Aging and tribological behavior of styrene butadiene rubber conveyor belts under combined seawater dry-wet conditions

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Keywords: styrene butadiene rubber, conveyor belt, seawater, dry–wet cycles, wear mechanisms

Abstract

In this study, the aging and tribological behaviors of styrene butadiene rubber (SBR) conveyor belts exposed to seawater dry–wet cycles were investigated. Using hardness as a measure of the aging performance, the worst seawater dry-wet (W-SDW) cycle conditions were selected using an orthogonal design method, the study was conducted based on such conditions. The changes in SBR surface properties and tribological properties with aging time before and after aging and the degree were investigated by using a hardness tester, SEM, EDS, etc. The performance degradation, microscopic morphological changes of wear surface, and evolutionary behavior of wear mechanism of styrene-butadiene rubber conveyor belt after aging by dry and wet cycles of seawater were discussed. The results show that the most severe combination of wet-dry cycles of seawater for the aging of SBR conveyor belts comprised a soak temperature of 45 °C, soak time of 12 h, drying temperature of 100 °C, and drying time of 9 h. The total surface discoloration of the conveyor belt increases as the number of W-SDW cycles increases, along with the hardness. The friction coefficient of the belt increases with increasing load and decreases with the increasing number of W-SDW cycles. The mass loss increases gradually with the number of W-SDW cycles and load. The wear mechanism gradually changes from fatigue wear to the damage mechanism of coexistence of adhesive wear and fatigue.

1. Introduction

With the advantages of a long conveying distance, large conveying volume, and high operational reliability, belt conveyors are widely used in coal, construction, and marine engineering. The belt conveyors used in offshore projects are in a complex marine environment for a long time, especially with alternating sunny and rainy days, high temperatures and high humidity, and the dry and wet cycles of seawater caused by the alternating action of sea winds and waves. The conveyor belt is the carrying and pulling mechanism of the belt conveyor, and accounts for more than 40% of its total cost [1, 2]. The actual working conditions of the belt conveyor are more complex, and they inevitably face aging and wear problems. These problems directly or indirectly affect the performance of the conveyor belt and can cause problems such as belt runout and reduced strength [3, 4], which greatly shorten the service life of the belt and can even cause belt breakage accidents. It is therefore essential to investigate the ageing properties and tribological patterns under the wet and dry cycles of seawater.

Aging and wear are the main factors leading to belt failure during the service of a belt conveyor [5–7]. The problem of aging and wear of rubber products such as conveyor belts has received extensive attention from scholars at home and abroad. Matthews et al [8] focused on the friction and surface properties of polytetrafluoroethylene and silicone rubber conveyor belts. They showed that silicone rubber has a more stable adhesion at high temperatures as well as a higher coefficient of friction. Zhang et al [9] studied the tribological behaviour of steel wire rope and nylon skeleton conveyor belts under different loads and different rates. Hardened steel balls were used to form a friction pair with the conveyor belt. The study shows that the wear of both conveyor belts increases with increasing load and the friction coefficient of both belts increases and then
decreases with increasing pressure. However, there are few reports on the systematic evaluation of the tribological properties of rubber after aging. Dong et al.\cite{10} carried out dry sliding wear experiments on ageing NBR and mating metal pin-disc contact. The results show that the friction factor, wear rate and surface roughness of the mating metal increase with increasing ageing temperature and time, and the wear mechanism is mainly fatigue wear. Li Bo et al.\cite{11} found that the wear mechanism of nitrile butadiene rubber under thermal and oxygen aging environments was mainly based on fatigue wear and abrasive wear. He et al.\cite{12} investigated the mechanical and tribological properties of cerium oxide/silicon blended rubbers after thermal oxidative aging, and observed increases in the crosslink density, elongation at break, tensile strength and tribological behavior in the later stages of thermal oxidative aging. Roche et al.\cite{13} also investigated the tribological properties of ion-modified hydrogenated NBR after ageing, while the results showed that thermal-oxidative ageing and tensile fatigue had little effect on the tribological properties of the rubber material.

As most of the studies on the aging and tribological behavior of conveyor belts have been conducted in land-based environments, very little consideration has been given to the application of belt conveyors in the coastal engineering sector. Belt conveyor belts are permanently exposed to a complex coastal environment represented by wet and dry seawater\cite{14}. In view of this, this study conducted dry-wet cycle experiments on styrene butadiene rubber (SBR) conveyor belts. On the basis of accelerated aging tests on conveyor belts, the influence of the degree of aging on the performance of conveyor belts was analyzed. Subsequently, reciprocating friction wear experiments were carried out using the ball-plane contact method, and the effects of belt aging on the time-varying curve of the friction factor, wear weight loss, and damage mechanisms were systematically investigated. In order to provide a theoretical reference for the prevention of aging failure and anti-wear and friction reduction of conveyor belts.

2. Experimental

2.1. Sample and seawater preparation
SBR conveyor belts and 316L stainless steel were selected as the test materials for the friction subsets in the experiments. In particular, the upper specimen was an AISI 316L stainless steel ball (7.94 mm diameter). The lower specimen is an SBR conveyor belt with 1721 SBR as the cover layer and cotton canvas as the tensile body. 1721 SBR composition is 137.50 parts SBR, 3 parts zinc oxide, 1.75 parts sulphur, 1.00 parts stearic acid, 68.75 parts carbon black N220 and 1.38 parts TBBS. Table 1 lists the main physical properties of the friction substrate.

Seawater with a pH of 8 was prepared using deionized water according to ASTM D 1141–1998 (2013) standard practice for alternative seawater preparation. The chemical composition of the simulated seawater is shown in table 1. The reagents listed in table 2 were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Orthogonal design
The soak temperature, soak time, drying temperature, and drying time were selected as the key factors for the orthogonal design of L9 (34) based on a single-factor test. Base on the time–temperature equivalence principle, the maximum temperature of the tropical sea surface (30 °C) and land surface temperature in summer (70 °C) were selected as the lower limits of the seawater and drying temperatures\cite{15}, respectively, as summarized in table 3.
One seawater dry-wet cycle was divided into two steps: (i) immersion in seawater for a given time and temperature, and; (ii) drying in an oven for a given time and temperature. After every five completed cycles, the specimens were ultrasonically cleaned in distilled water at 30 kHz for 5 min, dried at 100 °C for 30 min, and sealed for use. Using hardness as a measure of ageing, the worst cycle combination for ageing was analysed by orthogonal tests and used as the worst combination of wet-dry seawater (W-SDW) cycles. The seawater immersion and oven baking is a minor cycle and five minor cycles are a major cycle, the test goes through four major cycles in total.

2.3. Characterization

2.3.1. Surface properties
Color difference tests were performed according to CIE 1976 (L a b) using an SR-62 precision colorimeter. The results were averaged from at least 10 replicates and expressed as the total degree of discoloration (ΔE) for quantification, using equation (1).

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\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}
\] (1)

In the above, ΔL, Δa, and Δb represent the differences in black-white, red-green, and yellow-blue, respectively.

Hardness tests were performed in accordance with GB/T 531.1–2008 using an LX-D-1 shore hardness tester. The results were averaged over a 0–44.5 N indenter pressure range for at least five replicate tests.

2.3.2. Wear tests
Friction experiments were conducted according to GB/T 40721–2021 using an MMW-1A microcomputer-controlled universal friction and wear testing machine (as shown in figure 1) at a speed of 50 mm min\(^{-1}\) and a friction time of 30 min. Loads of 10, 50 and 100 N were chosen. The driving motor drives the main shaft, and the friction pair is connected with the main shaft through the tie rod to rotate synchronously with the main shaft. During the test, the loading system transfers the experimental force to the experimental force transducer, which

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**Table 3. Factors and levels of orthogonal test.**

| Factors          | Codes | Units | Levels |
|------------------|-------|-------|--------|
| Soaks temperature| X₁    | °C    | 30 45 60 |
| Soaks time       | X₂    | h     | 4 8 12 |
| Drying temperature| X₃   | °C    | 70 85 100 |
| Drying time      | X₄    | h     | 3 6 9 |
in turn is transferred downwards from the spindle to the specimen. The experimental force is measured by the
force transducer on the specimen. The frictional sub is rotated under certain pressure and the frictional force is
transmitted to the frictional torque sensor via the spindle. The specimen had a thickness of 10 mm, inner
diameter of 38 mm, and outer diameter of 54 mm. All tests were performed at room temperature (25 ± 3 °C)
and all tests are repeated 3 times under the same conditions to ensure the reliability of the results.

The specimens were ultrasonically washed in distilled water for 5 min before and after the wear test, and were
dried at 100 °C, for 20 min. Mass loss tests were performed using an FA224 electronic analytical balance with a
0.1-mg accuracy. Before and after the experiment, the weighing was repeated three times and averaged to ensure
the reliability of the results.

2.3.3. Wear mechanisms
A FlexSEM 1000 scanning electron microscope was used to observe the morphological changes on the worn
and unworn surfaces. A layer of gold was applied to the wear surface to provide the electrical conductivity.

A 550i energy spectrometer was used to analyze the elemental changes in the specimens before and after wear
tear.

3. Results and discussion
3.1. Orthogonal analysis
Table 4 presents the schemes and results of the orthogonal tests. Nine tests were conducted based on the L9 (34)
orthogonal array. The hardness measurement of the rubber materials was used as an indirect method to assess
their aging degree [16, 17]. As can be seen from the results in table 3, after five seawater dry-wet cycles, the
hardness of the sample increased from 25.07 HD to a minimum of 26.48 HD, (an increase of 5.62%), and
maximum of 29.74 HD (an increase of 18.63%). This shows that seawater dry–wet cycles can greatly increase the
interaction between SBR rubber molecules. Owing to the presence of unsaturated C-C double bonds in the
molecules of SBR, oxygen is more likely to react with the molecular chains of SBR under the combined action of
seawater and thermal oxygen to produce free radicals. Under the action of the free radicals, the vulcanized
components of the rubber are further cross-linked while the polysulphide bonds are desulphurized to produce
more single and double sulﬁde bonds, thus increasing the hardness of the SBR [18].

The corrected model p-value is less than 0.01, indicating the high statistical significance; (ii) the soaking
temperature, soaking time, and drying time have significant effects on the hardness of the specimens, as the p-values
for the X1, X2, and X4 factors are less than 0.05; (iii) the F-values for X1, X2, X3, and X4 were 22.25, 4.98, 0.88, and 4.78 respectively.
The significance of each factor is represented by its contribution to the F-values [19]. The greater the F-values,
the more signiﬁcant the effect on aging. The order of influencing factors for seawater dry–wet cycle aging is
X1 > X2 > X4 > X3. The average standard deviations presented in table 6 show that the theoretical
combination of the highest hardness (i.e., the worst seawater dry–wet (W-SDW) cycles) is X_12 X_23 X_33 X_42
corresponding to a soaking temperature and time of 45 °C and 12 h, respectively, and a drying temperature and
time of 100 °C and 6 h, respectively.

3.2. Surface properties analysis
Table 7 summarizes the discoloration parameters of the specimens exposed to the W-SDW cycle. As can be seen
from table 6, ΔL and Δb are both positive values. The increases in the ΔL and Δb values with the index of the

| Experiment | X1 | X2 | X3 | X4 | Cycle-index | Shore hardness (HD) ± |
|------------|----|----|----|----|-------------|----------------------|
| 1          | 1  | 1  | 1  | 1  | 5           | 26.48 ± 1.15         |
| 2          | 1  | 2  | 2  | 2  | 5           | 26.88 ± 0.67         |
| 3          | 1  | 3  | 3  | 3  | 5           | 28.22 ± 0.96         |
| 4          | 2  | 1  | 2  | 3  | 5           | 29.68 ± 0.43         |
| 5          | 2  | 2  | 3  | 1  | 5           | 28.38 ± 0.45         |
| 6          | 2  | 3  | 1  | 2  | 5           | 29.74 ± 0.61         |
| 7          | 3  | 1  | 3  | 2  | 5           | 28.34 ± 0.82         |
| 8          | 3  | 2  | 1  | 3  | 5           | 27.10 ± 0.68         |
| 9          | 3  | 3  | 2  | 1  | 5           | 27.34 ± 0.76         |
W-SDW cycles indicate that the surface of the specimen changes to white and yellow, respectively. The Δa value decreases and then increases as the index of W-SDW cycles increases, indicating that the color of the specimen surface changes from red to green to red again. Furthermore, the ΔE value increases with the W-SDW cycle index. The analysis suggests that the coupling of seawater and thermal oxygen can accelerate the process of oxygen penetration into SBR while lowering the energy barriers during the oxidation reaction of SBR. Oxygen molecules can attack the active hydrogen on the chain segment of butadiene, and the generated macromolecular radicals containing oxygen atoms collide, resulting in the formation of aliphatic aldehydes, ketones, and ethers leading to discoloration. At the same time, the antioxidants in the rubber evaporate and leach out under the action of seawater and hot oxygen. In most cases, the loss of antioxidants owing to evaporation and leaching is more significant than that owing to chemical depletion [20–22].

The hardness of the specimens after 0, 5, 10, 15, and 20 W-SDW cycles is illustrated in figure 2, and shows an increase in the hardness of the specimen. The hardness quantitatively increases from 25.07 HD to 29.14, 30.57, 32.77, and 33.57 HD after 5, 10, 15, and 20 W-SDW cycles, respectively. As the W-SDW cycle index increase, the specimen hardness increased by 16.2, 4.9, 7.1, and 8.5%, respectively. The rapid increase in the hardness of the specimens after five cycles is mainly owing to the greater degree of the aging in the pre-W-SDW period. After immersion in seawater, free radicals are generated in the SBR, which re-polymerize with each other in the presence of heat. This corresponds to an increase in the cross-link density within the rubber, and increases the relative resistance to movement between the molecular chains resulting in a rapid increase in the hardness of the specimen. After 10, 15, and 20 W-SDW cycles, the increase in the hardness of the specimens decreases, owing to the excessive cross-linking of the SBR molecules in the hot air environment. The increase in the degree of cross-linking of the rubber molecules leads to an increase in the hardness [23]. Simultaneously, seawater enters the SBR matrix and disrupts the forces between the rubber-filler and the filler, causing a chain-breaking reaction. The chain-breaking reaction relaxes the relative motion constraints between the molecular chains resulting in a reduction in hardness. At this point, the water molecules do not disrupt to the same extent as the hot air the promotes cross-link density, and the cross-link reaction has a slightly greater effect than the chain-breaking; thus, the increase in the SBR hardness is reduced compared to what it was before [17].
3.3. Wear test analysis

The friction coefficient of the specimens is shown in figures 3 (a1)–(c1). The coefficient friction of the specimens fluctuates considerably for loads of 10 N and 100 N. At a load of 50 N, the friction coefficient fluctuates more smoothly. Specimens S0, S1, S2, S3, and S4 are the specimens that have gone through 0, 5, 10, 15, and 20 cycles, respectively. Under the same load, the friction coefficient of the specimen gradually decreases as the number of cycles increases (S0–S4). The friction coefficient of specimens S0 to S4 decreased by about 65% under 10 N load. At a load of 50 N, the friction coefficient is roughly about 59% reduction. At a load of 100 N, the friction coefficient is roughly about a drop of 57%. For the same number of cycles, the coefficient of friction increases as the load increases. The analysis suggests that the friction coefficient of the SBR depends primarily on the true contact and heat build-up at the friction interface. The higher the load, the larger the true contact area, and the closer the fit between the counterpart and the SBR, making it easier it is for heat to be generated and trapped at the friction interface. In other words, the greater the true contact area, the greater the heat build-up, and the higher the friction coefficient. The variation of the friction coefficient with the cyclic index under the same load can be attributed to the changes in the surface properties of the specimen. The higher the hardness, the higher the modulus of elasticity of the specimen. When the modulus of elasticity modulus increases, the actual contact area decreases and the hysteresis component of each constituent friction force decreases. As a result, the specimen reduces the adhesion and friction thus leading to a reduction in the measured friction coefficient.[24]

Figures 3 (a2)–(c2) shows the mass loss graphs for 30 min wear of specimens with different aging levels under 10 N, 50 N and 100 N loads respectively. At the same load, the mass loss of all specimens tends to increase with the cyclic index. At the same level of aging, the mass loss of the specimen tends to increase with increasing load. The maximum mass losses of specimens S0, S1, S2, S3, and S4 occur at a load of 100 N. The maximum mass losses for S0, S1, S2, S3, and S4 are 1, 1.6, 1.9, 1.9, and 2.9 mg, respectively. The analysis shows that as the number of W-SDW cycles increases, the surface properties of the specimen in the wet and dry coupled environment change, surface cracks increase, their hardness increases surface adhesion decreases and abrasive chips are more likely to fall off, leading to increased specimen wear. The higher load allows the micro-convex bodies on the surface of the friction sub to be subjected to a higher, normal load perpendicular to the friction interface, allowing them to wedge and plough into the SBR more easily. However, higher loads also mean that the SBR undergoes more severe viscoelastic deformation, making it difficult to resist the wedging and plowing of the micro-convex bodies on the surface of the counterpart.

3.4. Wear mechanism analysis

Figure 4 shows the microscopic views of the unworn and maximally worn surfaces of the SBR conveyor belt. Slight and smooth cracks can be observed on the unworn side of the specimen. As the W-SDW cycle index increases, the number of minor cracks gradually increases. Compared to the unworn surface, the number, width, and depth of the cracks on the worn surface of the specimen increase, cracking become evident, and plow deformation appear locally. The surface cracks on the worn specimens S0–S2 gradually increase in size and produce fatigue cracks. This indicates that fatigue wear occurs at the friction interface. Specimens S3 and S4 exhibit large areas of cracking and localized abrasive debris. The appearance of these morphological features indicates the occurrence of adhesive wear and fatigue wear at the friction interface. Thus, it can be seen that the
degree of dry and wet coupled aging of seawater effects the wear mechanism of SBR conveyor belts. The analysis suggests that the cracking phenomenon is essentially the result of fatigue wear, and specifically the fatigue of the surface of the SBR caused by reciprocal cycles of contact stress at the friction interface. After repeated cyclic loading, cracks are created on the sub-surface or surface. The subsurface cracks propagate, join with other cracks, reach the surface and produce wear particles. Due to a combination of frictional and tensile stresses, some of the long and curved SBR protrusions are stripped from the surface and participate in the wear process as a third body. It is believed that the deformation, stretching, fracture, and tearing effects of SBR and frictional sub-wear processes coexist throughout the wear process, in line with fatigue wear and adhesive wear processes. Abrasive swarf can also be the result of adhesive wear, specifically, the actual contact between the friction sub and SBR occurs in the micro-convex body on the surface of both, the micro-convex body in contact with each other to form an adhesion when the adhesion point material adhesion strength is greater than the tear strength of the material in its vicinity, the friction interface shear stress under the adhesion point material will be torn into abrasive swarf.

To investigate the wear mechanism of the SBR conveyor belts in-depth, the energy-dispersive x-ray spectroscopy spectra of the unworn and most severely worn surfaces was further investigated in this study, a shown in figure 5. O and S are representative elements in the SBR, and are closely related to the aging mechanism. On the unworn surface, the S content first increases and then decreases as the W-SDW cycle index increases. This is consistent with the initial cross-linking process and later chain-breaking process, which breaks
Figure 4. Scanning electron microscope (SEM) micrograph of the unworn and maximally worn surfaces of the specimen: (a1), (b1), (c1), (d1) and (e1) unworn surfaces, (a2), (b2), (c2), (d2) and (e2) worn surfaces.

Figure 5. Energy-dispersive x-ray spectroscopy spectra of unworn and worn surfaces of specimens: (a) unworn surfaces, and (b) worn surfaces.
the S-S bond in the rubber. However, the S content of the worn surface is relatively low, and the oxygen content is relatively higher than that of the unworn surface. This suggests that the interaction of the SBR with the friction substrate accelerates the combination with oxygen in air, and weakens the adhesion of the surface to produce more wear.

4. Conclusions

This study investigates the effect of seawater dry-wet cycles on the aging surfaces and tribological properties of SBR conveyor belts for belt conveyors. Based on the experimental results the following conclusions can be drawn:

(1) Using hardness as an indicator of aging, the soaking temperature, soaking time, drying temperature, and drying time show more significant effects on the aging of SBR conveyor belts. The highest theoretical combination of aging is a seawater temperature of 45 °C, immersion time of 12 h, drying temperature of 100 °C, and drying time of 6 h.

(2) After the W-SDW cycling, the surface color of the conveyor belt changes to white, yellow, and red to green to red. The shore hardness increases with the number of cycles. Compared to the unaged surface, the aged surface show increases in fine cracks, irregular cracks, and small bumps between the cracks.

(3) Under the cyclical action of frictional stress, the friction coefficient of the SBR conveyor belts gradually decrease with an increase in the number of aging cycles, and the mass loss gradually increase with an increase in the number of aging cycles. Small cracks on the surface gradually evolve into large cracks, cracks within the rubber matrix spread to the surface, and fatigue cracks are evident. Craters are formed due to fatigue spalling of the material. Signs of fatigue wear are gradually becoming apparent at this point.

(4) In the later stages of aging, the performance of the belt decreases significantly. Fatigue cracks within the substrate spread to the surface and the material becomes harder and more brittle. The probability of direct contact between frictional substrates increases, the number of cavities in the wear surface increases, and abrasive chips from cutting action accumulate at the wear marks. At this point, the damage mechanism of the conveyor belt is mainly fatigue wear and adhesive wear.

Acknowledgments

This work is fully supported by the Nation Natural Science Foundation of China (51874004, 51904007, and 51641501), Key Research and Development Project of Anhui Province (202004a07020043), Research on multi-dimensional intelligent inspection technology of belt conveyor and its equipment research and development (ALW2021YF10). We would like to thank the Wuhu Research Institute for its funding.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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