Indian Journal of Fibre & Textile Research
Vol. 48, March 2023, pp. 61-72
DOI: 10.56042/ijftr.v48i1.54696

Effects of carbon chain length of acrylate monomer on sizing properties of sesbania gum-*g*-polyacrylate

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Received 6 September 2021; revised received and accepted 19 May 2022

A series of acrylate monomers with different carbon chain lengths including methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) has been grafted onto molecular chains of native sesbania gum (SG) to obtain SG-*g*-polyacrylate with similar grafting ratios through Fenton's initiator respectively. Effects of carbon chain length of the series of acrylates on sizing properties of the grafted SG on polyester yarn have been studied. It is found that, by grafting acrylates onto the molecular chains of SG, its sizing properties are improved markedly. Under the condition of similar grafting ratios, SG-*g*-PMA shows the highest apparent viscosity, tenacity of sizing film, wettability and adhesion strength to polyester fibre in all the grafted SG prepared. SG-*g*-PEA and SG-*g*-PEHA show the highest wear resistance and elongation of sizing film respectively. The polyester/cotton (65/35) warp yarns sized by SG-*g*-PMA, SG-*g*-PEHA and SG-*g*-PEA possess the highest tensile strength, tensile elongation and abrasion resistance respectively, in all the sized conditions. The SG grafted with acrylate monomers with different carbon chain lengths can meet various requirements in sizing polyester yarn.

Keywords: Acrylate monomer, Carbon chain length, Graft copolymerization, Polyester yarn, Polyester/cotton yarn, Sizing property, Sesbania gum

1 Introduction

Sesbania is a kind of wild annual legume plant and grows widely in many Asia-Pacific countries. Sesbania gum (SG) is derived from endosperm of sesbania seed, has no edible value, but can be used as a vegetable size in textile industry. SG is considered as a polycondensate of galactose and mannose with a molar ratio of 1:2, contains a number of hydroxyl groups in its molecular chain and exhibits strong polarity[1,2]. It has good sizing properties for natural and regenerated fibre yarns. However, SG exhibits poor affinity to the most widely used synthetic fibre, such as polyester, which possesses numerous phenyl and ester groups and thus shows very weak polarity[3,4]. The poor affinity limits the varieties of the SG's sizing objects seriously. In order to break the use limit, methyl acrylate (MA) monomers were grafted onto the molecular chains of native SG through Fenton's initiator to prepare SG-*g*-PMA with a grafting ratio (GR) of 18.7%[5]. The introduction of numerous ester groups decreased the macromolecular polarity of SG and enhanced the polarity similarity between SG size and polyester fibre. The grafting of MA opens up a new way for the application of SG in polyester yarn sizing. Nevertheless, textile researchers still have a question whether the SG grafted by MA possesses satisfactory sizing property in all aspects, such as appropriate apparent viscosity, high mechanical property of sizing film, strong adhesion to polyester fibre, mechanical properties and hairiness index of sized high content polyester warp yarn.

Some investigations have proved that the physical and chemical properties of a polysaccharide substrate will change in different aspects after the grafting of acrylate monomers with different carbon chain lengths. For example, under the condition of similar grafting ratios, viscosity stability of the sizing paste of the allyl starch grafted with acrylate monomer with shorter carbon chain was higher[6]. Water-resistance of the thermoplastic film of the camelina grafted with methacrylate monomer with longer carbon chain was found to be better[7]. Similarly, it can be speculated that SG grafted with acrylate monomers with different carbon chain lengths should exhibit various properties as well.

In order to select the molecular structure of the SG-*g*-polyacrylate which possesses the best sizing properties for polyester yarn, acrylates monomers with various carbon chain lengths, i.e. methyl acrylate

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(MA), ethyl acrylate (EA), butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA), were grafted onto native SG respectively through Fenton's initiator in the present study. Effects of carbon chain length of the acrylate monomers on sizing properties of the grafted SG were systematically evaluated in terms of apparent viscosity and its stability, contact angle of sizing paste on polyester fibres, mechanical property of sizing film, adhesion to polyester fibres, and application performance for high content polyester warp yarn. The four grafted SG were controlled at similar grafting ratio (GR) so as to remove the influence of the amount of grafted branches upon above properties and reveal true effects of carbon chain length of the acrylates. On comparing the application performance, the acrylate monomers with appropriate carbon chain length are recommended for the preparation of grafted SG sizes, which meet various application requirements.

2 Materials and Methods

2.1 Materials

Native SG powder was provided by Qianlixing Science and Technology Co. Ltd. MA, EA, BA, EHA; H_2O_2; $(NH_4)_2Fe(SO_4)_2·6H_2O$ and paradioxybenzene, supplied from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), were used as acrylate monomers with different carbon chain lengths, oxidant, reductant and terminator in the graft polymerization respectively. All the reagents used were chemically pure. The all-polyester rovings (483 tex) used for evaluating the adhesion were obtained from Yizheng Chemical Fibre Co. Ltd (Yizheng, China). The length and fineness of the polyester fibres of the rovings were 35 mm and 1.90 dtex respectively. The polyester/cotton 65/35 (T/C65/35) warp yarns (13.0 tex) used for sizing experiment were obtained from Zhenghua Textile Co. Ltd (Weifang, China).

2.2 Graft Copolymerization

Before the graft copolymerization, 10 g of native SG powders were dispersed in distilled water and then transferred into a 100 mL four-neck flask on a thermostat water bath. The flask was maintained at 45°C in the water bath. The flask was then deoxygenated by passing pure N_2 for at least 30 min before adding reactants. The Fenton's reagent including 3.360 g of oxidant (H_2O_2) and 0.774 g of reductant [$(NH_4)_2Fe(SO_4)_2·6H_2O$] were dissolved in distilled water respectively. The molar ratio of $H_2O_2/(NH_4)_2Fe(SO_4)_2·6H_2O$ was kept at 50/1. The acrylate monomers (MA, EA, BA or EHA), oxidant and reductant solutions were added into the flask simultaneously. In order to eliminate the influence of GR of the grafted SG on the sizing properties, the GR of all the SG samples were controlled at similar values. Sizing properties of the grafted SG for polyester yarn were proved to be satisfactory when the GR was around 19%[5]. Therefore, the GR was controlled within a fixed range (19±1.5%) after many tentative experiments in this study. The feed weight of MA, EA, BA and EHA monomers was 2.2, 2.3, 2.5 and 2.7 g respectively. The addition was completed in 10-20 min and final bath ratio of SG to distilled water was kept as 1/7. The graft copolymerization was carried out under mechanical stirring at 400 rpm under pure N_2 protection for 6 h. About 2% of paradioxybenzene solution was added to terminate the polymerization. The product was filtered, washed thoroughly with ethanol, dried in vacuum oven, ground to fine powders and stored in desiccator. Each graft polymerization was repeated 3 times. The graft polymerization of the SG with acrylate monomers is shown in Fig. 1.

2.3 Measurement of Grafting Parameters

The amount of residual acrylate monomers after grafting was determined by titrating double bonds of the monomers in the filtrate after the graft polymerization. Conversion of monomer to polymer (MC) was analyzed and calculated using the following equation:

$$\mathrm{MC}(\%)\frac{W_1-W_2}{W_1}\times 100 \qquad \ldots (1)$$

where W_1 and W_2 denote the weights of total and residual monomers respectively.

Then, the grafted SG with homopolymers (polyacrylate), such as PMA, PEA, PBA or PEHA, was extracted by repeated refluxing in Soxhlet with distilled acetone, which was a good solvent for the polyacrylate[5,8], for 24 h to remove the homopolymers thoroughly. The grafted SG product obtained was dried at 80°C for 4 h in a vacuum oven in order to remove acetone.

In this paper, grafting ratio (GR) describes the weight percentage of polyacrylate branches grafted onto SG to the SG. Grafting efficiency (GE) describes the weight percentage of polyacrylate branches grafted onto the SG to the sum of polyacrylate branches and homopolymers. GR and GE were determined using the following equations:

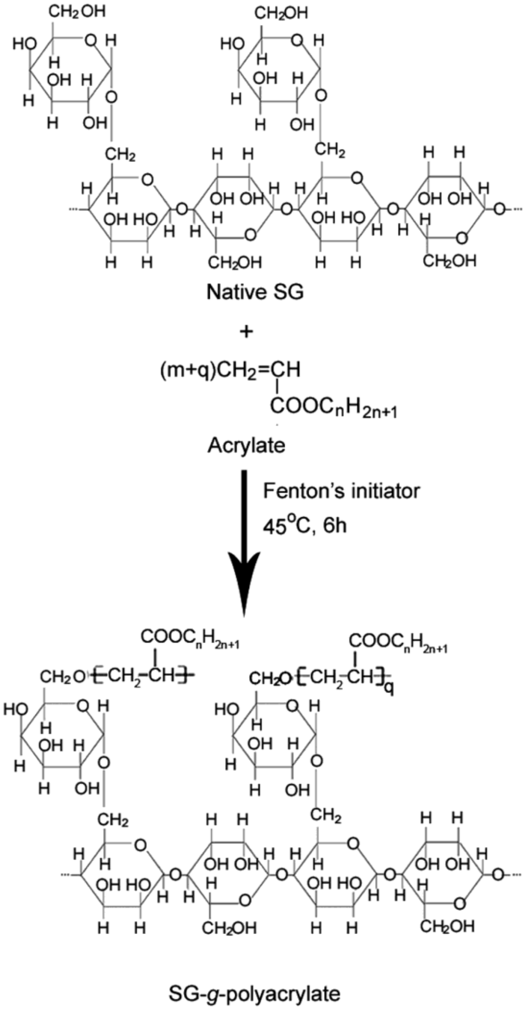

Fig. 1 — Graft copolymerization of native SG with acrylate monomers through Fenton's initiator

$$W_3 = W_b - W_a \qquad \dots (2)$$

$$\text{GR}\,(\%)\,\frac{W_1 - W_2 - W_3}{W_1}\times 100 \qquad \dots (3)$$

$$\text{GE}\,(\%)\,\frac{W_1 - W_2 - W_3}{W_1}\times 100 = \frac{\text{GR}}{\text{MC}}\times\frac{W_0}{W_1}\times 100 \qquad \dots (4)$$

where W_b and W_a are the weights of products before and after the extraction by acetone respectively; W_3 and W_0, were the weights of the homopolymers and SG respectively.

2.4 Characterization

Fourier transform infrared spectrometer (FTIR) spectra were collected using a Thermo Nicolet (Avatar 380) spectrophotometer with samples dispersed in KBr with a scan range of 400-4000 cm^{-1}. ^{1}H-NMR spectra were also measured on a Bruker ARX 400 spectrometer. SEM images were taken using an SNE-3000M SEM operating at 30 kV. Thermogravimetric analyses (TGA) were also carried out on a TG/DTA6300 (Seiko) analyzer under air atmosphere at a heating rate of 10°C/min and within a temperature range of 30-700°C. Contact angle of the SG solution on polyester fibres was measured using a JC2000D2 contact angle meter. Surface tension of the SG solution was measured with pendant drop method, using Droplet Shape Analyzer KRüSS DSA100 at 20°C.

2.5 Measurement on Apparent Viscosity

Apparent viscosity of the SG paste was measured using an NDJ-79 viscometer purchased from Electrical Machinery Plant of Tongji University (Shanghai China). The sample was suspended into distilled water to form 6% (w/w) dispersion. The dispersion was heated to 95°C and maintained at the temperature under mechanical stirring for 1 h. At this time, the apparent viscosity (*V*) of the paste was measured with a shear rate of 2028 s^{-1}. Viscosity stability of the paste denoted the percentage of the viscosity invariability over a period of 3 h at 95°C. The viscosity of the SG paste was measured in every 30 min and the stability was calculated using the following equation:

$$Vis\cos ity\; stability\,(\%) = (1 - \frac{V_{\max} - V_{\min}}{V})\times 100 \qquad \dots (5)$$

where V was the apparent viscosity of the paste; and $V_{\max}$ and $V_{\min}$ were the maximum and minimum of the viscosity over the period respectively.

2.6 Measurement of Mechanical Properties of Sizing Film

Sizing film was cast with 400 g of the SG paste (6%, w/w). The steps in the preparation of the paste were the same with those in viscosity measurement. The paste was poured onto a 650 × 400 mm polyester plastic film as a substrate spread on a same size glass plate and dried at 65% RH and 20°C. Then, the dried SG film was peeled off carefully from the polyester plastic film. The SG sizing film was cut into rectangular strips (220×10 mm), which were conditioned at 65 % RH and 20°C for 24 h before the measurement.

Tensile strength and tensile elongation of the SG film were measured on a BZ2.5/TNIS Zwick Material Tester. Twenty samples were measured to obtain the mean value. The abrasion resistance of the SG film was evaluated in the value of wear loss of film weight using a G552 Zweigle abrader. Ten samples were abrased reciprocatively for 1000 times to obtain the mean value[9]. The abrasion material was KP915C abrasion paper produced by ITAS Co. Ltd. The wear loss was obtained from the following equation:

$$\text{Wear loss}\,(\text{mg}/\text{cm}^2) = \frac{W_1 - W_2}{S} \qquad \ldots (6)$$

where W_1 and W_2 were the weight of the film measured before and after the abrasion, respectively; and S was the abrasion area of the film.

2.7 Measurement of Adhesion to Polyester Fibre

Roving sizing method was used to measure adhesion of the SG size to polyester fibre. In the measurement, a slightly sized roving is drawn to tensile failure. It is the failure loads that were adopted to exhibit the adhesion. The SG powders were suspended into distilled water to form 1% (w/w) dispersion. The dispersion was heated to 95°C and maintained at the same temperature under mechanical stirring for 1 h. Then the SG solution obtained was decanted into a stainless steel box placed in water bath at 95°C. The polyester rovings carefully wound onto a special frame were impregnated with the SG solution for 5 min. The frame was hung and dried in air. Finally, the rovings were kept at 65% RH and 20°C for 24 h before the measurement. Tensile strength and work-to-break of the sized rovings were measured as adhesion strength & work. Twenty samples were measured for obtaining the mean value of the data required.

2.8 Sizing Experiment

Cooking process of the grafted SG sizing paste was the same as the one described in the measurement on apparent viscosity except that concentration of the sizing paste was 12% (w/w). The sizing experiment for T/C65/35 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 size box adjusted to 95°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 used in drying chamber, in which it was adjusted to 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 the performance test of the sized T/C65/35 warp yarn.

2.9 Measurement of Mechanical Properties of Sized Yarns

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 resistance to reciprocating friction of the yarns was evaluated in the reciprocal motion times of the yarns until breakage using an LFY109B electric yarn abrader purchased from Textile Science Research Institute of Shandong Province (Qingdao, China). The measurements of mechanical properties of the sized yarns were carried out according to the previous study[3]. For every sample, fifty replications were taken and their mean values were obtained.

2.10 Measurement on Hairiness Amount of Sized Yarns

The amount of the hairiness (length, 3-9 mm) of the yarns 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 yarn with a drawing speed of 30 m/min.

2.11 Statistical Analysis

The data were analyzed using SAS software (SAS Institute, Inc., Cary, NC). The confidence interval was set at 95% and a ‘p’ value smaller than 0.05 was considered to be a statistically significant difference by Tukey’s HSD test. According to the operation results of the analysis software, small letters, such as (a, b or c), were inserted above or below the data points. The data points with the same small letter were not statistically significantly different from each other.

3 Results and Discussion

3.1 FTIR Analysis

FTIR spectrum of the native and grafted SG is shown in Fig. 2(a). The figure shows two peaks appeared at about 3380 cm^{-1} and 2910 cm^{-1} in all the SG curves due to stretching vibrations of hydroxyl and methyl/methylene[5,6] respectively. The curve of each SG-*g*-polyacrylate shows a new characteristic absorption band at about 1736 cm^{-1} in addition to the absorption bands of native SG. The peak at about 1736 cm^{-1} corresponds to stretching vibration of carbonyl group of acrylic ester[5,6] and confirms the successful grafting of acrylate monomers onto SG.

3.2 ^{1}H-NMR Analysis

^{1}H-NMR spectra of the native and grafted SG are displayed in Figs 2(b)-(f). Chemical shifts at about 2.5

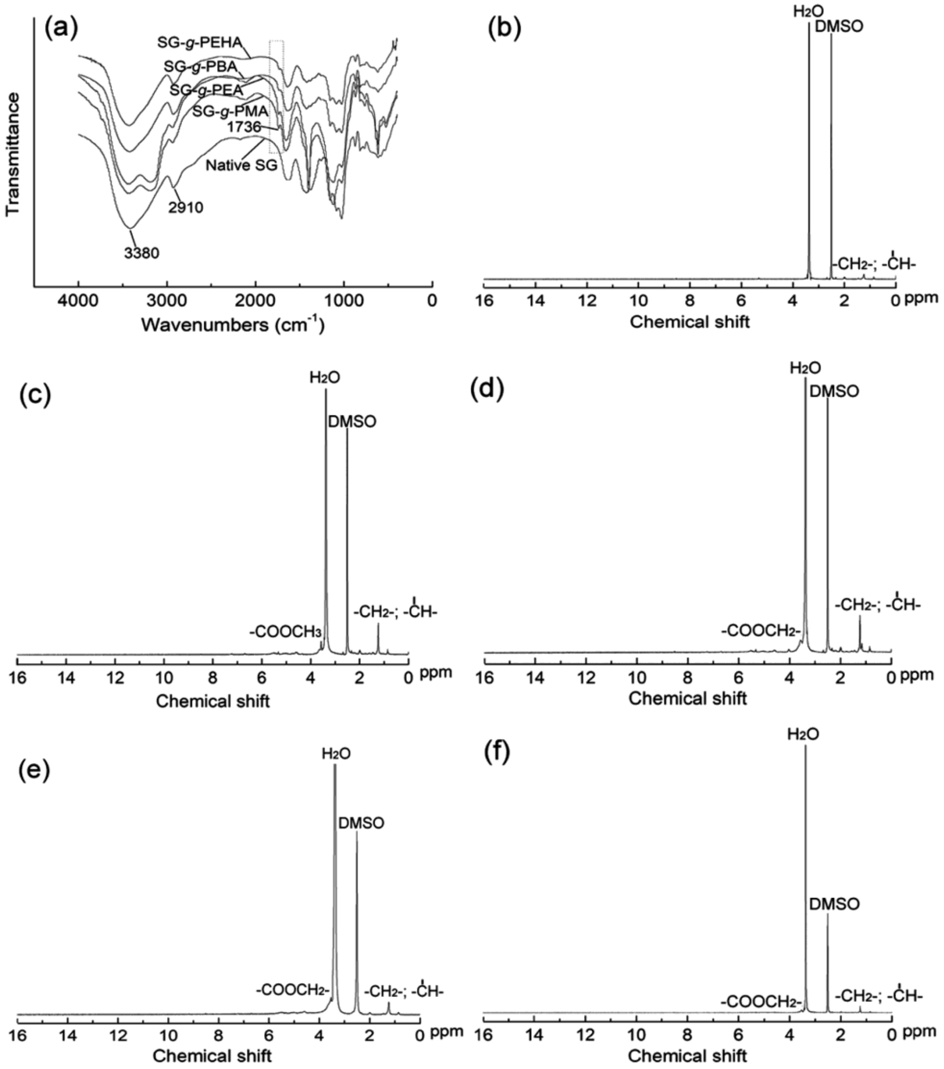

Fig. 2 — FTIR spectra of native SG and SG-*g*-polyacrylate (a); and ^{1}H-NMR spectra of native SG (b), SG-*g*-PMA (c), SG-*g*-PEA (d), SG-*g*-PBA (e), and SG-*g*-PEHA (f)

and 3.3 ppm in all the spectra could be attributed to proton peaks of the solvent (DMSO) and residual H_2O respectively. Besides the chemical shift peaks of native SG, e.g. the alkyl proton peaks (e.g. $–CH_2$- and >CH-) in the range of 0.9-2.0 ppm[10,11], a new chemical shift peak at about 3.5 ppm is also found in the spectra of all the SG-*g*-polyacrylate which could be considered as the proton peaks of methyl/methylene directly linked to the carbonyl of acrylic esters[10,11]. The new peak confirms the existence of various acrylic esters in the polyacrylate branches. Moreover, the increase in the intensities of alkyl proton peaks appearing in the range of 0.9-2.0 ppm in the spectra of the grafted samples could be considered as another evidence of the presence of the polyacrylate branches on the grafted SG.

3.3 Effects of Carbon Chain Length on Grafting Parameters

According to the measurement results, with the increase in the carbon chain length, the MC values are all around 97% and show no significant variation. In order to eliminate the impact of GR of the grafted SG sizes on their properties, the GR of all the modified SG grafted by acrylates with various carbon chain lengths are controlled within an appropriate range (19±1.5%). When it comes to GE, it decreases from 88.8% to 76.6% with the increase in the carbon chain length.

No matter what kind of acrylate monomer is employed in the study, 6 h is long enough due to the achievement of the MC close to 100%. In the graft polymerization, the formation of grafted branches (i.e. PMA, PEA, PBA, and PEHA) is based on the bonding of SG macromolecule free radicals with various acrylate monomers. The alkyl space volumes of side groups of MA, EA, BA and EHA monomers increase in turn. Increasing the carbon chain length of the acrylate would unavoidably enhance the difficulty for the acrylate to take part in the graft polymerization when the acrylate monomers were in the vicinity of the SG macromolecule free radicals due to the increasing steric hindrance. As a result, the feed quantity of acrylate monomers must be increased with the increase in the carbon chain length in order to obtain the expected GR (~19%). In other words, the longer the carbon chain, the lower is the GE.

3.4 Thermogravimetric Analysis

Figure 3 reveals thermal degradation behaviors of the native and grafted SG samples. As shown in Fig. 3(a), the degradation process of the native SG could be divided into three main stages, viz. (1) dehydration (< 130°C), (2) thermal degradation (220-320°C), and (3) carbonization and carbon oxidation (> 580°C). In Stage 1, both bound water and absorbed water of SG are removed. In Stage 2, numerous hydrogen bonds between spiral carbohydrate chains of SG are broken and such gas as water vapor is released. Depolymerization and decomposition of SG macromolecules occur. In Stage 3, SG is carbonized and some carbons are oxidized.

As compared to the thermogram of native SG, thermal behaviors of the grafted SG are quite similar in Stage 1. However, thermal degradation trends of the native and grafted SG in Stage 2 and Stage 3 are quite different. In Stage 2, weight loss rate of the grafted SG is much higher than that of the native one.

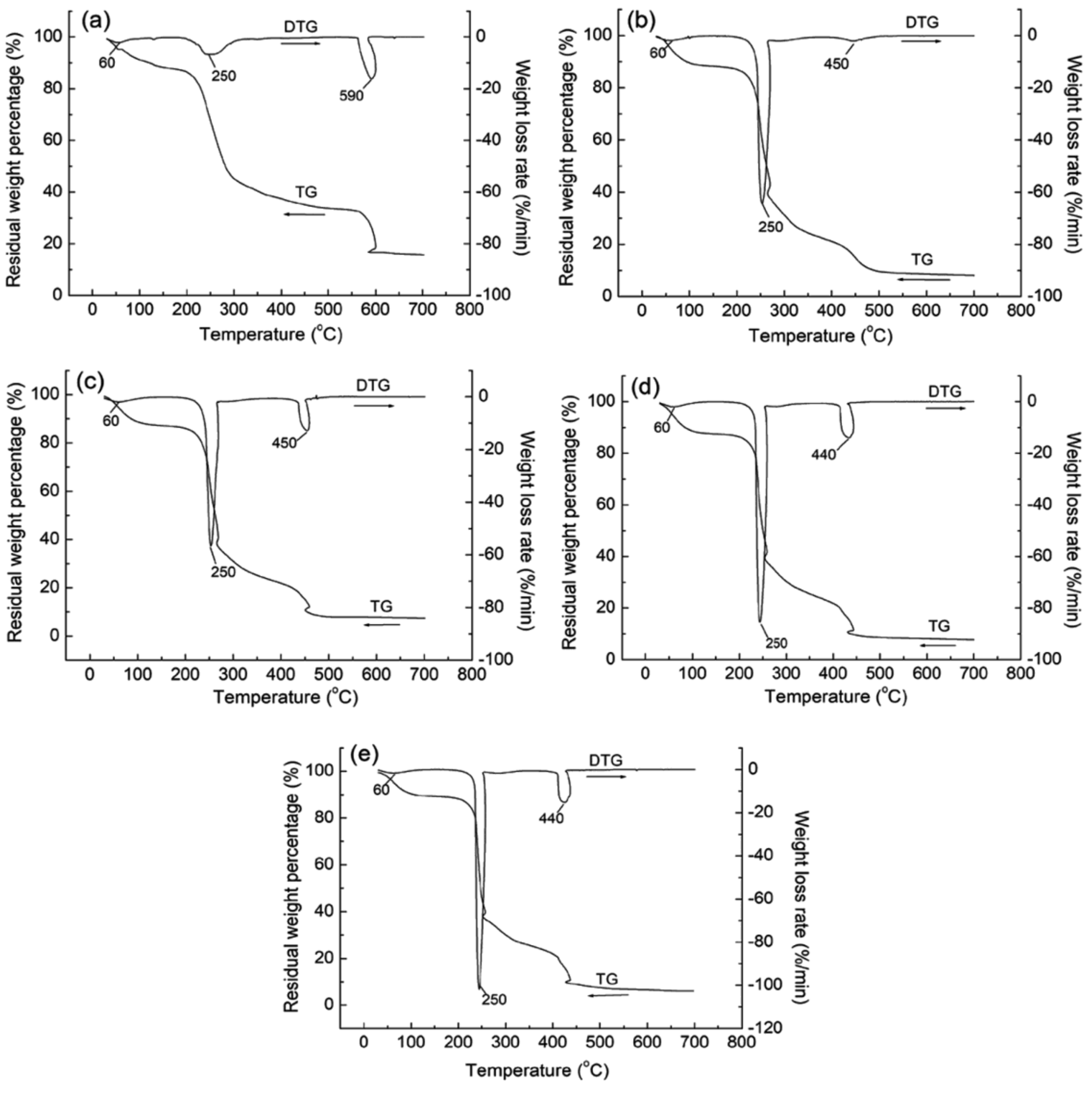

Fig. 3 — TGA thermograms of native SG (a), SG-*g*-PMA (b), SG-*g*-PEA (c), SG-*g*-PBA (d), and SG-*g*-PEHA (e)

In Stage 3, the most striking difference between the native and the grafted SG is that, starting temperature of carbonization of the latter is decreased to only about 430°C. The higher weight loss rate in Stage 2 and the lower carbonization temperature in Stage 3 both indicate that the grafted SG samples exhibit lower thermal stability than the native one at high temperature.

There are two major reasons for the decrease in the thermal stability of the grafted SG. On one hand, the grafting of polyacrylate branches onto the backbone of SG could enhance branching degree of the macromolecules, widen the distance between the macromolecular chains, and decrease the amount of hydrogen bonds. On the other hand, excessive H_2O_2 during the graft polymerization oxidizes the SG macromolecules and cut off their molecular chains. The grafted SG samples possess much lower molecular weight than the native one. As far as the same kind of polymer is concerned, the lower the molecular weight, the higher is the thermal decomposition rate. All the four kinds of SG-*g*-polyacrylate show similar thermal degradation behaviors due to the nearly same GR. During the actual sizing process, the highest temperature that SG withstands generally occurs in drying chamber for sized yarn (~110°C). In the temperature range of 20-130°C, the native and grafted SG sizes can be considered to possess similar thermal stability through the analysis of the thermograms.

3.5 Effects of Carbon Chain Length on Paste Viscosity

Effects of carbon chain length of acrylate monomer on apparent viscosity and viscosity stability of SG sizing paste is described in Table 1. All the grafted SG pastes possess much lower viscosity than native SG, while the former exhibits higher viscosity stability than the latter. In addition, with the increase in carbon chain length of the acrylate monomer, the viscosity of the grafted SG paste decreases slightly but their viscosity stability shows no remarkable difference.

When the molar ratio of $H_2O_2/(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ is controlled at 50/1, H_2O_2 could play two important roles. Initially, enough H_2O_2 could be guaranteed to participate in the redox reaction and initiate the graft copolymerization of SG with acrylate monomers. Moreover, excessive H_2O_2 could oxidize the SG macromolecule and thus reduce the excessively high apparent viscosity (200-400 mPa·s) of native SG paste to an appropriate range (8-20 mPa·s) for warp sizing[12-14]. Furthermore, most long molecular chains of native SG are cut off after the oxidation of H_2O_2. The chain length of SG becomes uniform and the molecular weight distribution of SG turns narrow. Therefore, viscosity fluctuation of the SG paste could be reduced under high-speed shearing and high temperature.

As for the grafted SG, with the increase in carbon chain length of the acrylate monomer, side chains of the grafted SG are easier to extend and their hydrophobicity keeps increasing. Long hydrophobic side chains show a more remarkable trend to tangle or aggregate in water[15]. The hydrophobicity could reduce the intermolecular forces between the grafted SG and the water molecule. Consequently, the apparent viscosity of the grafted SG paste is decreased therewith.

3.6 Effects of Carbon Chain Length on Wettability to Polyester Fibres

Effects of carbon chain length of acrylate monomer on the wettability of the SG paste to polyester fibres are also shown in Table 1. Each grafted SG paste exhibits a smaller contact angle and lower surface tension than the native one. In addition, with the increase in carbon chain length of the acrylate monomer, both of the contact angle and surface tension of the grafted SG paste increase gradually.

Young's equation provides a quantitative calculation method for the contact angle of a solution on fibres. The smaller the contact angle, the better is the wettability of the solution to the fibres. Young’s equation is shown in the following equations:

Table 1 — Apparent viscosity, viscosity stability, contact angle and surface tension of native SG and SG-*g*-polyacrylate sizing paste

Sizing agent	Apparent viscosity mPa·s	Viscosity stability, %	Contact angle deg	*CV* of contact angle, %	Surface tension mN/m	*CV* of surface tension, %
Native SG	210	85.7	76.4	1.47	46.7	2.38
SG-*g*-PMA	19.0	92.1	62.3	1.93	34.6	2.67
SG-*g*-PEA	18.5	91.9	64.3	1.45	37.0	3.03
SG-*g*-PBA	17.5	91.4	65.6	2.30	38.4	2.28
SG-*g*-PEHA	17.0	91.2	68.5	2.35	40.7	3.10

CV denotes coefficient of variation.

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad \ldots (7)$$

where θ is the contact angle; γ_S and γ_L are the surface tension of the solid and the liquid respectively; and γ_{SL} is the solid-liquid interfacial tension.

Surface tension of polyester fibre (γ_S) in Young's equation, is a constant. It can be deduced from the equation that the contact angle is mainly determined by the surface tension of SG paste (γ_L) and the interfacial tension between SG paste and polyester fibre (γ_{SL}). Decreasing γ_L and γ_{SL} will cause the cosine of θ to increase. In other words, θ angle will turn small. Native SG is composed of numerous mannose and galactose rings, which contain a large number of hydroxyl groups. Thus, native SG exhibits strong polarity. Polyester fibre macromolecule contains many aromatic rings & ester groups and belongs to typical nonpolar polymer. Based on similar dissolve mutually theory, the interfacial tension between native SG solution and polyester fibre is bound to be extremely large. Polyacrylate branches of the grafted SG contain numerous ester groups, which exhibit weak polarity. The introduction of ester groups onto the molecular chain of SG could remarkably reduce its polarity and decrease both the surface tension (γ_L) of SG solution and the interfacial tension (γ_{SL}) between SG solution and polyester fibre. Therefore, the contact angle of the grafted SG paste on polyester fibres is smaller than that of the native one. In other words, the wettability of SG paste to polyester fibres is improved through the grafting of acrylates.

The grafting ratio of the SG-*g*-polyacrylate samples prepared in this study is very close, which means that the weight of polyacrylate branches of each grafted SG is basically the same. Obviously, the shorter the carbon chain of acrylate monomer, the lower is the molecular weight of the structural unit of the polyacrylate branch. On the premise that the weight of the polyacrylate branches is close, the lower the molecular weight of the structural unit of the polyacrylate branch, the larger is the mole number of ester groups introduced onto the molecular chain of SG. The increase in the mole number of ester groups is quite helpful to decrease the γ_{SL} between SG paste & polyester fibre and to increase the compatibility between the two. As depicted in Fig. 2(a), with the decrease in carbon chain length of acrylate monomer, the amplitude of the stretching vibration (~1736 cm^{-1}) of carbonyl group in the weak polar group - ester of the grafted SG gradually increases. The increasing stretching vibration amplitude can prove the increase in the number of the ester introduced onto the SG. A similar change in trend of proton peak of ester group is also observed in ^{1}H-NMR spectra. For the same type of polymer, the weaker the polarity, the lower is the surface tension of its aqueous solution[16]. The finding in Table 1 also confirms this conclusion. It can be inferred that with the decrease in carbon chain length of acrylate monomer, the surface tension of the grafted SG paste and the interfacial tension between the grafted SG paste and polyester fibre are reduced. As a result, the contact angle turns small and the wettability to polyester fibres becomes strong.

3.7 Effects of Carbon Chain Length on Mechanical Properties of Sizing Film

Effects of carbon chain length of acrylate monomer on mechanical properties of SG sizing film are displayed in Fig. 4. The grafting is able to improve mechanical properties of the SG film efficiently. With the increase in carbon chain length of the acrylate monomer, tensile elongation of the SG films is increased stepwise at the expense of tensile strength. The SG-*g*-PEA sizing film exhibits the highest wear resistance. SEM images of sizing films of native SG (a) and the four kinds of SG-*g*-polyacrylate (b-e) are shown in Fig. 5.

The sizing film is prepared by aqueous casting method. The enhanced paste fluidity, which results from the oxidation of H_2O_2 during the grafting, is found beneficial for the formation of continuous and uniform SG film. More shrinkage and crack of native SG film are observed in drying process. During the mechanical evaluation, most fracture is found to occur at excessively thin part of native SG film. The grafting greatly reduces the possibility of such mechanical failure. Thus, all the grafted SG films exhibit

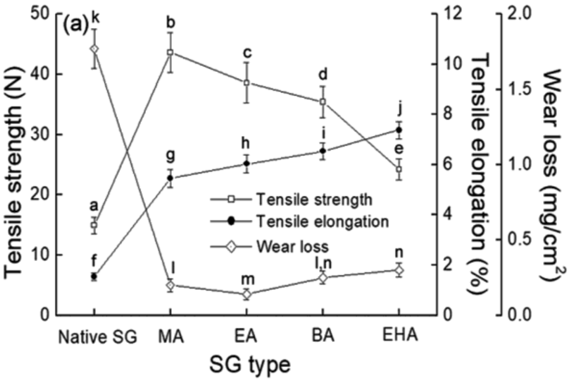

Fig. 4 — Mechanical properties of native SG and SG-*g*-polyacrylate sizing films

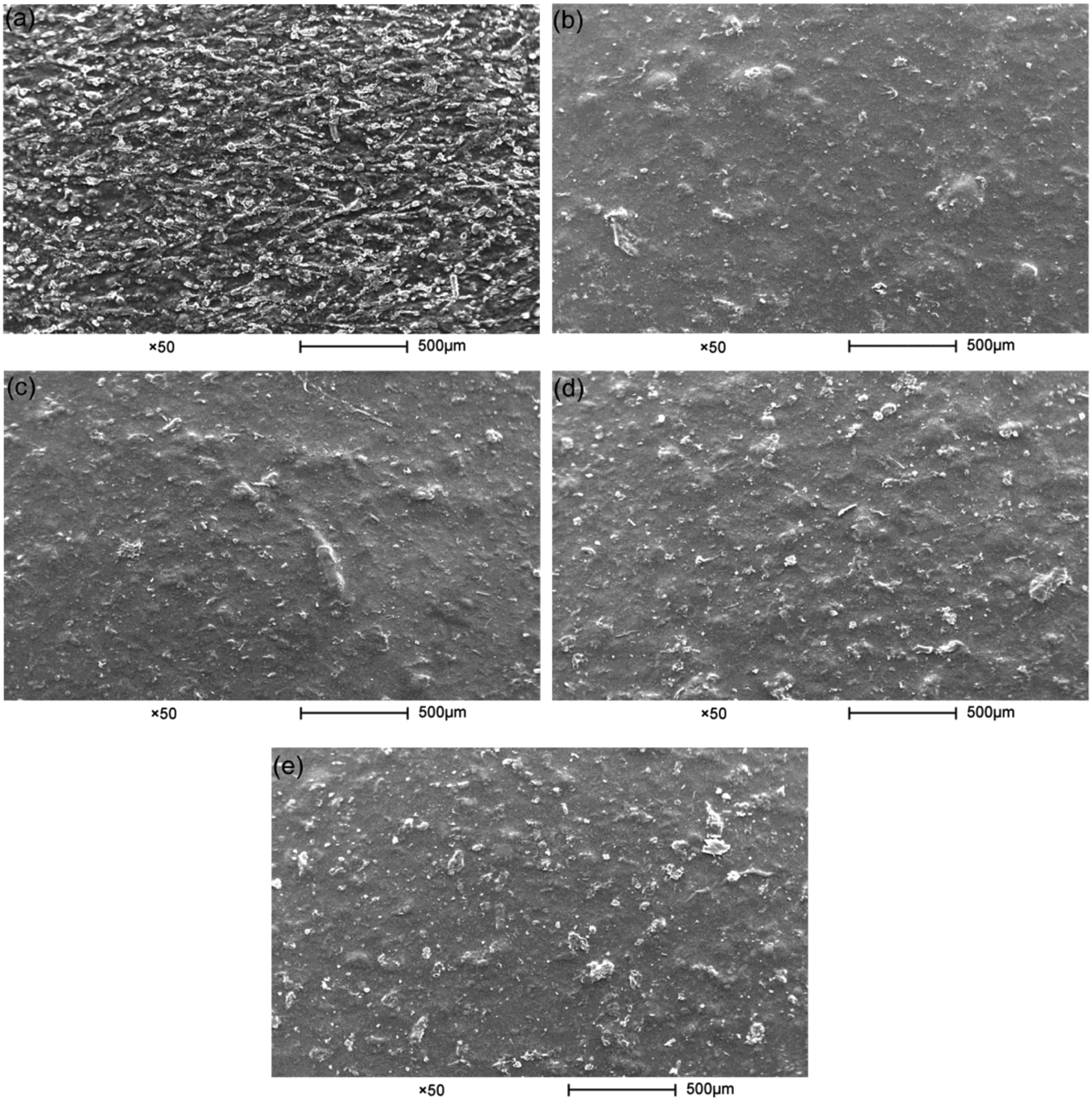

Fig. 5 — SEM images of native SG (a), SG-*g*-PMA (b), SG-*g*-PEA (c), SG-*g*-PBA (d), and SG-*g*-PEHA (e), sizing films

higher tensile properties and wear resistance than the native one. According to the surface morphology observation, native SG film is much rougher and more uneven than the grafted ones, as shown in Fig. 5.

Grafting ratios of all the SG-*g*-polyacrylate are controlled at about 19%. The introduction of such a considerable quantity of polyacrylate branches destroys the original excessive regularity of SG molecular chains, breaks intermolecular hydrogen bonding of SG and imparts good flexibility to the molecular chains. The flexibility of polyacrylate molecular chain largely depends on the carbon chain length of side group of its structural unit. Increasing the carbon chain length of alkyl group is an efficient way to increase the intermolecular distance and reduce the intermolecular force. Consequently, the motion ability of macromolecular segments of polyacrylate is enhanced and the flexibility of the molecular chain of the polyacrylate is improved. As a result, the longer the carbon chain of acrylate monomer, the more flexible is the molecular chain of the SG-*g*-polyacrylate. It can be speculated that the grafted SG film will exhibit higher elongation at the expense of breaking strength by tensile stress when increasing carbon chain length of the acrylate. The results in Fig. 4 confirm the speculation well. SG is a polycondensate of galactose & mannose and the polysaccharide structure causes SG film to exhibit excessive brittleness and hardness. The grafting of SG with acrylate with long carbon chain can become an effective method to make up for its structural defect.

Wear resistance of a polymer film is determined comprehensively by the strength and elongation of the film. The SG-*g*-PEA film possesses both moderate tensile strength and elongation in all the grafted samples. Therefore, wear loss of the SG-*g*-PEA film is lower than that of any other grafted one. The high wear resistance of the SG-*g*-PEA film enables it to form a solid covering layer for warp to resist the severe friction with weaving machine elements.

3.8 Effects of Carbon Chain Length on Adhesion to Polyester Fibres

Effect of carbon chain length of acrylate monomer on adhesion of the SG to polyester fibres is displayed in Table 2. The grafted SG exhibits much better adhesion to polyester fibres than the native one. With the increase in carbon chain length of the acrylate monomer, adhesion strength and adhesion work of the grafted SG to polyester fibres show decreasing trends, while their decreasing amplitudes are different.

The impossibility of the formation of strong bonding between native SG and polyester fibre stems from their great difference in polarity. It is unpractical to obtain sized polyester yarns with good mechanical property when using native SG as sizing agent due to its poor adhesion to polyester fibres. After grafting acrylates onto molecular chain of SG, numerous ester groups are introduced and thus the polarity of the SG is decreased efficiently. The polarity similarity between the modified SG and polyester fibre is enhanced and the affinity of the SG sizes to polyester fibres is increased. Moreover, the grafting of acrylates improves the wettability of the SG paste to polyester fibres. Good wettability of sizing paste on fibre surface provides a necessary prerequisite for its full penetration into the yarn. As a result, the improved affinity and wettability to polyester fibres endow the grafted SG with stronger adhesion.

As for the four grafted SG, on the basis of similar grafting ratios, the mole number of the ester groups introduced onto the grafted SG decreases gradually with the increase in carbon chain length of acrylate monomer. Due to the decrease in both the affinity and the wettability to polyester fibre, the adhesion of the SG-*g*-polyacrylate decreases with the increase in the carbon chain length. However, the decreasing amplitudes of adhesion strength and adhesion work are different. It can be interpreted that adhesion work is determined not only by adhesion strength, but also by the elongation of the adhesive layer that sizing agent forms between fibres. Obviously, it is impossible for researchers to strip adhesive layer between the fibres to evaluate its elongation with no mechanical damage. Therefore, tensile elongation of the film cast by a sizing agent is tested to simulate the elongation of its adhesive layer[17]. As depicted in Fig. 4, the tensile elongation of the grafted SG film increases with the increase in carbon chain length. In other words, the elongation of SG adhesive layer between polyester fibres kept increasing. With the increase in the carbon chain length, the adverse effect caused by the decrease in adhesion strength of the SG to polyester fibres on adhesion work could be offset to some extent by beneficial effects brought by the improvement in the elongation of the SG adhesive layer. Consequently, the decreasing amplitude of the adhesion work is found smaller than that of the adhesion strength.

3.9 Effects of Carbon Chain Length on Mechanical Properties of Sized Yarns

Effects of carbon chain length of acrylate monomer on mechanical properties of the T/C65/35 yarns sized by the series of SG-*g*-polyacrylate are shown in Table 3. Briefly speaking, there are three main reasons why native SG is not suitable for sizing pure polyester filament or high content polyester yarn (T/C65/35), viz. (i) poor compatibility between native SG and polyester due to large polarity difference, (ii) high viscosity of native SG paste leading to excess

Table 2 — Adhesion of native SG and SG-*g*-polyacrylate sizes to polyester fibres

Sizing agent	Adhesion strength N/1000tex	*CV* of adhesion strength, %	Adhesion work J/1000tex	*CV* of adhesion work, %
Native SG	185.3	7.29	1.72	10.70
SG-*g*-PMA	339.4	6.08	2.74	8.11
SG-*g*-PEA	314.8	8.82	2.73	6.21
SG-*g*-PBA	301.3	7.98	2.65	7.69
SG-*g*-PEHA	200.6	9.67	2.48	8.04

Table 3 — Mechanical properties of T/C65/35 raw yarn and the yarns sized by native SG and SG-*g*-polyacrylate

Sizing agent	Tensile strength		Tensile elongation		Abrasion resistance	
	Value, N	*CV*, %	Value, %	*CV*, %	Value, cycle	*CV*, %
Raw yarn	2.36	8.39	8.30	8.10	90	9.41
Native SG	2.59	6.08	5.80	9.80	219	9.26
SG-*g*-PMA	3.12	5.72	7.68	9.22	700	6.40
SG-*g*-PEA	2.97	4.87	7.76	6.67	755	5.67
SG-*g*-PBA	2.92	5.85	7.79	7.53	505	9.89
SG-*g*-PEHA	2.83	4.38	7.82	8.17	420	8.52

coating and insufficient penetration to warp yarn, and (iii) low wettability of native SG paste to polyester fibre. As compared to native SG, mechanical properties of the T/C yarn sized by the SG-*g*-polyacrylate are significantly improved. With the increase in the carbon chain length of acrylate monomer, tensile elongation of the yarns is gradually increased at the expense of the tensile strength. In terms of abrasion resistance, the yarns sized by the SG-*g*-PEA have the most reciprocal motion times until their breakage.

The shorter the carbon chain of acrylate monomer, the smaller is the contact angle of the grafted SG solution on polyester fibre. Reducing the carbon chain length is able to improve the wetting & spreading of the grafted SG solution on the surface of polyester fibre and the penetration of the SG paste into the T/C65/35 yarn. Therefore, the fibres in the yarn could adhere to each other better. The cohesive force between fibres is enhanced and the tensile strength of the sized yarn is improved. Shortening the carbon chain of the side group of the acrylate monomer could damage the flexibility of the polyacrylate chain formed. As a result, decreasing carbon chain length of the acrylate could deteriorate the elongation of both the grafted SG sizing film coated on the yarn surface and the grafted SG adhesive layer between the fibres in the yarn at the same time. Therefore, the tensile elongation of the sized yarn decreases continuously with the decrease in the carbon chain length.

The abrasion resistance is the comprehensive embodiment of tensile strength and elongation of the yarn. Based on the tensile test results, the yarn sized by the SG-*g*-PEA possesses both favorable tensile strength and elongation. Therefore, the sized yarn shows the highest abrasion resistance, of which the number of friction until breakage even exceeds 8 times of that of the raw yarn.

3.10 Effects of Carbon Chain Length on Hairiness Amount of Sized Yarns

Effects of carbon chain length of acrylate monomer on the amount of harmful hairiness of the T/C65/35 yarns sized by the series of SG-*g*-polyacrylate are depicted in Fig. 6. Both the short and long hairiness of the T/C yarn sized by native SG are much more than those of the yarns sized by the SG-*g*-polyacrylate. As for the yarns sized by the SG-*g*-polyacrylate, the longer the carbon chain of acrylate monomer, the more is the hairiness on the yarn surface.

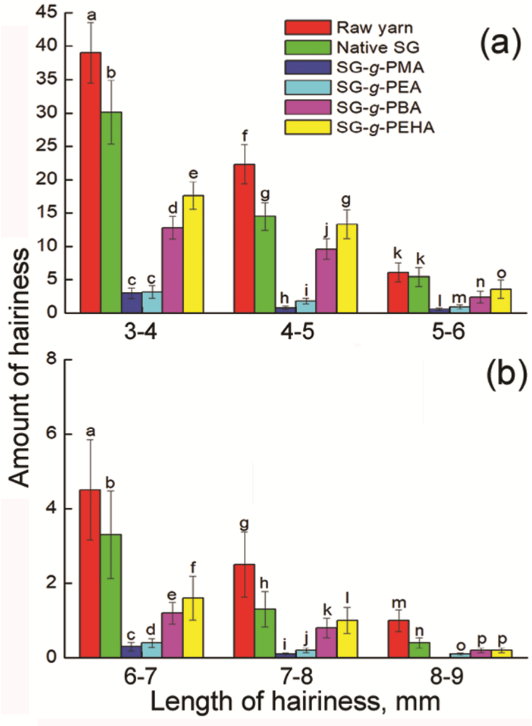

Fig. 6 — Amount of short (a) and long (b) harmful hairiness with different lengths of T/C65/35 raw yarn and the yarns sized by native SG and SG-*g*-polyacrylate

The molecular chains of the SG-*g*-polyacrylate and polyester fibre both contain a large number of ester groups. The introduction of polyacrylate branches onto the backbone of the SG could effectively improve the affinity of the SG size to polyester fibre, enhance the adhesion between the size and the fibre, and promote the ability of the SG size to adhere hairiness to the yarn body. As a result, the more the ester groups introduced, the better is the adhesion of SG-*g*-polyacrylate to polyester fibre. On the premise of similar grafting ratios, with the decrease in carbon chain length of acrylate monomer, the number of ester groups in the molecular chain of the SG-*g*-polyacrylate gradually increases. Thus, the SG-*g*-PMA exhibits the strongest ability to adhere the hairiness to the T/C65/35 yarn body among all the SG-*g*-polyacrylate. As described in Table 1, the shorter the carbon chain of acrylate monomer, the higher is the apparent viscosity of the grafted SG sizing paste. Increasing the viscosity of the sizing paste appropriately can increase the resistance which the hairiness encounters when warp yarns pass through the sizing paste and decrease the amount of the yarn hairiness. The two factors determine that the yarn sized by the SG-*g*-PMA has the least hairiness.

4 Conclusion

Carbon chain length of acrylate monomers has remarkable effects on grafting efficiency and sizing properties of SG graft copolymers for polyester yarn. Grafting efficiency, apparent viscosity, mechanical properties of sizing film, wettability & adhesion to polyester fibres, and application performance for high content polyester yarn of the grafted SG depend directly on the carbon chain length. The following conclusions are drawn from this investigation:

4.1 Carbon chain length of acrylate monomer closely relates to the grafting efficiency in the graft copolymerization of SG with acrylate monomers. Increasing the carbon chain length reduces the grafting efficiency markedly, while all the monomer conversions can stay at about 97.0%.

4.2 Carbon chain length of acrylate monomer directly determines the properties of the SG-*g*-polyacrylate sizing paste. Decreasing the carbon chain length can increase the apparent viscosity and decrease the surface tension of the grafted SG solution and the contact angle on polyester fibres. The SG-*g*-PMA possesses the highest viscosity and exhibits the best wettability to polyester fibre in all the SG-*g*-polyacrylate sizing pastes.

4.3 Mechanical properties of the SG-*g*-polyacrylate sizing film and the adhesion of the SG-*g*-polyacrylate to polyester fibres are greatly affected by carbon chain length of acrylate monomer. With the decrease in the carbon chain length, tensile strength of the grafted SG film and adhesion strength of the grafted SG to polyester fibres keep increasing, while tensile elongation of the grafted SG film gradually decreases.

4.4 Mechanical properties and the hairiness amount of the T/C65/35 warp yarn sized by SG-*g*-polyacrylate are significantly influenced by carbon chain length of acrylate monomer. With the decrease in the carbon chain length, tensile strength of the sized T/C yarn gradually increases, while tensile elongation and hairiness amount of the sized yarn decrease stepwise.

4.5 The investigation lays a solid foundation for future research on the preparation of bio-based sizing agent for pure polyester and high content polyester warp yarns. The graft copolymerization of SG with different acrylate monomers provides an innovative way to prepare a bio-based polymeric reagent with satisfactory sizing properties from agricultural by-products.

Acknowledgement

Authors gratefully acknowledge the financial support by technological research project for public welfare of Zhejiang Province (LGG21E030005; LGG22E030002), postdoctoral scientific research project of Zhejiang Province (276089) and project of key laboratory of clean dyeing and finishing technology of Zhejiang Province (QJRZ1902). Financial sponsors do not endorse the views expressed in this publication.

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