Fibers and Polymers 2016, Vol.17, No.6, 910-916
DOI 10.1007/s12221-016-5928-7

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Effects of Surface Treatments on Mechanical Properties of Continuous Basalt Fibre Cords and Their Adhesion with Rubber Matrix

Zhuo Li*, Tongliang Xiao, and Shugao Zhao*

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-plastics, Qingdao University of Science & Technology, Qingdao 266042, China

(Received December 16, 2015; Revised May 18, 2016; Accepted May 21, 2016)

Abstract: To improve the mechanical properties and the adhesion to a natural rubber (NR)/styrene-butadiene rubber (SBR) matrix, continuous basalt fibre (CBF) cords with and without a silane coupling agent (3-aminopropyl)triethoxysilane (KH550) treatment were dipped into a typical resorcinol-formaldehyde-latex (RFL) system. The breaking force and elongation at break of the cords were tested using a universal testing machine. The adhesive properties were evaluated by both static mode and dynamic (fatigue) mode with H-shape cord-rubber samples. An elastomer testing system was employed to conduct the fatigue test, and the evolution of the adhesive properties between the CBF cord and the NR/SBR matrix was tracked. The interfacial fracture caused by H pull out and fatigue were both observed with a scanning electron microscope (SEM). The results of this investigation show that the RFL-dipping treatment can significantly improve the mechanical properties of the CBF cord and its adhesion to the NR/SBR matrix, and the pre-treatment of the CBF cord with KH550 can further improve the interfacial fatigue property.

Keywords: Continuous basalt fibre, Adhesion, Fatigue property, Mechanical properties, Surface treatment

Introduction

Recently, high-performance fibres have gained more and more attention as reinforcements for polymer-based composites from both industrial and academic worlds. Continuous basalt fibre (CBF), known as a type of natural mineral fibre, has been introduced into this field and has been studied [1] due to its excellent resistance to heat and cold, mechanical properties, chemical stability and relatively low cost. In addition, the increasing concern regarding environmental issues has also promoted the use of natural fibres [2,3]. With similar basic components but exhibiting a better performance, CBF is considered a serious competitor to glass fibre. New potential applications have been intensively investigated, though applications in the rubber industry, such as the use of CBF as a skeleton material, have seldom been mentioned.

In addition to the mechanical properties of a skeleton material, understanding the adhesion between the skeleton material and the rubber matrix is also very important [4]. The surface of CBF is smooth and lacks sufficiently reactive groups (except -OH), which leads to a relatively poor adhesion to the rubber matrix. So far, several types of surface treatment methods, such as acid or alkali etching, modification with silane coupling agents, surface coating, and plasma treatment, have been studied [5-8]. However, the previous work mainly focused on either the mechanical properties of CBF or the adhesion to thermoplastic/thermoset resin matrices, while little research was conducted on CBF/rubber composites. Actually, to improve the adhesion between a skeleton material, for example, nylon, polyester and aramid cords, and a rubber matrix, the resorcinol-formaldehyde-latex (RFL) system and its modified versions have been shown to be an effective solution, and RFL-dipped cords have been widely used in a series of rubber products, such as tires [4,9, 10]. The structure of cured RFL has been viewed as a continuous resin phase with dispersed latex particles, and the morphology of RFL proposed is shown in Figure 1 [11-13]. During vulcanizing, the sulphur from the rubber matrix

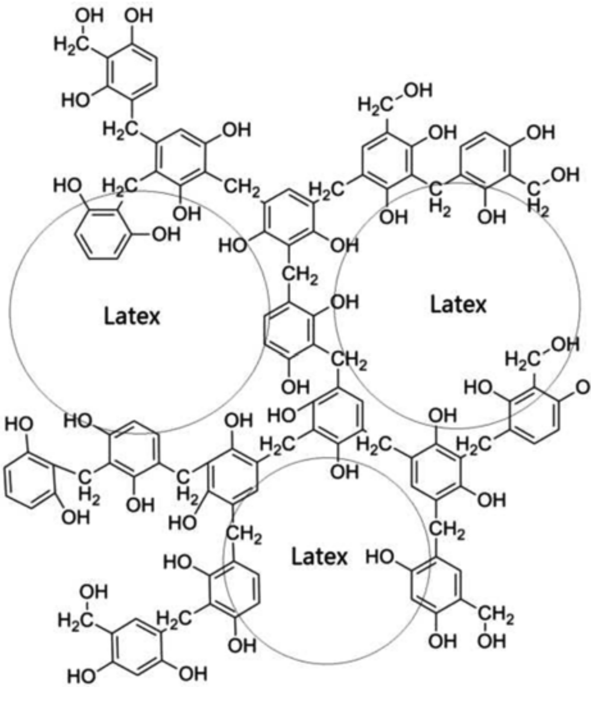

Figure 1. Proposed RFL morphology [13].

---

*Corresponding author: lizhuoqust@126.com

*Corresponding author: zhaosgqd@hotmail.com diffuses into the RFL layer, and sulphur cross-links form between the latex portion of RFL and the rubber matrix. Shirazi *et al*. [14] also reported that for a peroxide cured system, bonding happens between rubber and both the latex and resin parts of RFL. However, the effects of RFL dipping on the mechanical properties of CBF cord and its adhesion to a rubber matrix have not yet been studied.

An evaluation of the adhesive properties between CBF cord and the rubber matrix is also very important when considering the applicability of a CBF skeleton for rubber products. Normally, cord-rubber adhesion strength should be evaluated in both static and dynamic modes, considering the actual service conditions of rubber products. The H pull-out test is a type of standardized test method (ASTM D4776, GB/T 2942, etc.) and is usually employed to investigate the static adhesive property of raw materials to characterize the quality. For rubber products, the dynamic adhesive property is more important in determining the service life of an adhesive interface because under actual service conditions, rubber products normally experience periodic extensional and compressional forces. To date, there is no special standard for the testing of dynamic adhesive properties, but the fatigue test is a common approach to simulate the cyclic strain or stress an actual product might experience. Some studies have mentioned using the fatigue test on cord-rubber systems to estimate the dynamic adhesive properties for nylon, polyester and steel cord [15-19], and the fatigue resistance of the cord was also studied [20]. Jamshidi *et al*. [4] investigated the relationships between dynamic measurements and the static adhesion test, aiming to simplify the prediction of the durability of the system.

Based on a review of the literature, there is little information available on the applications of CBF as a skeleton material in rubber products, and the surface treatment method developed for rubber-based composites has not yet been mentioned. The present study was performed to focus on the effects of RFL dipping on the mechanical properties of CBF cords and their adhesion to a NR/SBR matrix. Aiming to further improve the adhesion, the use of a silane coupling agent (3-aminopropyl)triethoxysilane (KH550), which has been approved to be effective in improving the adhesion between basalt fibre and thermoset matrices [21-24], was also discussed as a pre-treatment that was applied to the CBF cords before RFL dipping, and the results were compared with those of directly RFL-dipped samples. An MTS Elastomer Test System (MTS) was employed to simulate displacement-control conditions and to record the evolution of interfacial adhesive properties; the interfacial fractures caused by fatigue were observed with SEM.

Experimental

Materials

CBF (BC11-200) was supplied by Sichuan Aerospace Tuoxin Industrial Co., Ltd., and CBF cord (200 tex/3) was produced by Shandong Tianhengfiber Co., Ltd. KH550 was purchased from Lvxun Chemical, Kunshan, China. The composition of the rubber compound used in this study is shown in Table 1. NR (SMR 10) was from Malaysia, and SBR (ESBR 1502) was supplied by Sinopec Qilu Co., Ltd. ZnO was supplied by Zhenjiang Hakusui Chemical Co., Ltd. Stearic acid was supplied by Qingdao Kangan Rubber Technical Co., Ltd. Carbon black N330 and carbon black N660 were purchased from Kabote (China) Investment Co., Ltd. Polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ) was supplied by Sinopec Nanjing Chemical Industries Co., Ltd. Dibenzothiazole disulfide (MBTS) and tetramethyl thiuram disulphide (TMTD) were supplied by Puyang Willing Chemicals Co., Ltd. Aromatic oil (VIVATEC 500) was supplied by Hansen & Rosenthal Group. The adhesive agents RA (methylene donor) and RE (Acetaldehyde-resorcinol copolymer) were supplied by Wuxi Huasheng Rubber Technical Co., Ltd. Insoluble sulphur was supplied by China Sunsine Chemical Holdings Co., Ltd. The RFL (resorcinol-formaldehyde-latex) dipping system was supplied by Shandong Tianhengfiber Co., Ltd. Other reagents were commercially available and used as received.

Table 1. Rubber compound composition

Component	Content (phr)
NR	90
SBR	10
ZnO	3
Stearic acid	2
Carbon black N330	5
Carbon black N660	30
TMQ	2
Aromatic oil	3
RA	0.8
RE	0.6
MBTS	1.2
TMTD	0.03
Insoluble sulphur	2.5

Surface Treatments of CBF Cords

Desizing

To remove the sizing and any other dirt on the surface, CBF cords were desized by soaking in acetone for 50 min, then washed with distilled water, and dried in vacuo at 105 °C for 30 min to obtain CBF-D.

Modification with KH550

A water/alcohol (1:1 mass ratio) solution containing 0.75 wt% KH550 was prepared, and it was left standing for 5 min. The desized CBF cords were soaked in the solution for 30 min at room temperature, and then the wetted cords were dried at 120 °C for 1 h to obtain CBF-K.

RFL Dipping

Each of the CBF-D and CBF-K cords was fixed at one end and stretched with a 50 g weight, then dipped into the RFL solution for 6 s and dried at 170 °C for 2 min. CBF-DRFL and CBF-KRFL were correspondingly obtained in this step.

H-shape Specimen Preparation

H-shape specimens were prepared separately using CBF-D, CBF-K, CBF-DRFL, CBF-KRFL and the rubber compound, and the H-shape specimens were named H-D, H-K, H-DRFL, and H-KRFL, respectively. According to ASTM D4776, the rubber compound parts were placed in the channels of a die, and the cords were placed on the rubber and then another set of rubber pieces was used to cover the top. Each cord was stretched with a 50-g weight. Samples were vulcanized at 145 °C for 14 min under a pressure of 6 MPa. Finally, the vulcanized samples were cut into H-shape specimens.

Measurement

The curing characteristics of the rubber compound were measured with a moving die rheometer (MDR) 2000 from Alpha Technologies, America. The tensile properties of the CBF cords were tested with a GOTECH AI-7000-M universal testing machine at a drawing rate of 200 mm/min; the gauge length of the tested cord was 250 mm. The morphological characterization of the surface of the CBF cords and the interfacial fracture of the composites were tested with a JEOL JSM-7500F scanning electron microscope (SEM). Energy dispersive X-ray spectrometer (EDS) results of desized CBF were obtained with an SEM equipped with an EDS Inca X-Max manufactured by Oxford Instruments. The H pull-out tests were performed on a Zwick Z020 materials testing machine according to ASTM D4776. The dynamic adhesive properties were tested on an MTS Elastomer Testing System (831.50) under displacement-control mode with a loading frequency of 5 Hz, and the loading mode was a sine wave. The applied displacements were 5 mm, 6 mm and 7 mm.

Results and Discussion

Surface Treatments of the CBF Cords

To remove the sizing agent applied during the production and any other dirt on the surface of CBF, desizing is usually required before further surface treatments of CBF cords. Normally, there are two options for desizing, namely heat treatment and immersion with acetone or toluene. In the case of the CBF cord, thermal treatment, usually requiring 300 °C or above, does not represent a feasible solution. In this study, a tensile test showed that after exposure to 300 °C for 1 h, the breaking force and elongation at break of the CBF cord dropped to 49 % and 61 %, respectively. This severe decrease in mechanical properties can be attributed to a change in the crystalline structure of CBF [25]. By contrast, immersion with acetone had little effect on the mechanical

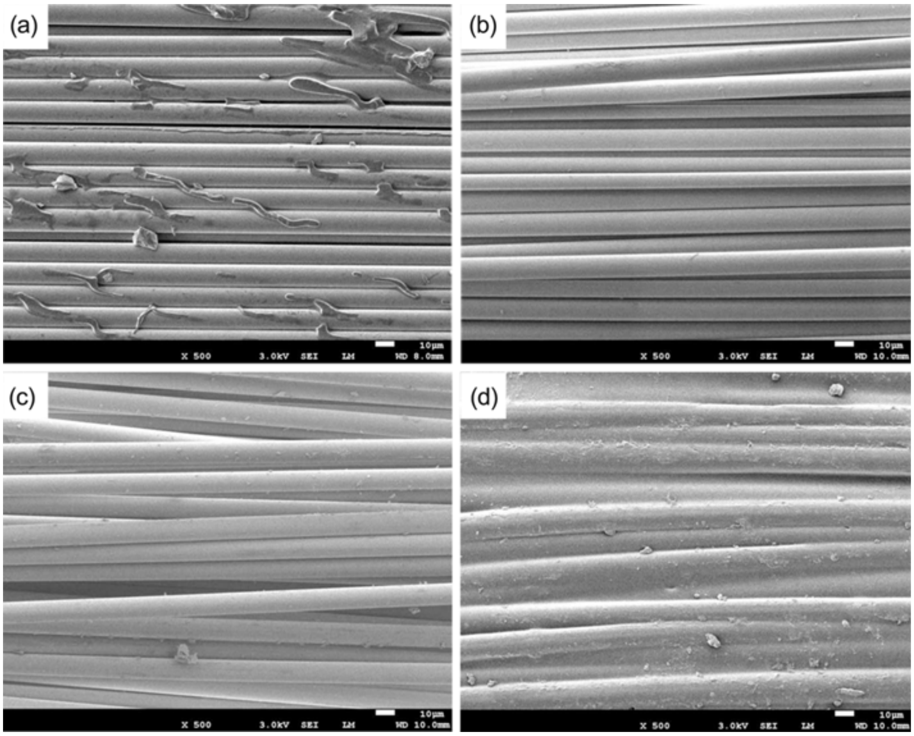

Figure 2. SEM images of the CBF cords (500X); (a) the initial CBF cord, (b) CBF-D, (c) CBF-K, and (d) CBF-KRFL.

Table 2. The EDS results of desized CBF cord surface

	Si	Al	Fe	Ca	K	Na	Mg	Ti
Element content (wt. %)	45.58	12.00	17.32	14.52	1.37	2.08	4.81	2.31

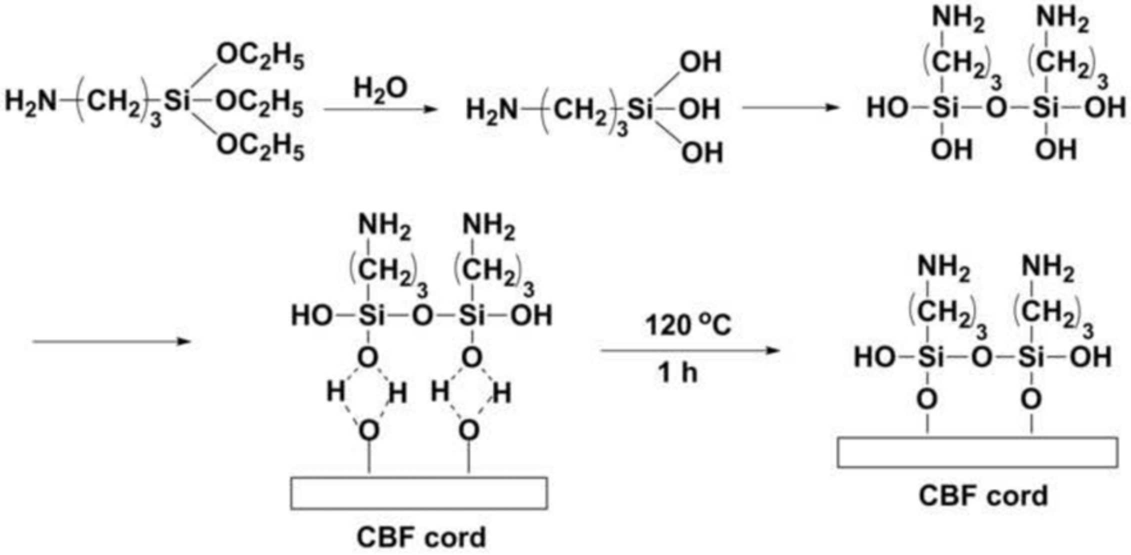

Figure 3. Mechanism for the grafting reaction of KH550 onto the CBF cord.

properties of the CBF cord.

SEM images of the initial CBF cord and CBF-D, which is the CBF cord that was desized by immersion in acetone, are shown in Figure 2(a) and (b), respectively, and the EDS results of the surface of the desized CBF cord are given in Table 2. The findings show that acetone can successfully remove the sizing agent from the surface of CBF. The desized CBF has a very smooth surface, which is not conducive to adhering to the rubber matrix. Therefore, a modification with KH550 and an RFL dipping treatment were applied in this study. The mechanism behind the grafting reaction of KH550 onto the CBF cord is shown in Figure 3. A covalent bond between the -OH groups on the CBF cord and KH550 is formed. The morphological characterizations of CBF-K and CBF-KRFL are shown in Figure 2(c) and (d).

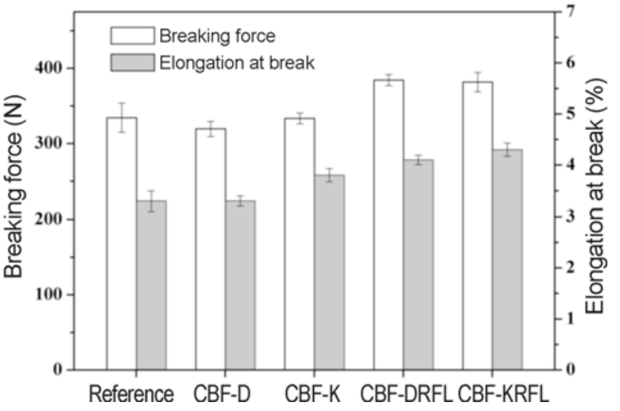

Figure 4. Mechanical properties of the CBF cords. Reference: the initial CBF cord without any treatment.

Mechanical Properties of the CBF Cords

The mechanical properties of the CBF cords, including breaking force and elongation at break, were evaluated by a tensile test, and the results are shown in Figure 4. As a type of inorganic fibre cord, the CBF cord has a good breaking force but a limited elongation at break. After the desizing process, the sizing agent, which is applied to improve the bundling and to reduce the abrasion between CBF filaments during production, is removed, and the breaking force is slightly reduced. To some extent, KH550, besides providing a good sub-base for the following treatment with the RFL system, plays a similar role as the sizing agent.

As is presented in Figure 4, the RFL dipping greatly helped to improve the tensile properties of the CBF cord. Compared with CBF-D, the breaking force and elongation at break of CBF-DRFL were enhanced by 20 % and 24 %, respectively. It can be observed from Figure 2(d) that a layer of the RFL adhesive system was sufficiently coated on the CBF cord. The RFL layer is flexible, bonds the filaments together, and covers microcracks or other defects in the filaments. When the cord was stretched, the stress was evenly distributed, so the breaking force significantly increased. The results also indicated that the pre-treatment with KH550 did not improve the mechanical properties of the RFL-dipped CBF cord. This may be due to the major enhancements in thickness and flexibility that were already provided by the RFL layer.

H Pull-out Test

Figure 5 shows the H pull-out results for the different cords. Though the desizing process could help improve the adhesion to the matrix due to the cleaning effect, the H pull-out force was only 48.2 N for the H-D sample. As shown in Figure 2(b), the smooth surface of CBF, apart from lacking enough reactive groups, is also a big disadvantage to achieving adhesion to the rubber matrix. After the RFL dipping of the CBF cord, the H pull-out force increased to 119.0 N, which is approximately 147 % higher than that of H-D. A possible mechanism behind the interfacial adhesion between the RFL-dipped CBF cord and NR/SBR is shown in Figure 6. Stable interactions form between the molecular chains of latex and the matrix during vulcanization, and hydrogen bonds form between the -OH groups of the CBF cord and -OH or pyridine groups of RFL. Furthermore, the mechanical friction force may also contribute to this improvement. In addition, the modification by KH550 as a pre-treatment can slightly improve the adhesion; the H pull-out force of H-KRFL was raised to 128.1 N, which is approximately 8 % higher than that of H-DRFL. This slight improvement may be due to the increase in surface groups capable of hydrogen bonding that was introduced by KH550, but the effect of this

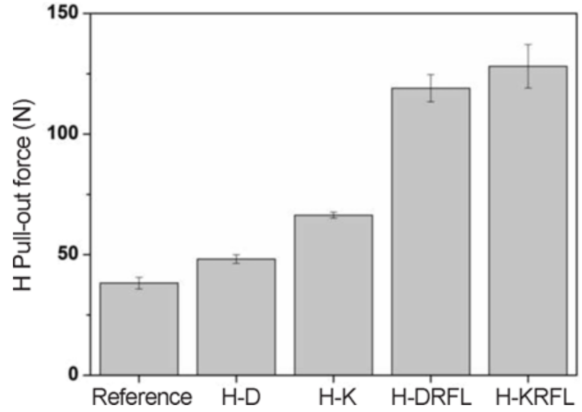

Figure 5. H pull-out force of the CBF cords. Reference: the initial CBF cord without any treatment.

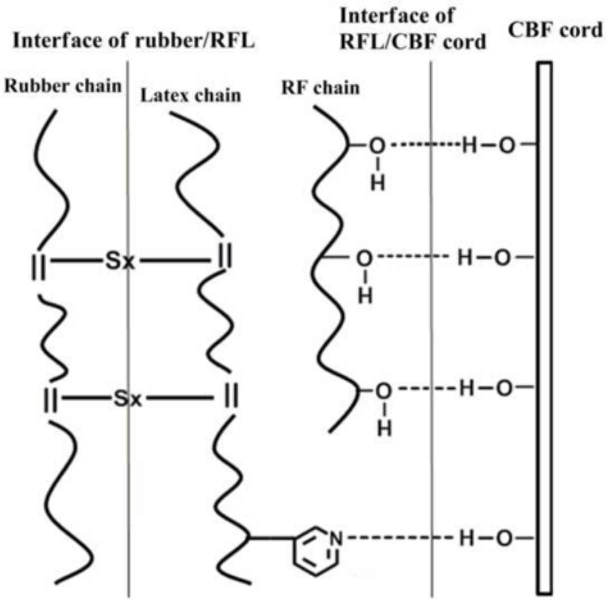

Figure 6. Possible mechanism for the adhesion between the RFL-dipped CBF cord and the NR/SBR rubber matrix.

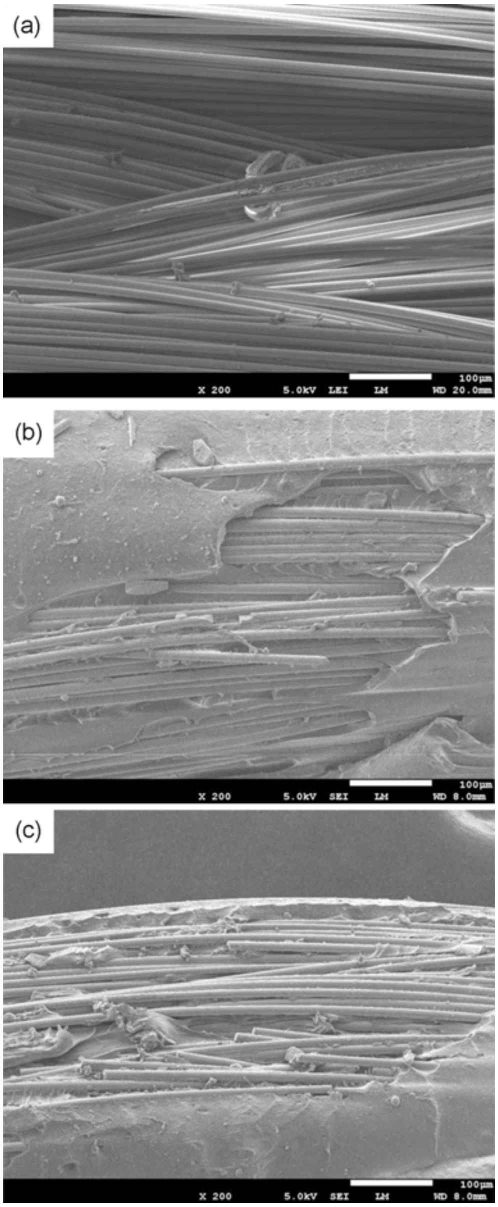

Figure 7. SEM images of the interfacial fracture morphologies after the H pull-out test (200X); (a) H-D, (b) H-DRFL, and (c) H-KRL.

pre-treatment is limited when considering static adhesion. Figure 7 shows the interfacial fracture morphology after the H pull out of H-D, H-DRFL and H-KRFL. The rubber pulled out with the RFL-dipped cord was greater than the desized one because of the improved adhesion, but H-DRFL and H-KRFL showed very similar interfacial fracture morphologies after the H pull-out test.

Fatigue Test

To study the adhesion between the CBF cord and the rubber matrix under dynamic mode conditions, a fatigue test was conducted with the MTS, and the H-shape specimens were used. The tensile force was loaded along the direction of the cord as a sine wave under a series of displacement-control modes [26]. As is shown in Figure 8, in pace with the number of fatigue cycles as they increased, the change in load was recorded. The change in the tensile force could reflect the interfacial shear force, and in this study, the number of fatigue cycles that led to a decrease in load to 10 N was defined as the "fatigue life" of the adhesive interface. At this point, the cord and matrix were mostly separated. The fatigue life should be affected by both initial adhesion strength and the damage rate of the interface. In this study, the RFL dipping significantly improved the fatigue properties of the adhesive interface. As tested, at a 5-mm displacement, the adhesion failure of H-D happened within only 1000 cycles, and the fatigue life of H-D dropped to a few cycles if the displacement was raised to 6 mm or 7 mm, which was attribute to the limited adhesion strength. In addition to the chemical bonding between the RFL-dipped CBF cord and the NR/SBR matrix, the 3-D network structure of the RF resin and the flexibility of the latex also contributed to the fatigue life improvement by evenly distributing the shear stress across the surface of the cord, so that the damage rate was slowed down.

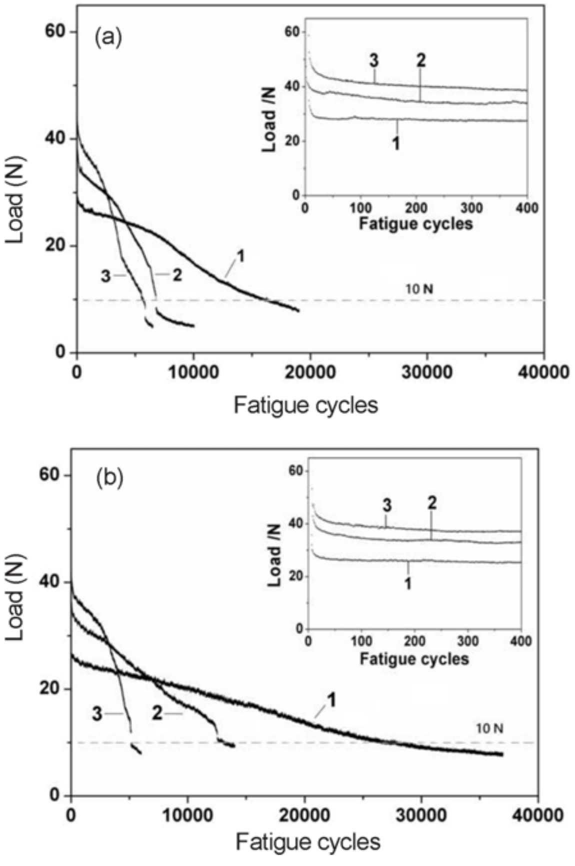

Figure 8. Fatigue curves for the displacement-control modes. Displacement: 1-5 mm, 2-6 mm, and 3-7 mm. Frequency: 5 Hz. (a) H-DRFL and (b) H-KRFL.

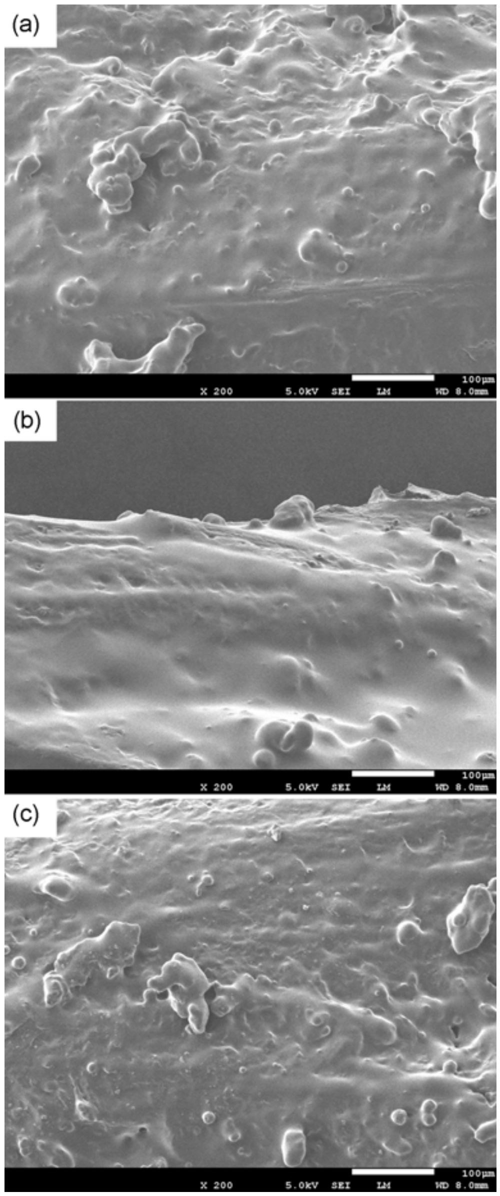

Figure 9. SEM images of the surfaces of pulled-out cords of H-KRFL caused by fatigue failure (200X); (a) 5 mm, (b) 6 mm, and (c) 7 mm.

Though pre-treatment with KH550 provided a limited effect on the static adhesion between the RFL-dipped CBF cords and the rubber matrix, the MTS result indicated that the fatigue properties were significantly improved when the CBF cord was modified with KH550, especially under low displacement conditions. As shown in Figure 8, when the displacements were the same for H-DRFL and H-KRFL, the initial loads of the two were similar. However, H-KRFL exhibited an extended fatigue life, particularly at displacement of 6 mm and 5 mm. For example, the fatigue life of H-KRFL was approximately 27,000 cycles, while that of H-DRFL was approximately 16,000 cycles with a displacement of 5 mm. This improvement may be due to the ability of KH550 to enhance the adhesion between the CBF and RFL layer, which can further mitigate the local concentration of the shear stress during fatigue, and the RFL layer becomes more effective as a flexible transition layer. When the displacement was increased, the initial load increased and the fatigue lives were reduced for both H-DRFL and H-KRFL. The effect of the KH550 pre-treatment was limited when the displacement was 7 mm, which was similar to the results of the H pull-out test, which should be due to the relative large initial load.

The interfacial fracture morphologies of H-KRFL, after being under a series of displacement-controlled conditions, are shown in Figure 9. Different from the H pull out, the failure caused by fatigue happened inside the rubber matrix, and the change in controlled displacement did not show much of an effect on the fracture morphologies. It can be speculated that the breaking of rubber molecular chains should be the main reason for the fatigue failure of the composites.

Conclusion

We conclude the following:

1. Dipping with RFL is an effective method to improve the mechanical properties of the CBF cord.
2. The H pull-out force of the CBF cord increased by approximately 147 % after being dipped in the RFL system; the fatigue properties of the adhesive interface between the CBF cord and the NR/SBR matrix were also significantly improved.
3. Modification with KH550 as a pre-treatment of the CBF cord had a limited effect on improving the mechanical properties of the cord and its static adhesion to the NR/SBR rubber matrix, but it can significantly improve the fatigue properties of the adhesive interface.

Acknowledgement

This work was supported by the Postdoctoral Foundation of Qingdao.

References

1. V. Fiore, T. Scalici, G. Di Bella, and A. Valenza, *Compos. Pt. B-Eng.*, **74**, 74 (2015).
2. V. Lopresto, C. Leone, and I. De Iorio, *Compos. Pt. B-Eng.*, **42**, 717 (2011).
3. A. Greco, A. Maffezzoli, G. Casciaro, and F. Caretto, *Compos. Pt. B-Eng.*, **67**, 233 (2014).
4. M. Jamshidi and F. A. Taromi, *J. Adhes. Sci. Technol.,* **20**, 1693 (2006).
5. V. Manikandan, J. T. W. Jappes, S. M. S. Kumar, and P. Amuthakkannan, *Compos. Pt. B-Eng.*, **43**, 812 (2012).
6. J. M. Espana, M. D. Samper, E. Fages, L. Sanchez-Nacher, and R. Balart, *Polym. Compos.*, **34**, 376 (2013).
7. B. Wei, H. L. Cao, and S. H. Song, *Compos. Pt. A-Appl. Sci. Manuf.*, **42**, 22 (2011).
8. G. J. Wang, Y. W. Liu, Y. J. Guo, Z. X. Zhang, M. X. Xu, and Z. X. Yang, *Surf. Coat. Technol.*, **201**, 6565 (2007).
9. T. S. Solomon, *Rubber Chem. Technol.*, **58**, 561 (1985).
10. G. R. Hamed and C. Ruksakulpiwat, *J. Appl. Polym. Sci.*, **91**, 1993 (2004).
11. G. Gillberg, L. C. Sawyer, and A. L. Promislow, *J. Appl. Polym. Sci.*, **28**, 3723 (1983).
12. M. Shirazi, M. B. de Rooij, A. G. Talma, and J. W. M. Noordermeer, *J. Adhes. Sci. Technol.*, **27**, 1886 (2013).
13. W. B. Wennekes, R. N. Datta, and J. W. M. Noordermeer, *Rubber Chem. Technol.*, **81**, 523 (2008).
14. M. Shirazi, A. G. Talma, and J. W. M. Noordermeer, *J. Adhes. Sci. Technol.*, **27**, 1048 (2013).
15. A. I. Abou-Kandil, A. Awad, N. Darwish, A. B. Shehata, and B. K. Saleh, *Int. J. Adhes. Adhes.*, **44**, 26 (2013).
16. M. P. Wagner and N. L. Hewitt, *J. Elastomers Plast.*, **10**, 95 (1978).
17. Y. M. Chen and Y. Zhang, *Tire Industry*, **34**, 188 (2014).
18. M. Jamshidi, F. Afshar, and B. Shamayeli, *J. Appl. Polym. Sci.*, **101**, 2488 (2006).
19. X. Y. Shi, M. Q. Ma, C. B. Lian, and D. W. Zhu, *Polym. Test.*, **32**, 1145 (2013).
20. A. K. Naskar, A. K. Mukherjee, and R. Mukhopadhyay, *Polym. Degrad. Stabil.*, **83**, 173 (2004).
21. J. M. Park and R. V. Subramanian, *J. Adhes. Sci. Technol.*, **5**, 459 (1991).
22. J. M. Park and R. V. Subramanian, *J. Adhes. Sci. Technol.*, **8**, 1473 (1994).
23. T. Deak, T. Czigany, P. Tamas, and C. Nemeth, *Express Polym. Lett.*, **4**, 590 (2010).
24. Y. L. Liu, S. J. Shen, L. Zhang, and L. M. Shao, *Adv. Mater. Res.*, **236-238**, 1467 (2011).
25. J. Militky, V. Kovacic, and J. Rubnerova, *Eng. Fract. Mech.*, **69**, 1025 (2002).
26. X. Y. Shi, C. B. Lian, Y. Y. Shang, and H. Y. Zhang, *Polym. Test.*, **48**, 175 (2015).