Abridged version

KAWASAKI STEEL TECHNICAL REPORT

No.45 (November 2001)

"Developed Machinery Maintenance Technology in Steelmaking Plant"

Improvement of Rubber Toughness by Cross-linking Effect and Techniques for Extending Service Life of Rubber Rolls in Steel Production Processes

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Synopsis :

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Improvement of Rubber Toughness by Cross-linking Effect and Techniques for Extending Service Life of Rubber Rolls in Steel Production Processes*

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Rubber rolls are widely adopted to process rolls for cold rolling and surface treatment processes. Studies on the materials and forming techniques of rubber rolls have been carried out to improve the product quality and productivity. As for the technical development of materials, tough-hardening rubbers have been developed as a result of an experiment in that an excellent acid proof EPDM polymer including -CH_2- bond was compounded with methacrylic acid Zn, which acted as co-cross-linking agent. It is found that 1/Eσ-index is applicable to the evaluation of wear resistance. Concerning the development of forming-technology, new mold forming at high-pressure vulcanizing has been developed to reinforce rubbers instead of sheet-lining cure forming that has been customarily used. This new forming rubbers have a superior wear resistance. These activities have made the rubber rolls more reliable and their span of service-life longer.

1 Introduction

Rubber rolls are widely used as process rolls in cold rolling and coating lines and stainless steel lines. Among these rolls, wringer rolls are used to remove acid, alkaline, and warm water washing solutions (hereinafter referred to as process solutions) from the surface of steel strips in pickling and alkaline washing lines. Various improvements were made to prevent line stops due to peeling, wear, and cut defects on these rolls, and to prevent quality-related rejections due to the transfer of streak and flow patterns to the steel strip and rubber powder pickup by the strip.

Countermeasures against peeling include improvement by changing the material to H-NBR (hydrogenated nitrile butadiene rubber), which has the strength enough to withstand high speed, high screw-down service environments, changing the raw rubber material used in lining from sheet to ribbon to reduce air entrainment, and forming a resin underlining to prevent corrosion at the interface between the rubber and the steel core due to immersion in the process solution.

As countermeasures for wear and cut defects, the wringing structure has been clarified,[1] and based on this, high rigidity epoxy type resin rolls have been developed[2,3] and applied.

Countermeasures against streak and flow patterns, which have their origin in the rubber manufacturing process, include the introduction of warm water vulcanizing in place of steam vulcanizing, aimed at increasing the vulcanizing pressure, and large volume pouring into the mold so that pouring will be completed before the urethane hardening reaction. As a countermeasure against rubber powder pickup, the material has been changed from synthetic rubber to urethane.

However, there are cases in which high product quality and high productivity cannot be adequately realized in steel strips, and the amount of rubber waste cannot be reduced by these conventional material changes and improvements in the manufacturing process.

* Originally published in *Kawasaki Steel Giho*, 33(2001)1, 48–52

For this reason, development of rubber materials was carried out to realize improved performance from the rubber material design stage. This included improving various properties, beginning at the molecular bonding level, and improving performance by compounding. Moreover, the forming method was improved by developing a high pressure press vulcanizing forming technology using a new metal mold, which replaces forming by the conventional vulcanizing process of covering the steel core with raw rubber in sheet or ribbon, from followed by wrapping and curing with a heater.

This report describes the development of a chemical corrosion resistant, wear resistant rubber material that realizes higher toughness in the rubber by a cross-linking reaction with the compounding agent, using a base rubber with the optimum molecular bonding, and the development of a forming technology that realizes higher toughness in rubber by press vulcanizing using metal dies.

Table 1 Effective factor to improve rubber properties

Main required properties	Improvement factor for unvulcanized rubber		Improvement factor for compounding ingredient
	Polymer chain	Solubility parameter	
Chemical corrosion resistance	Saturation compound	Smaller	—
Thermal resistance	Saturation compound	Bigger	Addition of amine type antioxidant
Water resistance	—	Smaller	
Oil resistance	—	Bigger	—
Abrasive wear resistance	—	Bigger	(1) Addition of fine carbon black (2) Addition of co-crosslinking agent

2 Development of Chemical Corrosion Resistant, Abrasive Wear Resistant Rubber

2.1 Performance Requirements and Problems

Rubber rolls that are used to wring pickling acid and warm water washing solutions from the surface of steel strips in pickling lines must possess not only chemical corrosion resistance and abrasive wear resistance, but must also have the proper elasticity to prevent the solution from being drawn onto the strip from the strip edges. Conventionally, low cost SBR (styrene butadiene rubber) was used as a lining, but the physical properties (tensile strength, elongation at time of rupture, etc.) of this material were reduced by deterioration because it lacked adequate chemical corrosion resistance, and it showed a drum shaped wear mode due to wear in the areas corresponding to the steel strip edges. Consequently, its service life was short. Recently, moreover, with use under high loads accompanying higher line speeds, use of additives to increase washing performance, and an increase in the treatment of thin gauge steel strips, it has become necessary to replace the SBR lining in a period even shorter than the conventional replacement cycle.

2.2 Concept of Development

Generally, rubber is a compound material that is synthesized by combining compounding agents (vulcanizing agent, vulcanizing accelerator, antioxidant, filler, etc.) and reinforcing agents with unvulcanized rubber (CR (polychloroprene rubber), CSM (chlorosulfonated polyethylene), SBR, NBR (nitrile rubber), H-NBR, EPDM (etylene propylene rubber). etc.). Items that contribute to improvement of the various required properties of rubber, such as chemical corrosion resistance, thermal resistance, and abrasive wear resistance, are shown in **Table 1**. In order to improve chemical corrosion resistance and thermal resistance, it is important to increase the amount of saturated bonds in the polymer chain of the unvulcanized rubber. If the number of saturated bonds is small, in other words, if the number of double bonds (>C=C<) is large, the rubber will tend to decompose because its reactivity will be large, making unstable, which has a negative effect on these properties. Accordingly, excellent chemical corrosion resistance and thermal resistance can be expected as the number of saturated bonds ($-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$) increases. Where water resistance, oil resistance, and abrasive wear resistance are concerned, quality is basically determined by the size of the polarity (SP value) resulting from the difference between plus and minus polarities in the polymer. Because the polarity of water is large, water resistance improves as the polarity of the rubber decreases; on the other hand, because the polarity of oil is small, oil resistance improves as the polarity of the rubber increases. Further, if the polarity is large, abrasive wear resistance is high because the strength of the rubber is increased by the electrical bonding force. In other words, water resistance on the one hand, and oil resistance and wear resistance on the other, stand in a mutually contradictory relationship. When a material has been selected with priority given to chemical corrosion resistance, a rubber with a large number of saturated bonds and a small SP value is appropriate because the pickling bath is generally an environment that also contains water. Conversely, as the negative side of this selection, abrasive wear resistance will not be adequate. **Figure 1** shows a comparison of the SP values[4] of various rubbers. EPDM has superior hydrochloric acid resistance, and NBR and ester type urethane have superior oil resistance and abrasive wear resistance. The general practice for improving abrasive wear resistance is addition of reinforcing agents such as carbon black. Strength is improved in proportion

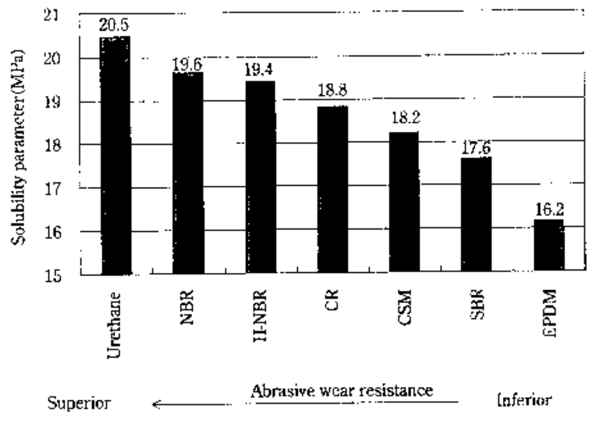

Fig. 1 Comparison of solubility parameter for various kinds of rubber parameters

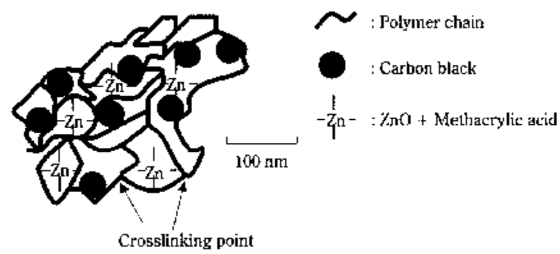

Fig. 2 Microstructure of developed rubber

to the addition of substances with a small particle size, but improvement of abrasive wear resistance by adding these reinforcing agents has already reached its upper limit.

Therefore, the authors considered the application of a rubber strengthening and toughening method using a co-cross-linking agent,[5] which had not previously been applied to high strength rubbers such as those in rubber rolls for steel manufacturing processes. Here, the material selected was EPDM, which has a large number of saturated bonds and a small SP value, and therefore has superior chemical corrosion resistance. The aim was to improve the abrasive wear resistance of this material to a higher level than is possible with reinforcing agents by using a co-cross-linking agent to toughen the material.

2.3 Material Design and Compounding Results

The toughening method that was introduced in this development work is a method that improves abrasive wear resistance by using ZnO + methacrylic acid as a cross-linking agent. This increases tensile strength by ion cross-linking with peroxides. However, it was necessary to establish the optimum amount ZnO + methacrylic acid because excessive addition invites a reduction in strength by the chemical solution. The molecular microstructure of the developed rubber is shown in **Fig. 2**. Because the particles of ZnO + methacrylic acid are on the order of nm in size and are dispersed, improvement in abrasive wear resistance by the formation of a high order structure is expected.

Table 2 shows the specifications of the compounding ingredients used in the EPDM, developed rubber, and SBR, together with the ratio of the tensile strength and Young's modulus to those of EPDM after vulcanizing. With SBR, sulfur was used as the vulcanizing agent, whereas, with EPDM and the developed rubber, an organic peroxide was used. As the reinforcing agent, carbon black was the main ingredient used with all the rubbers. With the developed rubber, tensile strength was increased to approximately 1.4 times that of EPDM by using ZnO + methacrylic acid as a cross-linking agent, and strengthening to the same level as SBR was possible. The Young's modulus of the developed rubber was increased to approximately 1.4 times that of EPDM and approximately 1.27 times that of SBR. Using these ratios of the tensile strength and Young's modulus, values were substituted into the Eσ equation, which is generally used to evaluate the abrasive wear resistance of rubber. It has been reported that abrasive wear resistance improves as the value of Eσ increases.[6] These results are shown in **Fig. 3**. The developed rubber showed a value approxi-

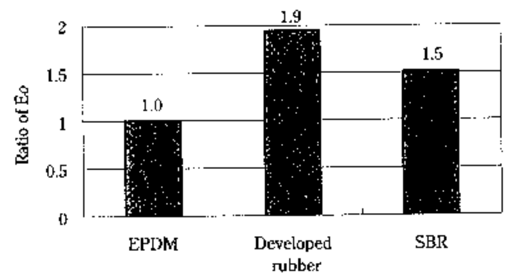

Fig. 3 Comparison of ratio of Eσ

Table 2 Specifications of compounding ingredient, ratio of tension strength and ratio of Young's modulus for EPDM

Rubber materials	Compounding ingredient			Ratio of tensile strength	Ratio of Young's modulus
	Crosslinking agent	Reinforcing agent	Co-crosslinking agent		
EPDM	Organic peroxide	Carbon black	—	1.0	1.0
Developed rubber	Organic peroxide	Carbon black	ZnO + methacrylic acid	1.4	1.4
SBR	Sulfur	Carbon black	—	1.4	1.1

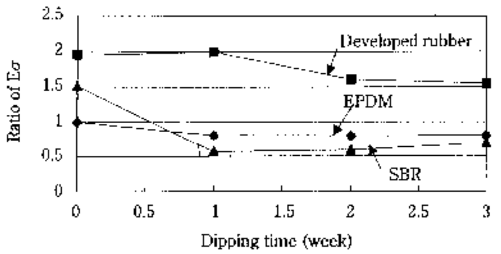

Fig. 4 Change of the ratio of $E\sigma$ during dipping experiments

mately 1.9 times and SBR approximately 1.5 times that of EPDM. Thus, the developed rubber has a value approximately 1.3 times that of SBR, and therefore can be expected to provide abrasive wear resistance superior to that of SBR.

2.4 Performance Evaluation in Laboratory Tests

2.4.1 Evaluation of chemical corrosion resistance by dipping test

A dipping test was performed by immersing samples of the EPDM, developed rubber, and SBR shown in Table 2 in a standing solution for three weeks. The samples were removed at intervals of one week, and tensile strength and Young's modulus were measured. The test solution was prepared from a pickling line pickling tank (HCl 9%). The temperature was maintained at 80°C, which is the same as in the actual pickling line. The test results are shown in **Fig. 4**.

Comparing the $E\sigma$ ratio to that of EPDM before immersion, the SBR showed an extreme decrease from 1.5 to 0.6 (approximately 60%) in one week. In contrast, the $E\sigma$ of the developed material decreased from 1.9 to 1.6 (approximately 16%) in two weeks. The EPDM showed a decrease of 20%, from 1.0 to 0.8.

Because these results show that the decrease ratio of the developed material was extremely small in comparison with that of the SBR, it can be estimated that the developed rubber will provide acid resistance, and excellent abrasive wear resistance over the long term.

2.4.2 Evaluation of abrasive wear resistance by rotating wear test

Specimens of the same materials as those in the dipping experiment were used with the rotating abrasive wear test apparatus shown in **Fig. 5**. In order to reflect wear at the edges of the steel strip, a steel roll with steps at its edges was placed above the rubber test roll. As test conditions, the same load, difference in the peripheral speed of the rolls, and test time were used with all specimens.

The test results are shown in **Fig. 6**. Wear of the developed rubber was approximately 0.79 times that of the EPDM, and was approximately 0.73 that of the SBR.

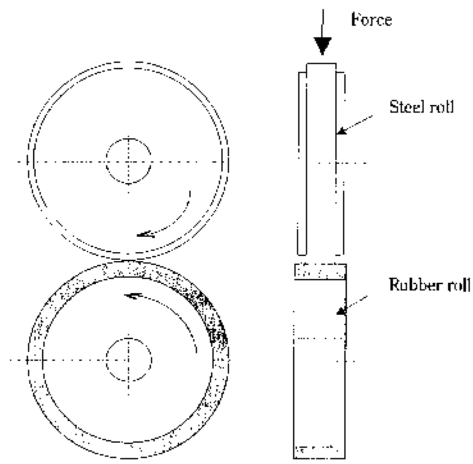

Fig. 5 Schematic diagram of abrasive wear test

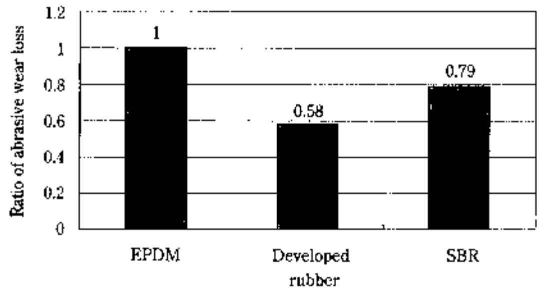

Fig. 6 Comparison of the ratio EPDM to other rubber for abrasive wear loss

Considering also the results of the dipping test, it can be estimated that the developed rubber has greatly improved abrasive wear resistance in comparison with the SBR.

Figure 7 shows the correlation of $1/E\sigma$ and the wear ratio. Because the three point plot of the data for the test materials shows a good correlation between $1/E\sigma$ and the amount of abrasive wear loss, it is considered that $1/E\sigma$ can also be used to evaluate the abrasive wear resistance of rubber rolls.

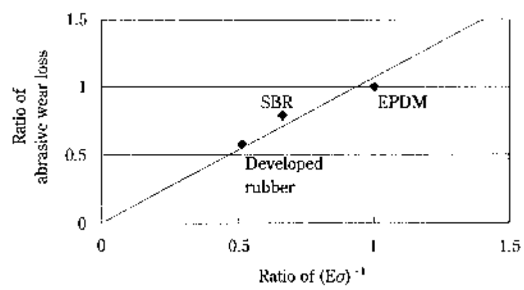

Fig. 7 Relation between the ratio of $(E\sigma)^{-1}$ and the ratio of abrasive wear loss

2.5 Total Evaluation in Production Equipment

From the laboratory tests described thus far, it can be understood that the developed rubber, in which ZnO + methacrylic acid is added as a cross-linking agent to EPDM, has excellent chemical corrosion resistance and abrasive wear resistance.

The developed rubber was installed in the wringer roll at the delivery side of a pickling-line pickling-tank for comparison with the conventional SBR roll. The results showed that wear can be reduced to approximately 50% that of the conventional SBR roll, and furthermore, there were no rejections of strip due to quality-related problems such as rubber peeling or rubber powder pickup, indicating that stable use is possible.

3 Development of Rubber Roll by Press Vulcanizing Forming with Metal Dies

3.1 Problems with Conventional Forming Method and Purpose of Development

The conventional method of forming rubber rolls is shown in **Fig. 8**. Conventionally, the main method was lining using raw (unvulcanized) rubber in sheet form, followed by wrapping. As typical conditions, vulcanized was performed in a steam atmosphere at a temperature of 150°C for 11 h at a pressure of 1.0 MPa. In this steam vulcanizing manufacturing method, because the pressure during vulcanizing was of the order of 1.0 MPa, the cross-linking density tended to be low in comparison with that in high pressure press forming. **Figure 9** shows the respective values of $E\sigma$ when press forming was performed at 1.0 and 21.0 MPa using CR. The value of $E\sigma$ is larger when the press pressure is high, and in the case shown here, increased by approximately 1.4 times. With the conventional forming method, a good lining property (processing property) is generally required in the raw rubber. Therefore, the compounding design is characterized by reduced tensile strength in comparison with that of the raw rubber used in press forming, although tensile strength is an important property for securing abrasive wear resistance. As other disadvantages of the conventional manufacturing process, because lining is performed manually, quality deviations occur and the manufacturing process is complicated.

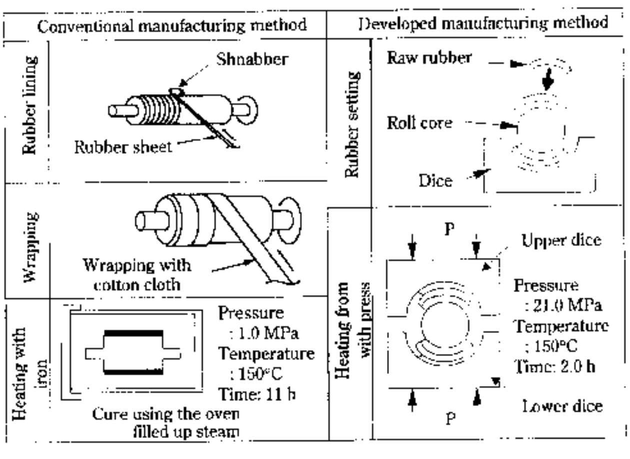

Fig. 8 Comparison of manufacturing process

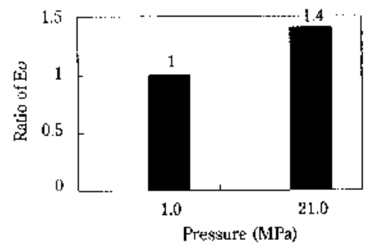

Fig. 9 Comparison of the ratio of $E\sigma$

Therefore, a vulcanizing forming technology employing pressing forming with metal dies was developed. The new technology makes it possible to omit processing steps and toughen the rubber by vulcanizing with a high pressure press, contributing to longer roll life and stable roll quality.

3.2 Establishment of Press Forming Technology

Figure 8 shows the press vulcanizing forming process. As the metal mold, a type which is divided into two dies (upper half and lower half) is used. After the raw rubber has been laid in the lower dice, the steel core is put in place, and raw rubber is then laid on top of the core. Finally, the upper dice is set over the roll, and vulcanizing forming is performed by the press.[7~11)] In establishing technology, the factors that have a particularly strong effect on the quality of the roll are shown in **Fig. 10**. The factors that determine quality are the proper viscosity and amount of raw rubber to enable plastic flow, the raw rubber shape and dimensions, the press pressure and duration, and the timing of dumping, and a heating pattern and temperature that ensure a uniform temperature in all parts of the rubber. If the proper combination of these conditions cannot be determined, swelling and fusing defects in joint parts may occur.

Therefore, the respective conditions were narrowed by trial manufacture tests of rubber rolls. In narrowing the heating pattern and temperature conditions, experimen-

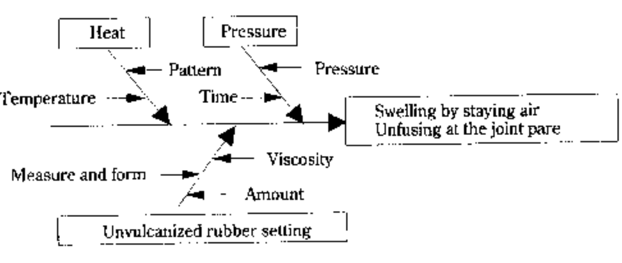

Fig. 10 Diagram of the characteristic factor

tal scale rolls were trial manufactured with an outer diameter of ϕ255 mm, and a steel core diameter of ϕ215 mm and barrel length of 1 400 mm. The temperature in various parts of the roll during vulcanizing forming was measured for each of the heating patterns using thermocouples, and the heating pattern and heating temperature were narrowed so that the temperature in all parts would increase as uniformly as possible to find the conditions that enable vulcanizing forming in a short time. In narrowing the other conditions, miniature rolls with an outer diameter of ϕ190 mm and a steel core diameter of ϕ165 and barrel length of 400 mm were trial manufactured, and the optimum viscosity and amount of unvulcanized rubber, rubber shape and dimensions, press pressure and duration, and bumping timing were determined. Quality confirmation was done by inward grinding 4.0 mm intervals on the diameter, checking the appearance, and measuring the hardness with a hardness gauge. As a result, no fusing defects of the joint parts were found, and it was possible to narrow the heating conditions, press conditions, and unvulcanized rubber setting conditions to obtain stable quality.

3.3 Total Evaluation in Production Equipment

A rubber roll that was manufactured by press vulcanizing forming with metal dies was installed adjacent to a conventional roll in the wringer rolls at the delivery side of an electrolytic pickling line spray tank and compared with the conventional roll. The material used in this test was the same CR as the conventional material. The results confirmed that the amount of wear was reduced to approximately 50% that of the conventional roll, and no defects of the steel strip due to rubber peeling or rubber pickup were observed, indicating that rolls manufactured by the developed method can be used stably.

4 Conclusion

Research and development on toughening of rubber using the cross-linking reaction with a co-cross-linking agent and a forming technology that realizes toughness in rubber by press vulcanizing with metal dies were carried out to achieve longer life in rubber rolls. The following results were obtained.

(1) In material development, toughening of rubber was achieved by ion cross-linking with peroxides by compounding ZnO + methacrylic acid, which acts as a co-cross-linking agent, with a EPDM polymer, which has a large number of saturated bonds, a small SP value, and $-CH_2-$ bonds, and thus possesses excellent chemical corrosion resistance. This made it possible to obtain rubber rolls with high abrasive wear resistance. As a result, the conventional roll life was extended by two times in an actual pickling line.

(2) In evaluating the abrasive wear resistance of rubber rolls, it is possible to use an index ($1/E\sigma$) which is the reciprocal of the product of tensile strength and Young's modulus.

(3) In the development of a rubber roll forming technology, a vulcanizing forming technology was developed which toughens the rubber by high pressure press forming using metal dies, superceding the conventional method of vulcanizing forming by sheet lining. This made it possible to obtain rubber rolls with excellent abrasive wear resistance and stable quality. As a result, approximately two times the conventional life and stable product quality were obtained with rolls used in actual equipment.

The authors believe that these results will contribute to higher quality and higher productivity in steel sheets through wider application of these new technologies in the future.

In closing, the authors wish to express their sincere thanks to all those concerned at Kinyosha Co., Ltd. and Mutsubishi Gomu Corp. for their cooperation in the development of the rubber toughening technologies described in this paper.

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