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Investigation of the Potential of Using Liquid Rubbers in Rubber Industry

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Abstract

Along with the developing technology in the rubber industry, the use of natural and synthetic rubbers as well as liquid rubbers has increased significantly in recent years. The formulation of the tread compound, which directly affects the performance of a tire, is generally produced from natural and synthetic rubbers. Intensive scientific studies have been carried out on liquid rubbers because they reduce the consumption of process oils used in the tire production phase and increase dispersion. In this study, the rheological and physico-mechanical properties of rubbers developed using only liquid rubber (liquid isoprene and liquid SBR) with four different viscosities and without using process oil (Styrene Butadiene Rubber—SBR) were investigated. It has been observed that the rubber blends produced by adding four different liquid rubbers to the same recipe caused changes in rheological and physico-mechanical properties compared to the reference sample. It was observed that the minimum torque/viscosity (ML), maximum torque/viscosity (MH) and curing time (t90) in some of the formulas tested decreased significantly due to the use of liquid rubber.

Keywords

Natural Rubber, Liquid Rubber, SBR, Isoprene

1. Introduction

Natural rubber products are obtained from latex, a milky liquid obtained from Hevea brasiliensis trees growing in tropical climatic conditions, whose chemical structure is cis-1,4-polyisoprene [1] [2] [3]. Charles Goodyear discovered by chance in the 1800 s that natural rubber can be cross-linked with sulfur (vulcanization) and this discovery led to a revolution in the rubber industry [4] [5].

Tires, a product of this invention, are used in all motor vehicles today. The Innovations made in vehicle technology over time are also made in tire technology [6].

Natural and synthetic rubber, carbon black, silica, oils and various chemicals are used in the production of standard tires [7]. Rubber materials are used successfully in many sectors apart from the transportation sector due to their abrasion resistance, high flexibility, excellent strength, easy processing, low deformation, good tearing and good dynamic properties [6] [8].

Liquid rubbers are divided into three groups as natural, styrene butadiene (SB) and butadiene liquid rubbers in viscous form with low molecular weight. Commercially, Japan-based Kuraray Co. Ltd. [9] produces liquid rubber in three different groups, namely isoprene (LIR), butadiene (LBR) and styrene-butadiene (LSBR). Due to the glass transition temperature (Tg) value, the products produced from these raw materials can maintain their properties at low temperatures [10] [11]. Industrially produced "Liquid Polymers"; It is widely used as a covulcanizable plasticizer in tires, mechanical rubber compounds, plastic products, printing inks, paints and coatings, or sealants [12]. **Figure 1** shows the chemical structures of the most commonly used types of liquid rubber in industry.

There are studies on the dispersion of SiO_2 as a plasticizer additive [13] [14] and increasing the Tg value [15] of liquid rubbers. In addition, studies have been conducted to improve abrasion resistance and low temperature properties in winter tires and wet and dry grip properties in racing tires [16]. In this study, the

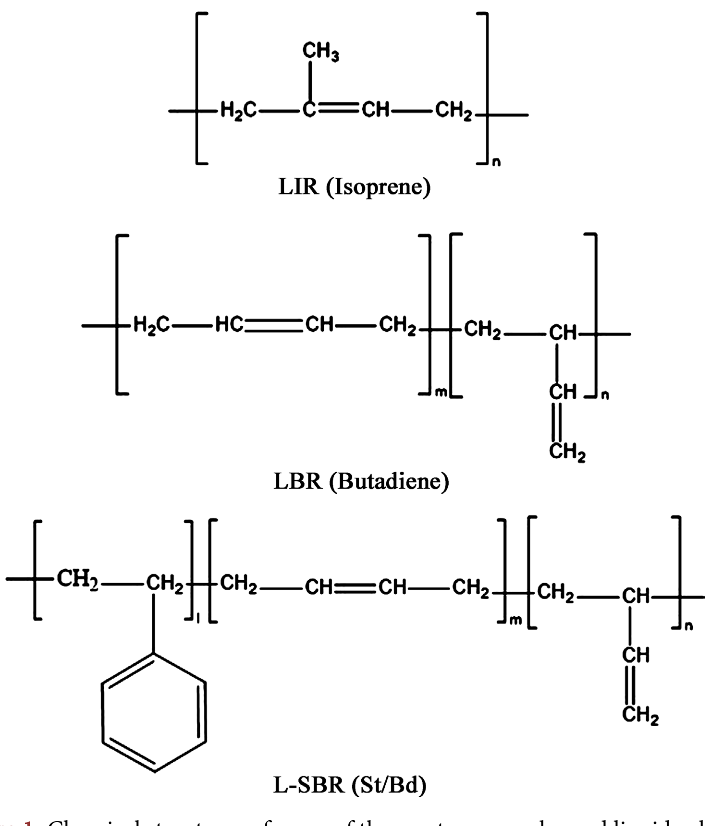


Figure 1. Chemical structures of some of the most commonly used liquid rubbers.

rheological and physico-mechanical properties of the rubbers developed using only liquid rubber (liquid isoprene-liquid SBR) type with four different viscosities and without using process oil with the reference recipe SBR created with process oil were investigated.

2. Material and Method

2.1. Sample Preparation

Synthetic rubber, liquid rubber, carbon black as filler, process oil, activator, accelerator, preservative, cooker and resin were used in the recipes. The raw materials used are the chemicals currently used in motorcycle tires at Anlas Tyre Company [17]. Apart from the reference mixture used, a total of 5 recipes were created using liquid rubber with 4 different properties. The liquid rubbers are coded as A, B, C and D in **Table 1** and were supplied by Kuraray Co., Ltd. [9].

The raw materials used in the recipes and their quantities in phr (Parts Per Hundred Rubber) are given in **Table 2**. The reference blend (containing process

Table 1. Features of liquid rubbers.

Liquid Rubbers	Viscosity at 38˚C (Pa·s)	Viscosity at 60˚C (Pa·s)	Molecular Weight	Tg (˚C)
A	500	-	54.000	−63
B	350	-	8.500	−14
C	-	100	10.000	−6
D	250	-	6.000	−18

Table 2. Rubber compound recipes.

Raw Materials	Reference (phr)	K1 (phr)	K2 (phr)	K3 (phr)	K4 (phr)
Synthetic Rubber	137.5	137.5	137.5	137.5	137.5
A (Liquid Rubber)			10.5		
B (Liquid Rubber)				10.5	
C (Liquid Rubber)		10.5			
D (Liquid Rubber)					10.5
Carbon Black	70.0	70.0	70.0	70.0	70.0
Process Oil	5.00				
Activator (ZnO + Stearic Acid)	4.5	4.5	4.5	4.5	4.5
Accelerator	1.5	1.5	1.5	1.5	1.5
Antidegradants and Antiozonants	5.0	5.0	5.0	5.0	5.0
Sulfur	1.5	1.5	1.5	1.5	1.5
Resin	10.0	10.0	10.0	10.0	10.0

*S-SBR: Solution Polymerized Styrene Butadiene Rubber; The designed mixtures were produced using a Banbury mixer [18].

oil) and the blends using different liquid rubber were named as K1, K2, K3 and K4.

2.2. Physico-Mechanical Tests

Physico-mechanical tests; After being cured in a press at 170˚C for 15 minutes, they were cut into bow tie specimens in accordance with ASTM D412-06 standards and tensile, elongation and 300% modulus values were measured with EKTRON-TS-2000 brand Tensile Testing Machine in accordance with ASTM D412 (Figure 2).

2.3. Rheological Tests

Rheological tests (Moving Die Rheometer, MDR) were performed with EKTRON MDR 2000S according to ASTM D5289 standard at 191˚C for 15 minutes (Figure 3).

Mooney Scorch (SC) tests were performed with EKTRON MV 2001M device at 135˚C according to ASTM D1646 standard (Figure 4).

3. Findings and Discussion

Physico-Mechanical and Rheological Tests

A total of 10 tests were carried out on 3 different devices (MDR, physico-mechanics and Mooney) on the reference (containing process oil) mixture and

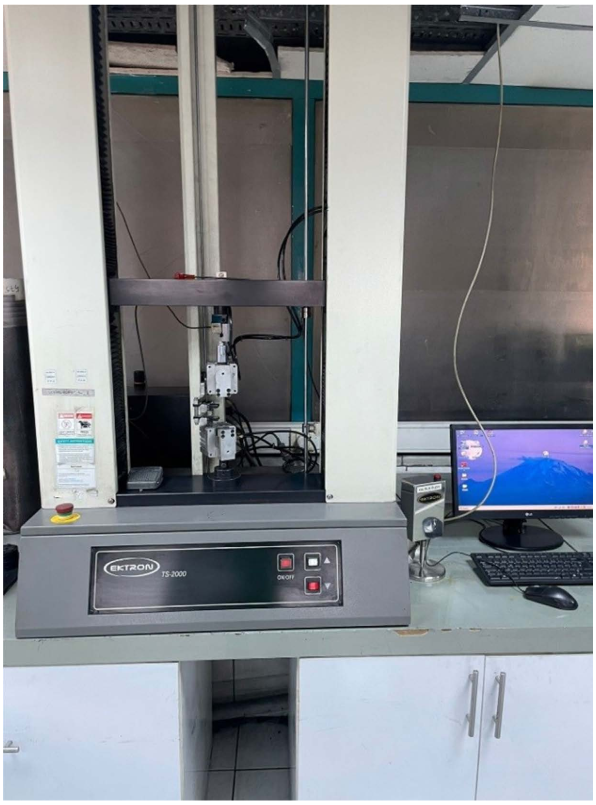


Figure 2. EKTRON TS 2000.

Figure 3. EKTRON MDR 2000S.

Figure 4. EKTRON MV 2001M.

the mixtures in which different liquid rubbers were used. The obtained results are given in Table 3.

In the MDR test (Table 3), the rheological properties of all mixtures measured at 191˚C were evaluated. The purpose of this test is to determine the curing characteristics of the product with the data obtained from the yield properties of the mixture. The curing curve (Figure 5) is found by creating a time-dependent graph of the torque value increasing with an increase in crosslink density [19].

Since rheological properties are parameters that give information about the behavior of mixtures in production processes, optimum mixture selection can be made by considering ease of processing, scorch safety and curing times.

The ML value indicated in Figure 5 refers to the minimum viscosity at the initial temperature of the test. This value is defined as the first point at which crosslinking begins. The MH value is the viscosity/torque value at the point where vulcanization and cooking are completed.

Table 3. Results of rubber compound.

Test Parameters		Reference	K1	K2	K3	K4
Moving Die Reometer, 191˚C, 15 min	ML (dNm)	3.09	2.15	2.13	2.30	2.08
	MH (dNm)	13.21	9.18	8.84	9.06	10.83
	ts2 (min)	01:09	01:13	01:13	01:18	01:21
	t90 (min)	08:32	06:41	05:18	07:07	08:39
Mooney Viscosity, 135˚C	ML1 + 4	59.51	45.32	44.10	45.37	55.31
	T5 (min)	16:46	17:59	21:25	18:07	14:19
Physico-Mechanical, 170˚C 15 min	Tensile Strength (kg/cm^2)	160.78	148.95	168.78	157.9	159.06
	Elongation, %	612.14	604.87	699.32	703.26	510.44
	%300 Modulus (kg/cm^2)	61.12	51.52	43.41	41.55	79.77
	Hardness (Shore A)	62.80	56.20	54.10	57.60	64.20

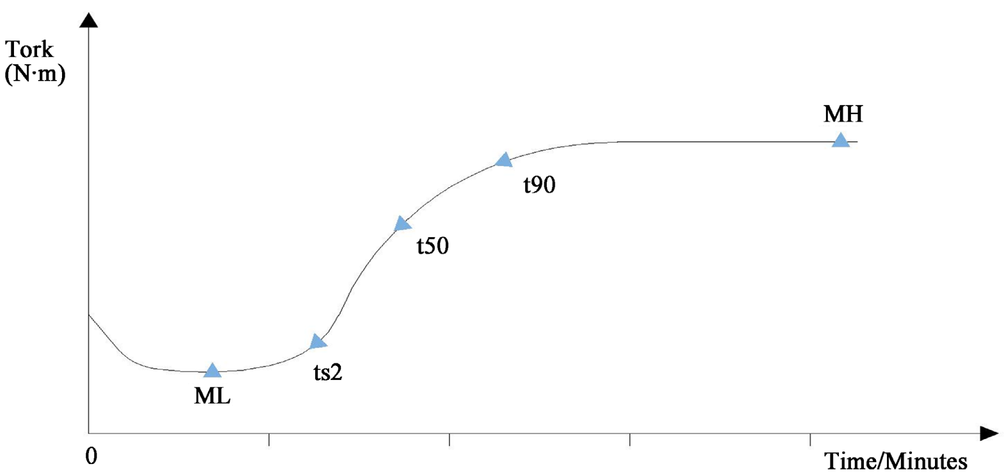


Figure 5. Rheometer curve parameters.

ts2 value is the scorch time defined as the first start time of curing. The ts2 value is very important to be able to observe the process. The t90 value is the time it takes to reach 90% of the maximum torque. The t90 value gives the optimal curing time.

When the results of rheological and physico-mechanical tests were analyzed in the mixture recipes given in **Table 3**, the following results were obtained.

It was observed that ML and MH values decreased significantly in K1, K2, K3, and K4 blends. This finding shows that the fact that the viscosity of liquid rubbers is quite low compared to normal rubbers is effective in the low viscosity of the blends. Thus, the ease of processing of the blends in the processes will increase and less energy will be used. An increase in the ts2 values of the other 4 different blends was observed compared to the reference blend. This increase indicates that the blends have a longer scorch time and therefore provide safer processing ease in the production process.

In the obtained t90 values; it was observed that the values of K1, K2 and K3 mixtures were lower compared to the reference mixture. The closest t90 value to the reference mixture belongs to the K4 mixture. K1, K2 and K3 mixtures will be cured in a shorter time, which will provide the advantage of obtaining more products and saving energy per product.

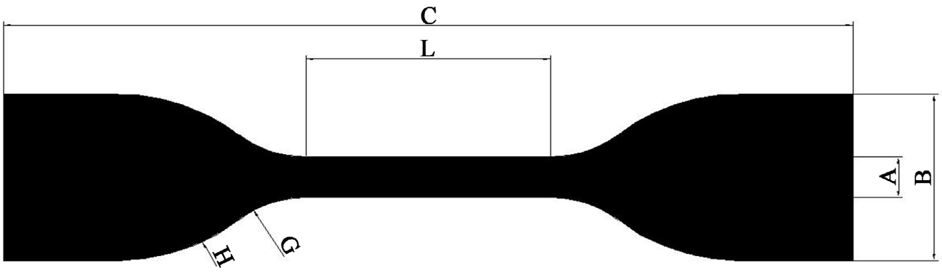
It was determined that there was a decrease in the ML1 + 4 values due to the use of liquid rubber, as in the ML value. The closest value to the reference recipe belongs to the K4 mixture; it is seen that K1, K2 and K3 values are lower.

The tensile strength of the liquid rubber used in K2 was found to increase compared to the reference sample, while the lowest value was measured in the K1 blend. In K3 and K4 recipes, values close to the reference were obtained. In terms of elongation percentages, while K2 and K3 recipes gave the highest values, K4 gave the lowest values. K1, on the other hand, gave a result close to the reference. K4 gave the highest modulus value, while K2 and K3 gave the closest and lowest values to the reference sample, respectively.

Hardness value; decreased with the use of liquid rubber, except for the K4 recipe. While the lowest result was obtained in the K2 sample, the hardness values of K1 and K3 gave close results.

The mixtures prepared for physico-mechanical tests are cured in plates at 170˚C for 15 minutes. A bow tie (**Figure 6**) sample in accordance with ASTM D412 Die C standard is cut from the plates and the thickness is measured from 3 different points and entered into the system of the device where the test will be performed manually. A certain force is applied to the bow tie specimen placed in the jaws of the tensometer, causing the specimen to break.

Physico-mechanical tests are used to determine the amount of elongation at break in % of the material and to measure the mechanical strength of the material. Physico-mechanical properties provide important information for the suitability of mixtures for the purpose under the ambient conditions in which they are used. For example, higher rupture and elongation values may be desired



A: Width off narrow section: 6 mm	B: Overall Width: 25 mm	C: Overall Length: 115 mm
L: Length off narrow section: 33 mm	E: Radius of curvature (out): 14 mm	F: Radius of curvature(in): 25 mm

Figure 6. Test specimen used in tensile-rupture test.

for moving products, while lower values may be desired for stationary products. Thus, after determining the working conditions, the mixture can be selected by focusing on the performance criteria expected from the product.

The Mooney test determines the viscosity value of the mixture. The data obtained with this test determines the flow, movement and shaping properties of the rubber. Thus, information about the behavior of the product during production can be obtained in advance.

4. Conclusions

In this study, the potential of using liquid rubbers, which have recently become widespread, instead of process oils used in rubber compounds was investigated. For this purpose, 4 different liquid rubbers with different viscosity values were included in a reference blend formed with process oil.

- This study proved that with the addition of liquid rubbers in the appropriate amount to the mix recipe, the process oils previously traditionally used are no longer required.
- It has been observed that basic rheological and physico-mechanical properties of the mixtures produced can be improved thanks to the liquid rubbers used.
- The potential of using liquid rubbers for further development of the properties expected from the tire, especially in cases where tire performance is specifically sought, has been revealed by this study.
- Liquid rubbers should be investigated in different recipes and usage quantities.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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