Article

A Facile Way to Modify Polyester Fabric to Enhance the Adhesion Behavior to Rubber

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Abstract: Due to the extremely inert surface of the polyester (PET) fabric, a toxic and traditional resorcinol-formaldehyde-latex (RFL) dipping solution is always needs to be used in in rubber composite industry. Unfortunately, other effective methods for fabric surface treatment are in urgent needed to improve the poor bonding interface between the fabric and the rubber matrix. In our study, a facile way to modify PET fabric was developed. Specifically, the fabric is treated by an alkaline solution and a coupling agent with magnetic agitation. Afterwards, the treated fabric/rubber composites are prepared through a co-vulcanization process. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA) were used to characterize the surface chemical compositions of the modified fabrics. The adhesion behavior is analyzed by the peel test. The results show that the fabric surface is successfully grafted with a coupling agent, and the peel strength reaches 9.8 N/mm after KH550 treatment, which is increased 32% compared with that of the original fabric/rubber composites. In addition, the vulcanization rate and interfacial fracture mechanism are also researched.

Keywords: polyester fabric; surface; rubber; composites; adhesion behavior

1. Introduction

Polyester (PET) Fabrics are used widely to reinforce rubber compounds such as conveyor belts, v-belts, tires and high-pressure hoses. They are important to develop the rubber-based industries [1]. However, the polarity and modulus of the synthetic fibers and the rubber matrix have a large difference each other, and the corresponding fabrics/rubber composites have a poor interface between the fabric and the rubber [2]. These phenomena constraint the overall properties, such as safety and durability, and which can be greatly improved by fabric [3,4]. Two ways are used to combine fabric and rubber. In the first way, the fabric and unvulcanized rubber are placed in steel mold and vulcanized [5,6]. In the second way, the fabric is merged with the vulcanized rubber by rubber adhesive [7]. Comparing the second way, the first one is simple and low cost because it avoids using expensive rubber adhesives.

As a synthetic fiber, polyester (PET) fibers are suitable for reinforcing rubber as skeleton materials because of their good mechanical properties and wear resistance. Physical or chemical treatment has been conducted intensively for improving the adhesion between PET fabric and rubber matrix, such as plasma treatment, γ-ray irradiation, electron

beam (EB) irradiation, coating method, UV-initiated grafting, oxidative acid etching and chemical grafting [8,9]. However, physical methods like plasma treatment and γ-ray irradiation are expensive and require specific reaction conditions. Thus, traditional chemical treatments, such as surface etching or grafting, still is a low-cost and effective strategy for surface modification of fabrics [10].

In this work, we chose a facile way to modify polyester fabric to enhance the adhesion behavior to rubber as well as a co-vulcanization process.We studied the chemical structure and interfacial adhesion mechanism between fabric and rubber by Fourier transform infrared spectra (FTIR), thermogravimetric analysis (TGA) and peel test. By changing the fabrics surface, the adhesion of PET fabrics to rubber can be reached to 9.8 N/mm, which provides a useful reference for the engineering application.

2. Experimental

2.1. Materials

Styrene-butadiene rubber (SBR, ESBR 1502) was supplied by Sinopec Qilu Co., Ltd, and nature rubber (NR, 1-0082) was from Yunnan Agricultural Reclamation Group Co., Ltd. Aromatic oil (VIVATEC 500) was supplied by Hansen & Rosenthal Group. Carbon black N330 was purchased from Kabote (China) Investment Co., Ltd. The adhesive agents RA and RS were obtained from Jiangsu national Huagong Technology Co., Ltd. ZnO was supplied by Liuzhou Zinc Products Co., Ltd. Stearic acid (SA) was supplied by Fengyi Oil Technology Co., Ltd. Accelerator was supplied by Qingdao Kangan Rubber Technical Co., Ltd. Silane coupling agent KH550 was purchased from Nanjing Chuangshi chemical additives Co., Ltd, China. Sodium hydroxide (NaOH) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Anhydrous ethanol was purchased from Tianjin Tianli Chemical Reagent Co., Ltd, China. Deionized water was made by the laboratory, and all reagents do not need to be purified again.

2.2. Surface modification of the PET fabric

The fabric was put into deionized water and anhydrous ethanol with ultrasonication for 2 h to remove lubricant and water-soluble and fat-soluble impurities on the fiber surface. Then, the fabric was dried in an oven at 70°C for 24 h. The fully dried fabric was soaked in 2 wt% NaOH solution for 2 h to hydrolyze the surface of PET fabric under magnetic agitation, which is labeled as NaOH-treated fabric. NaOH-treated fabric was soaked in the ethanol solution of 5 wt% silane coupling agent (KH550) with magnetic agitation for 2 h to alkylate, which is labeled as KH550-grafted fabric. Last, the fabric was dried in an oven at 70°C for 24 h.

2.3. Preparation of RFL dipping solution

Formaldehyde and resorcinol were mixed in water and then sodium hydroxide as a catalyst was added to the mixture and then the mixture was matured for 6 h at 25 ᵒC, forming matured RF resin. Ammonium hydroxide (to remove unreacted formaldehyde) and vinyl pyridin were added to the matured RF solution to prepare the RFL solution and left to mature for 20 h at 25 ᵒC. The components of traditional RFL dipping solution are given in Table S1.

2.4. Preparation of PET/rubber composites

As shown in Fig. 1, the sample preparation was as follows. The composition of the rubber compound as shown in Table S2 was used in our study. The weighed rubber compound was put into a two-roll mill, in which the rubber sheets with a thickness of 2 mm were obtained by adjust the space of the two-roll mill. Then, the rubber sheets were cut into the same size as fabrics with 25 × 25 cm². Finally, the fabric was laid on the rubber sheets carefully to avoid wrinkling between two rubber layers to form 1 layer of fabric-2

layers of rubber sheets sandwich structure. The uncured fabric reinforced rubber composites were placed into a 23 × 23 × 10 cm^3 stainless steel mold and vulcanized at 150 ^{o}C for 40 min under a pressure of 15 MPa. The vulcanized samples were cut into 180° peel test specimens.
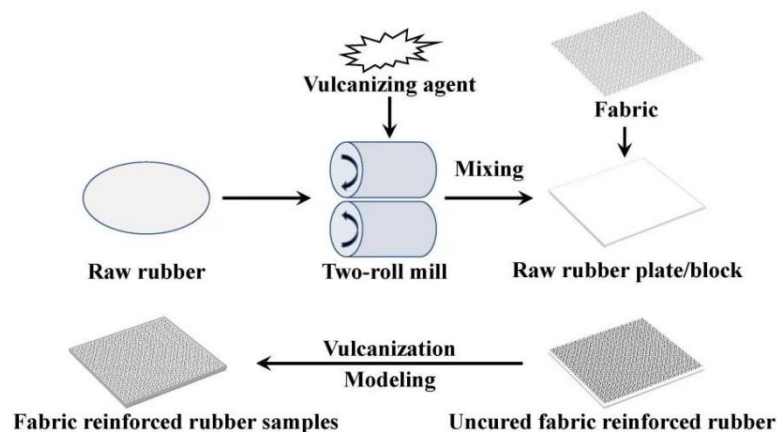

Figure 1. The preparation process of fabric rubber composites.

2.5. Characterizations

Fourier transform infrared spectroscopy (FTIR, INVENIO S, BRUKER, U.S.A) equipped with an attenuated total reflectance (ATR) accessory containing a diamond crystal was used to analyze the surface of the fabrics before and after treatment.

The tensile properties of the PET cords were carried out by using an universal testing machine (UTM5504, SUNS, China) at a crosshead speed of 2 mm/min, according to GB/T 3362-2005.

The morphological surface of the PET cords and the interfacial fracture surface of the composites were examined by scanning electron microscopy (GeminiSEM 360, Carl Zeiss, Germany) with an excitation voltage of 30 kV. The fracture surfaces were cleaned with alcohol in order to eliminate impurities, then were coated with a thin evaporated layer of gold.

The peeling strength between the fabrics and the rubber was tested according to ASTM D413-98 with a peeling speed of 50 mm·min-1 at room temperature. Strip samples of 250 mm length and 25 mm width were prepared.

A TGA instrument (TGA/DSC1/1600, Mettler, Switzerland) was used to characterize the grafting content coated on the PET fibers. Ground 5-10 mg specimens from the fibers randomly were proper for TG test, and were placed in a alumina crucible. A constant nitrogen flow of 50 mL/min was used in order to avoid oxidation of fibers. The temperature from room temperature to 700 ^{o}C at a heating rate of 20 ^{o}C/min was applied and then kept for 120 min at 700 ^{o}C.

The curing characteristics of the rubber compound were measured with a moving die rheometer (MDR3000Basic, Germany), in accordance with ISO 6502:2018 at 160 oC. Then, the curing rate index (CRI) was calculated according to the formula (1).

$$CRI = 100 / (T_{90} - T_{10}) \qquad (1)$$

in which T_{90} is the positive curing time, T_{10} is the scorch time.

3. Results and discussion

3.1. Influence of alkali treatment and grafting coupling agent on the fibers strength

Multifilament tensile strength of the PET fibers was carried out for studying the effect of alkali treatment and grafting coupling agent on the fibers strength. The relationship between multifilament tensile strength and treatment process modes was shown in Fig. 2. As a result, the tensile strength of fibers was decreased with alkali treatment, while it was

increased when KH550 is grafted on fibers. When the fabrics are immersed in a NaOH solution, the surface of the fabric will undergo hydrolysis to generate ethylene glycol and sodium terephthalate [11,12], leaving the -OH, -COONa and the -COOH groups on the fabric surface, whose the reaction process is shown in Fig. 3. Compared to the untreated fiber, the tensile strength is decreased by NaOH solution treatment, indicating some damage of fibers and causing a loss of tensile strength. From our results as shown in Fig. 2, the tensile strength of fibers was inversely recovered a little after KH550 treatment. Because the grooves and holes etched by alkali solution can be embedded by these polymer molecules and they can be repaired partly (as shown in Fig. 4), reducing the probability of stress concentration and avoiding fibers breakage.
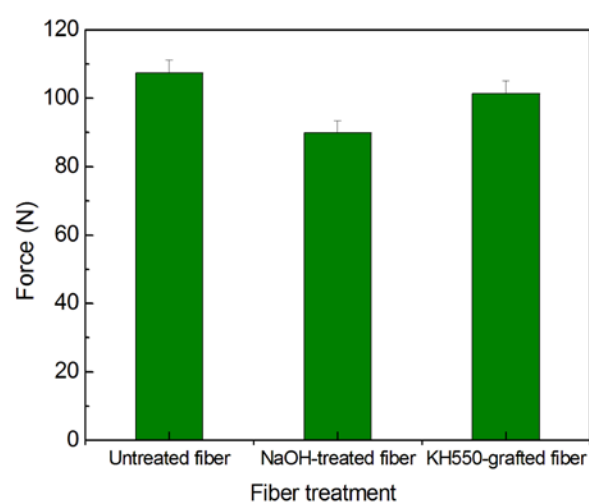

Figure 2. Effect of process mode on tensile strength of fibers.
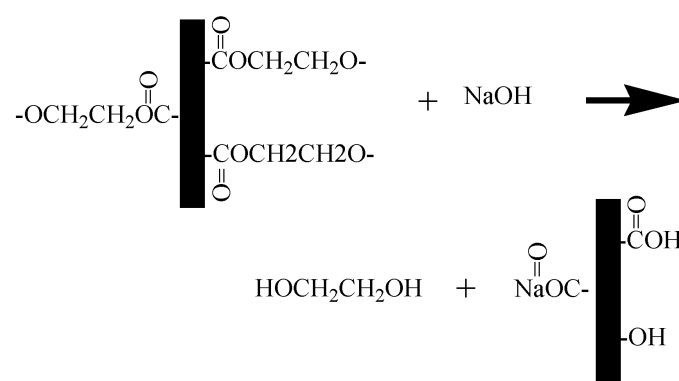

Figure 3. Hydrolysis of fiber with NaOH solution.

3.2. Surface modification analysis of the fabric

To further understand the tendency of fibers strength as shown in Fig. 2, the surface SEM was employed to characterize the morphology of untreated and treated fabric, which is shown in Fig. 4. As can be seen from Fig. 4(a1, a2), the fiber surface of the original fabric is very neat and smooth, and a few particles on the surface of the original fabric may be dust or sodium chloride particles not cleaned up during the preparation process [13]. After the fabric is treated with NaOH solution, extremely rough surface and cracks appear due to severe surface hydrolysis (etch effect), as shown in Fig. 7(b1, b2). It can be seen from Fig. 7(c1) that a white layer of KH550 coupling agent is coated on the fabric, and it is easy to think that some KH550 molecules can be filled into the defects (large holes and grooves) of the fabric (Fig. 7(c2)), which is the reason of the enhanced strength compared with that of NaOH-treated fabric (section 3.1).
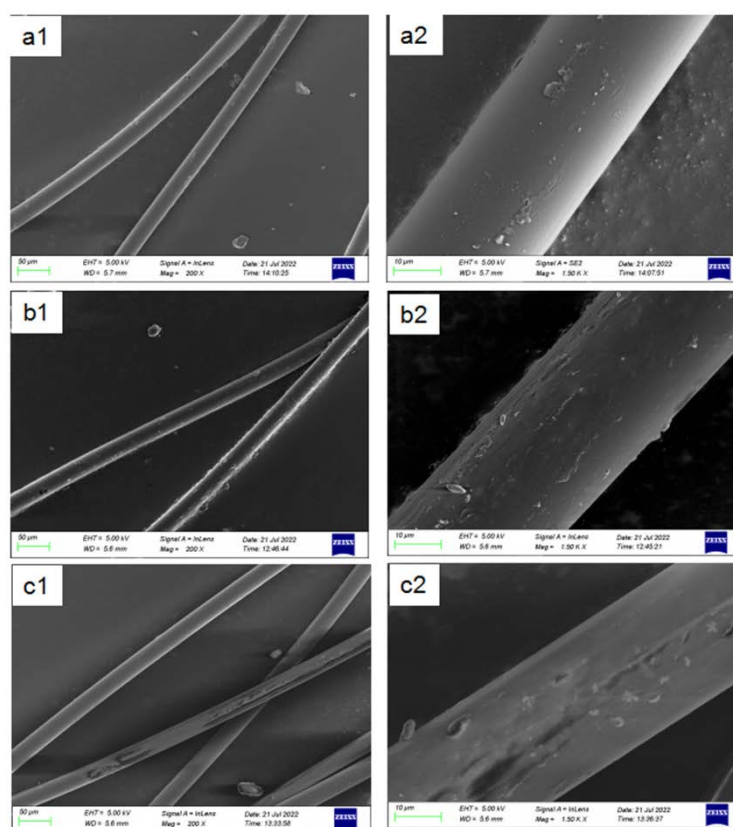
Figure 4. SEM images of fabric samples. (a1, a2) original fabric; (b1, b2) NaOH-treated fabric, (c1, c2) KH550-grafted fabric.

The chemical structures of KH550 is shown in Fig. 5(a), and it is hydrolyzed easily (Fig. 5(b)). When the NaOH solution treated fabric was immersed in the KH550 solution under ultrasonic condition, the sodium terephthalate on the surface was formed into terephthalic acid in aqueous solution, which reacted with the hydroxyl silane group (hydrolysate of KH550) and formed water molecule (Fig. 5(c)). Thus, the KH550 was grafted on the surface of the fabric and the strength was recovered after KH550 treatment.
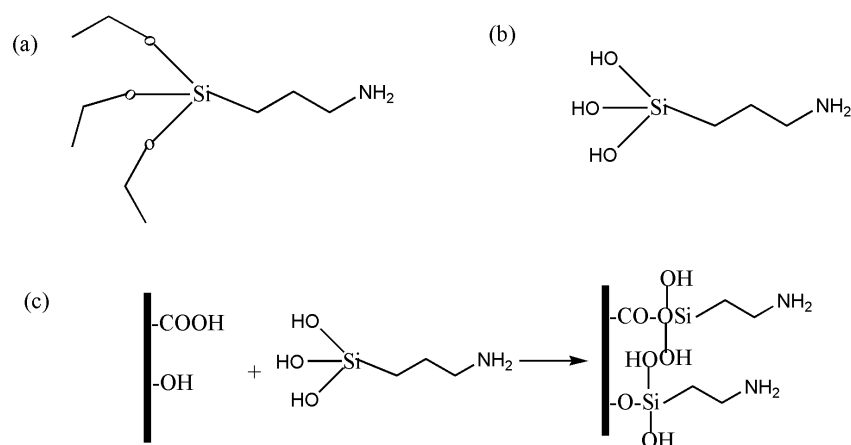

Figure 5. (a) chemical structures of KH550; (b)Schematic illustration of the hydrolysis of KH550 and (c) the reaction of KH550 with fabrics.

The infrared spectra of the fabrics modified by different process modes are shown in Fig. 6. The absorption peaks at 2969 cm^{-1} are the stretching vibration absorption peaks of

–CH$_2$–. The absorption peak at 1712 cm^{-1} is stretching vibration peak of C=O, and the absorption peaks at 1233 and 1013 cm^{-1} are the stretching vibration peaks of C–O–C, which are characteristic peaks of esters. The absorption peaks at 745 cm^{-1} are the bending vibration absorption peaks of –CH– in benzene ring [14,15]. As can be seen from the enlarged figure in Fig. 4(b), the characteristic peak of C-O of the polyester fabric changes from 1241 cm^{-1} to 1235 cm^{-1} after the NaOH solution and KH550 coupling agent which is caused by hydrolysis of ester group and the grafting coupling agent treatment [10].
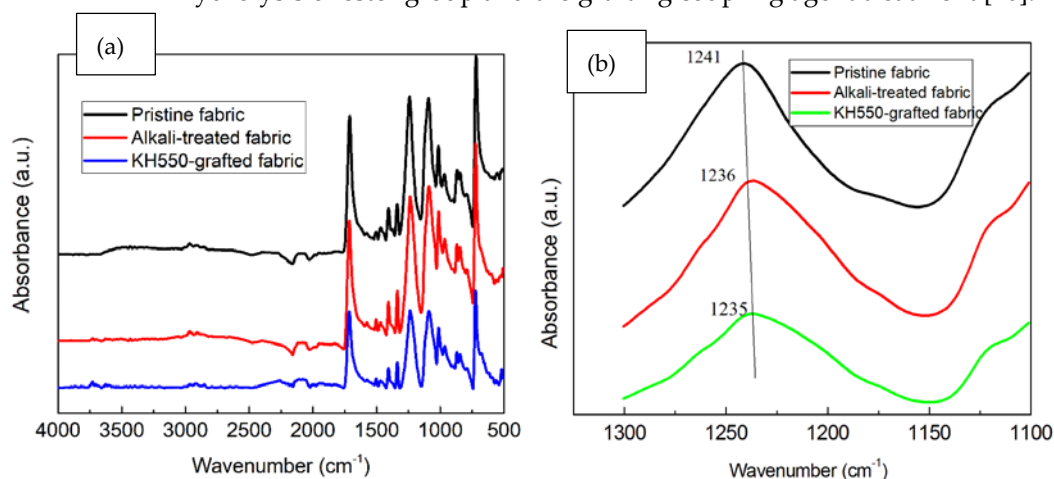

Figure 6. FTIR spectrum analysis of the fabric modified by different process modes. (a) wide scan spectra of FTIR; (b) FTIR spectrum with wavenumbers from 1300 cm^{-1} to 1100 cm^{-1}.

A TGA analysis of the pristine fabric, NaOH-treated fabric and KH550-grafted fabric is shown in Fig. 7. The residue rate of the pristine fabric is 14.1 wt%. In this temperature range (room temperature to 700 $^\circ$C), the PET fabric shows a large decomposition. After NaOH solution treatment, the residue rate of the NaOH-treated fabric is 11.1 wt%, because both severe surface hydrolysis of the NaOH-treated fabric and the resulting -OH and -COOH groups can be decomposed easily. The residue rate of 13.2 wt% is obtained after KH550 treatment, and at least the grafting rate of KH550 on fabric surface is 2.1 wt%. This also confirms that the KH550 molecules had been successfully grafted onto the fabric surface.
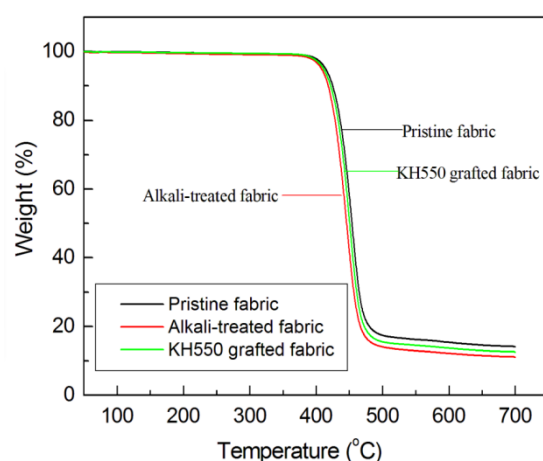

Figure 7. Weight loss as a function of time for pristine fabric, NaOH-treated fabric, KH550-grafted fabric.

3.3. Vulcanization characteristics of fabric rubber composite

The vulcanization process of the rubber is mainly divided into three stages, namely the induction period, the rapid vulcanization period and the flat vulcanization period [16].

The t_{10} is called the scorch time, also called the induction period, in which time the sample is gradually heated from the outside to the inside by the upper and lower cavities of the moving die. However, the rubber does not start to vulcanize and the rubber has good fluidity due to the shear thinning effect and increasing the temperature. The t_{90} is the time when the torque reaches 90% of the maximum torque and the rubber is rapidly cross-linked due to lots of free radicals generated by the rapid decomposition of vulcanizing agent, and the torque also increases rapidly.

The vulcanization curves of the fabric rubber composites are shown in Fig. 8, and the specific vulcanization parameters are shown in Table 1. As shown in Fig. 8 and Table 1, the vulcanization curves of fabric/rubber composites have a large change compared with pure rubber. It can be seen from Table 1 that the CRI of pure rubber is 17.95 min^{-1}, while the CRIs of fabric/rubber samples are lower than that of pure rubber. The reason for the decrease of the vulcanization rate maybe the diluting effect of fabric on vulcanizing agent. Obviously, the fabric and the coupling agent can postpone the vulcanization of rubber, especially at the interface between fabric and rubber in our research.
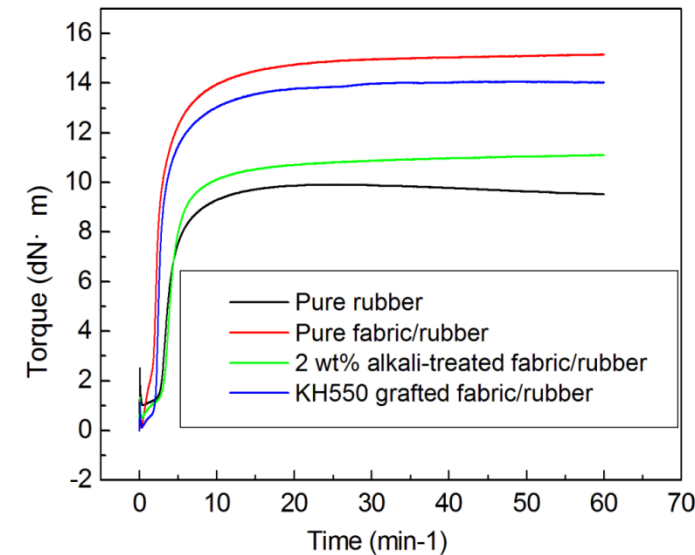

Figure 8. Vulcanization curves of samples (Pure rubber, Pure fabric/rubber, 2 wt% alkali-treated fabric/rubber, KH550 grafted fabric/rubber).

Table 1. Vulcanization parameters of samples (Pure rubber, Pure fabric/rubber, alkali-treated fabric/rubber, KH550 grafted fabric/rubber).

curing characteristics	pure rubber	original polyester/rubber	alkali-treated fabric/rubber	KH550 grafted fabric/rubber
M_H (dN·m)	9.91	15.16	11.11	14.05
M_L (dN·m)	1.01	0.12	0.50	0.12
t_{10} (min)	2.81	1.07	2.88	2.08
t_{50} (min)	3.62	2.33	4.02	2.66
t_{90} (min)	8.38	8.43	9.51	8.04
CRI (min^{-1})	17.95	13.59	15.08	16.78

3.4. Adhesion behaviors of the composites with alkali-treated fabric and KH550 grafted fabric

The peel strength tests are conducted to investigate the interfacial adhesion of fabric/rubber composites. The peel strength of fabrics under different treatments are shown in Fig. 9(a). The peel strength of the KH550 grafted fabric/rubber composites is higher than the others when the fabrics are modified by the KH550, which is increased 32% compared

with that of the original fabric/rubber composites. The peel curves of fabrics treated with different fabric surface treatment are shown in Fig. 9(b). It is also obvious that the KH550 grafted fabric treatment can improve the interfacial bonding effectively. In addition, it can be seen that the peeling curves of the alkali-treated fabric/rubber composites have greater modulus and fluctuations than the other peeling curves. This is because the peeling force is not only affected by the interfacial adhesion strength, but also by the shrinkage deformation of the fabric [17]. Obviously, the alkali-treated fabric can be deformed easily because the alkali-treated fabric is damaged to some extent.
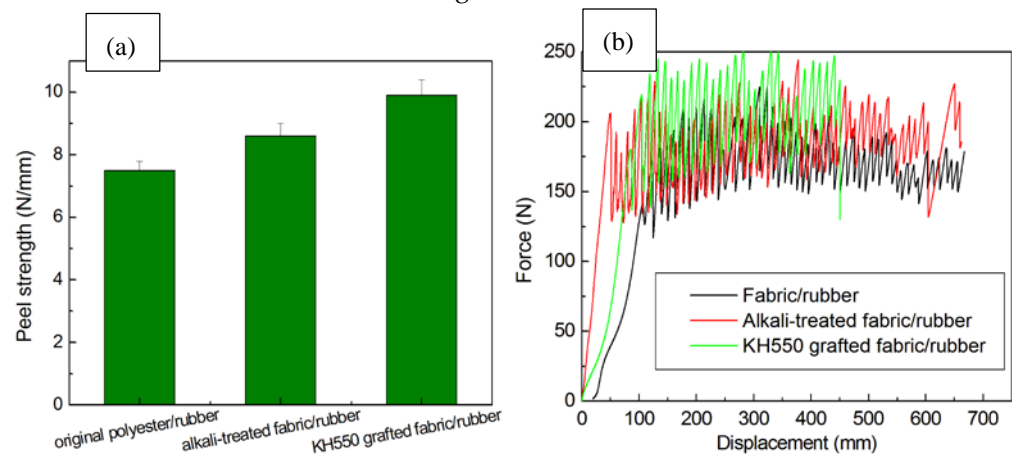

Figure 9. (a) Peel strength; (b) peel curves of fabric/rubber under different fabric surface treatments.

The photographs of the interfacial fracture surface of the fabric/rubber composites with alkali-treated and KH550 grafted after the 180° peel test are shown in Fig. 10. As can be seen from Fig. 10(a), the surface of the fabric is either bright and the rubber is black after the peeling test, and the visible surface of fabric can be observed, which indicates the interfacial adhesion is low. A wholly dark surface of fabric compared with that of the original fabric means that the surface of the fabric is partly covered by a layer of rubber, indicating the interfacial adhesion is larger than that the original fabric/rubber composites (Fig. 10(b)). A partly cohesive rubber failure occurs when the fabric is treated by alkali solution. As shown in Fig. 10(c), a large amount of rubber is adhered to the fabrics and the rubber layer also has a lot of holes (red circles). These characteristics indicate that a complete failure in the bulk of the fabric/rubber composites, not only the interfacial failure. Hence, KH550-grafted fabric/rubber composites have the strongest interfaces to resist stripping.
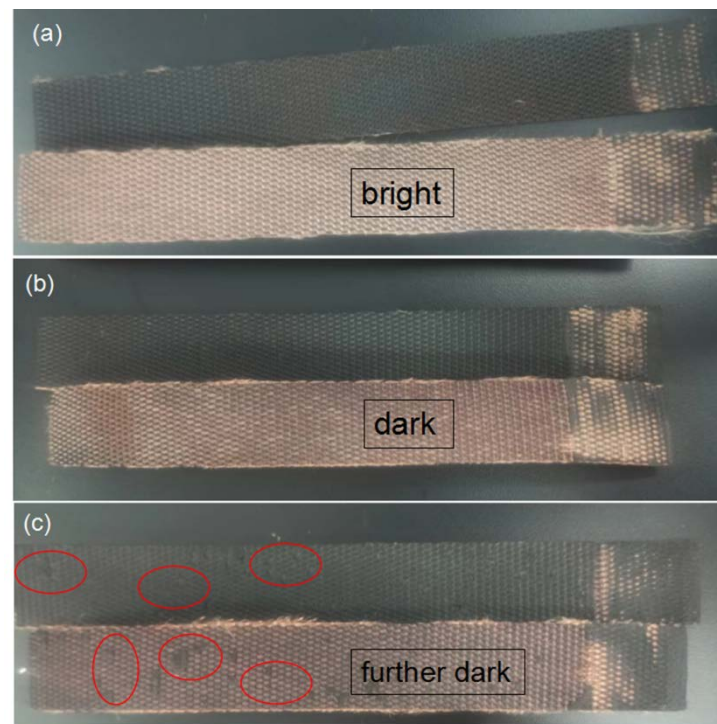
Figure 10. The photograph of interfacial fracture surface of fabric/rubber composites after the peel test. (a) original fabric/rubber, (b) 2 wt% alkali-treated fabric/rubber, (c) KH550-grafted fabric/rubber.

4. Conclusions

In this paper, an alkaline solution and a coupling agent treated fabric is developed to improve the problem of poor adhesion between the fabric and the rubber. The tensile strength of the fibers has not been seriously damaged after alkaline and coupling agent treatment. ATR-FTIR and TGA show the KH550 is grafted on the surface of the fabric and the strength is recovered after KH550 treatment. The peel strength is increased 32% compared with that of the original fabric/rubber composites. A complete failure in the bulk of the KH550-grafted fabric/rubber composites has been found, and this way can greatly improve the stripping resistance of fabric/rubber composites and expands their industrial applications.

Conflicts of Interest: The authors declare no conflict of interest.

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