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EFFECT OF LIQUID RUBBERS ON THE THERMAL AND ADHESION PROPERTIES OF THE TIRE SKIM COMPOUND

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Abstract

Polymeric textile cords, steel cords and steel cables are mainly reinforcing materials that are used in tire production. Polymeric textile cords such as Polyester (PEs), Nylon, Aramid and Rayon are commonly treated with bi-functional resorcinol formaldehyde latex (RFL) to obtain desired adhesion to rubber matrix. PEs cords are known as their poor adhesion to both RFL and rubber compounds due to limited reactivity on the surface and poor reaction extent between methylol and hydroxyl groups of RFL. Increasing carboxyl content on PEs surface or in the rubber compound is one of the best strategies to overcome this adhesion problem. Liquid rubbers, which can co-vulcanize with solid rubbers, are also strong alternatives of process oils with their excellent plasticizing effect without deterioration in mechanical properties of the resulting material. Co-vulcanization also improves the stability of this additive and prevents possible bleeding and migration during service life of the tire. In this study, carboxylated grafted liquid isoprene rubber has been incorporated to rubber compound to improve adhesion in PEs-RFL-Rubber ternary system. Rheological and dynamic-mechanical properties of reactive liquid rubber containing tire rubber compounds have been evaluated extensively, as well as H-adhesion behaviour of PEs cord-rubber composite matrix.
Key words: Polyester Fabric, RPA, Natural Rubber, Liquid Rubber, Adhesion

1. Introduction

The natural rubber is common used in tire skim compound which is that provide the endurance of the tire when it using. It can define exactly as the skeletal system of the tire. Polymeric textile cords, steel cords and steel cables are mainly reinforcing materials that are used in tire production. Polymeric textile cords such as Polyester (PEs), Nylon, Aramid and Rayon are commonly treated with bi-functional resorcinol formaldehyde latex (RFL) to obtain desired adhesion to rubber matrix. Generally, the polyester fabric is preferred when the radial tires are produced. The polyester fabric is cheaper than aramid, Kevlar, nylon and other hybrid fabrics and more durable than other popular fabric nylon 6 and nylon 6.6. The polyester fabric have less thermal shrinkage than nylon. It is more critical point for heavy duty vehicles tires. But adhesion property is the very low because of the it has non-polar groups. All this properties such as mechanical, rheological, adhesion properties affect the tire performance in the field. In order to obtain optimal values, the use of liquid natural rubber is preferred. Liquid rubbers have low molecular weight and its formation is viscos. There are 3 variants of the liquid rubbers;

1- LNR (Liquid Natural Rubber)

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2-LSBR (Liquid Styrene Butadiene Rubber)
3-LBR (Liquid Butadiene Rubber)

Liquid rubbers are added to the process as a plasticizer due to their low molecular weight. However, thanks to their cross-linking abilities, they participate in the reaction during curing. With these properties, they affect the efficiency and speed of the reaction, unlike conventional plasticizers. Due to their low glass transition temperature (Tg), they can maintain their properties at low temperatures [1].

For reinforcing of the tire the carbon black types are used common in the tire industry. Additionally talc, silica, kaoline etc. are used to as the reinforcing materials in compound. The carbon black has between 10 nm – 500 nm particular size. The particular sizes are determined with Bruner-Emmett-Teller (BET) nitrogen adsorption test. Due to the high specific surface area and surface energy of carbon, particles have a tendency to coalesce and aggregation. This trend creates two different structures. When large numbers of individual carbon black particles are brought together to form a long and branched chain, it is called a high structure. This kind of carbon black gives excellent strengthening effect for the mixture. Short, linear carbon blacks are combined to create a low structure [2].

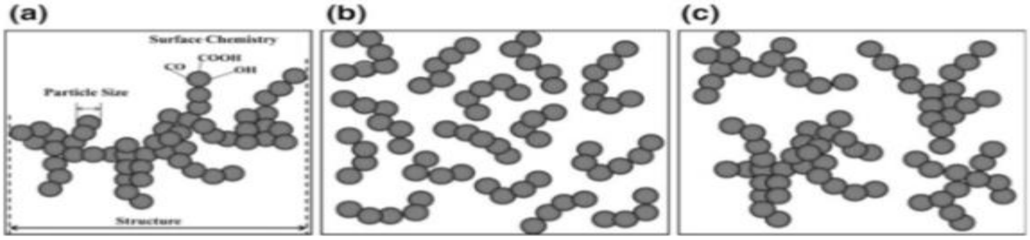


Figure 1. Microstructures that carbon particles tend to form

According to Figure 1., The smaller the particle size, the higher the darkness / gradation power of the carbon black, but the poorer the dispersion. This is because; There is a strong cohesive force between the carbon black particles and they tend to agglomerate. However, as the particle size increases, it becomes easier to disperse the carbon black in the matrix and process it in the process [3]. Generally, carbon black and silica are used to improve the final vulcanized properties. The reinforcing material improve the hardness, modulus, tensile, abrasion resistance and elastic modulus properties of the compound. The most important point for this improving is the filler-filler and filler-rubber interaction. More rubber-filler interaction is expected after the mixing for effective dispersed compound and high mechanical properties [4]. The vulcanization process is the very slow when lack of the accelerators. Due to that for vulcanization of the rubber compound are used accelerators which is the organic chemicals. In addition, accelerators or accelerating systems significantly increase the physical properties and aging resistance of the material. There are lots of type of the accelerators and it affect the process speed and degree of the crosslink density [5]. While the sulfur bridges are provided by accelerators, the number of sulfur in the sulfur bridges to be formed varies depending on the accelerators/sulfur ratio. Polysulfidic bonds provide the material with high fatigue strength. However, due to the low energy S-S bonds, dimensional stability and aging properties are reduced. The dimensional stability and aging tendency of the material improve as the sulfur content between the two carbons decreases. However, it shows low fatigue strength. There are 3 types of vulcanization systems created to define them;

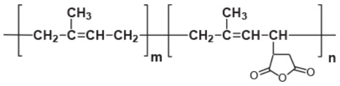
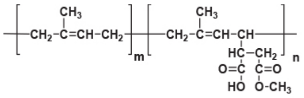
1. Efficient Vulcanization System (EV): Low sulfur content / High accelerator amount (S/Acc<1)
2. Semi-Efficient Vulcanization System (Semi-EV): Medium sulfur amount / Medium accelerator amount (S/Acc=1)
3. Conventional Vulcanization System (CV): It is defined as High sulfur content / Low accelerator amount (S/Acc>1).

Vulcanization is one of the most important processes in rubber technology, which is called crosslinking or baking. The process of cross-linking the elastomer molecules ensures that the rubber retains its elongation ability despite becoming harder and stronger. Sulfur is mainly used as a crosslinking agent. Long polymer chains participate in cross-linking with sulfur over their allylic hydrogens, thus reducing the flow properties of the chains. Sulfur can be linked by two opposing chains or cross-linked with neighboring carbons. The amount of sulfur bond (S-S) between the two chains affects the final properties of the vulcanizate [6].

2. Materials and Method

The natural rubber and synthetic rubbers are used in this study. Natural rubber (NR; SIR20(Standart Indonesia Rubber, LIR403(Liquid natural rubber, Kuraray Co.) and LIR410 (Liquid natural rubber, Kuraray Co.). These rubbers were filled with 55 phr of N326 type (Orion Carbon Black Co., high abrasion furnace black–high structure) carbon black. The liquid rubbers were defined chemical and physical properties at Table 1.

Table 1. Carboxylated isopren rubber chemical properties

Type	T_g (°C)	MW (g/mol)	Viscosity (Pa*s 38 °C)	Chemical Structure
LIR 403	-60	34000	200	
LIR 410	-59	30000	430	

The mixture with the code of Reference Coating Rubber (REF) is a traditional coating rubber content that does not contain any liquid rubber. In the coding of the test mixtures containing carboxylic isoprene liquid rubber, the first numbers indicate the phr ratio (2,5, 5, 10) and the remaining part indicates the liquid rubber type (L-403 and L-410). 100% natural rubber, silica and N326 type carbon black were used in the masterbatch content of the mixtures. It contains phenolic resin and traditional antioxidants TMQ and 6PPD. The masterbatch prepared in this way in the Banbury is diversified by the addition of liquid rubber at the final stage. The final stage contents are defined below Table 2 and Table 3 It have been mixed in the two rolls mill.

Table 2. Compounds of the prepared with LIR403

Compound	**REF**	**2,5 L-403**	**5 L-403**	**10 L-403**
	PHR			
LIR 403		2,5	5	10
INSULFUR	4,2	4,3	4,4	4,6
ZnO	1,5	1,5	1,5	1,5
DCBS	1,2	1,2	1,2	1,2
CBS	0,5	0,5	-	-
HMT80	1,04	1,04	1,04	1,04
PAVI	0,4	0,4	0,4	0,4

Table 3. Compounds of the prepared with LIR403

Compound	**REF**	**2,5 L-410**	**2,5 L-410**	**2,5 L-410**
	PHR			
LIR 410		2,5	5	10
INSULFUR	4,2	4,3	4,4	4,6
ZnO	1,5	1,5	1,5	1,5
DCBS	1,2	1,2	1,2	1,2
CBS	0,5	0,5	-	-
HMT80	1,04	1,04	1,04	1,04
PAVI	0,4	0,4	0,4	0,4

3. Results

In this study, the adhesion of natural rubber-based coating compound to isoprene-based carboxylic liquid rubbers and polyester cord, and the workability properties, change in rheological properties and crosslink density of the coating compound were evaluated.

3.1. Rheology

Figure 2 and Figure 3, the compound 150 °C and 150 minutes rheometer curves shown. In line with the results obtained, it was observed that the reversion tendencies of the liquid rubber added compound were less than the reference compound after the vulcanization time reached t100. After completing t100, the reversion rates of 5 L-403 and 5 L-410 mixtures are 20% lower than the reference mixing, and 30% lower for 10 L-403 and 10 L-410 compounds. These findings show that the thermal stability of the crosslinks formed in the presence of liquid rubber is higher [7].

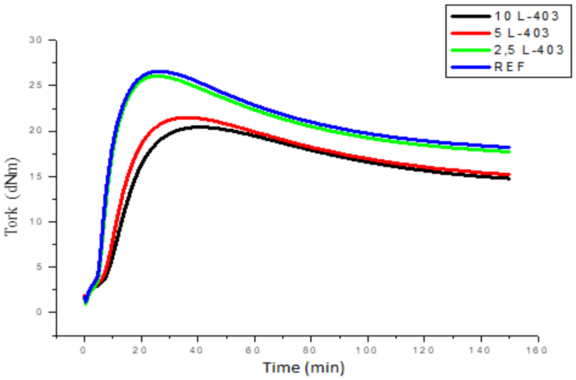


Fig. 2. 150 °C and 150 min rheometer curves of the LIR-403

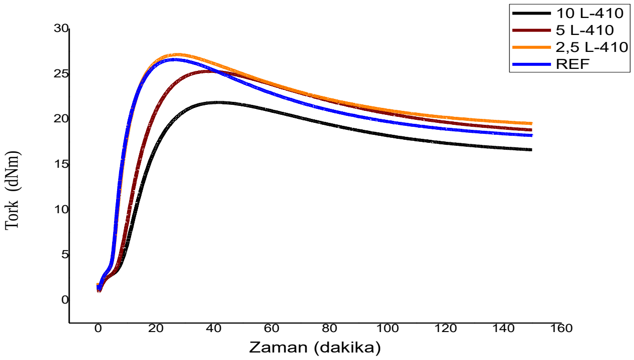


Fig. 3. 150 °C and 150 min rheometer curves of the LIR-403

Moreover, since the vulcanization condition of 150 °C and 150 minutes are the same as the conditions used in the preparation of adhesion test samples, it is emphasized that they can be used to correlate rheological properties with adhesion characteristics.

3.2. Lee-Pawlowski-Coran Crosslink Density

In rubber compounds, the network structure that exists due to the reactive interactions between fillers and polymer chains and the attachment of long polymer chains to each other is defined as physical crosslinking. The covalent network structure formed between crosslinking agents and polymer chains during vulcanization. It represents chemical crosslinks.

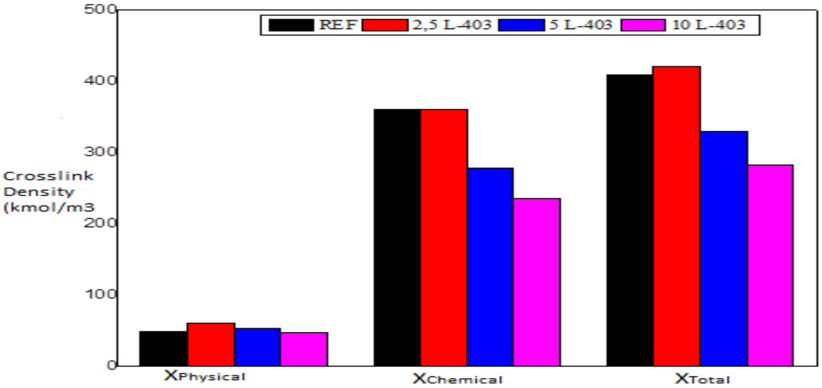


Fig. 4. Crosslink Density of LIR403

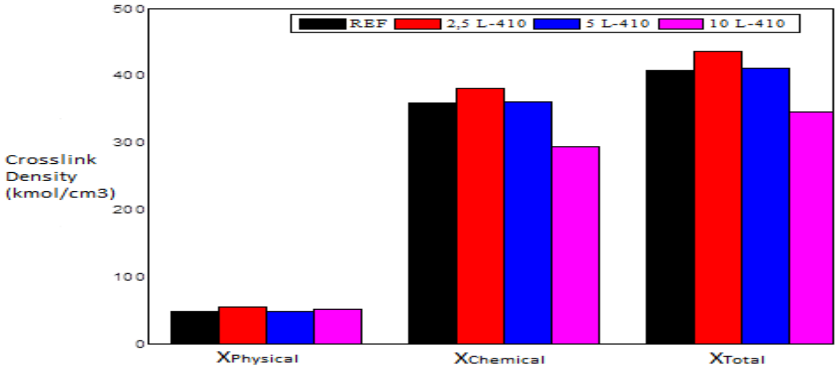


Fig. 5. Crosslink Density of LIR410

As the Figure 4 and Figure 5, the physical crosslinks increased with the addition of liquid rubber. This increase is thought to be due to the easier interaction of liquid rubbers with the filler [8]. Considering the chemical crosslinking, the highest crosslink density was obtained in 2.5 L-403 and 2.5 L-410 vulcanizates. In parallel, the total crosslink density is higher in 2.5 L-403 and 2.5 L-410 vulcanizates. It is seen that the crosslink density decreases with the addition of 5 and 10 phr liquid rubber. This finding is in line with the curing amplitude results obtained for the same mixing and confirms that the addition of high amounts of liquid rubber adversely affects the vulcanization performance. While high crosslink density of up to 421 kmol/m^3 can be obtained in L-403 compounds and this value is at most 437 kmol/m^3 for L-410 compounds. At high rates (5 and 10 phr) the crosslink density of L-410 compounds haves higher crosslink density than L-403 compounds. This finding also comply with the curing amplitude data measured by rheometer.

3.3. Frequency Sweep

The Frequency Sweep test was carried out at 100 C , %7 deformation (strain) and between 0.1 – 33 Hz. The compound was tested at determinated condition and measure the tand value. It show that below graphics. After the uncured value of the tand, the compound was cured at specific curing characteristic and then the tand value was measured again on the cured compounds. The G” loss modulus of rubber materials is related to the viscous properties of the material. The tan δ values recorded at different frequencies from the uncured form of the samples provide information about the processability of the compound [9].

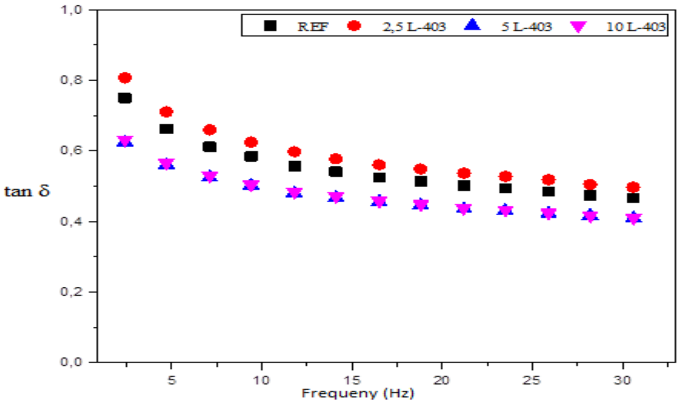


Fig. 6. Frequency sweep of uncured LIR403

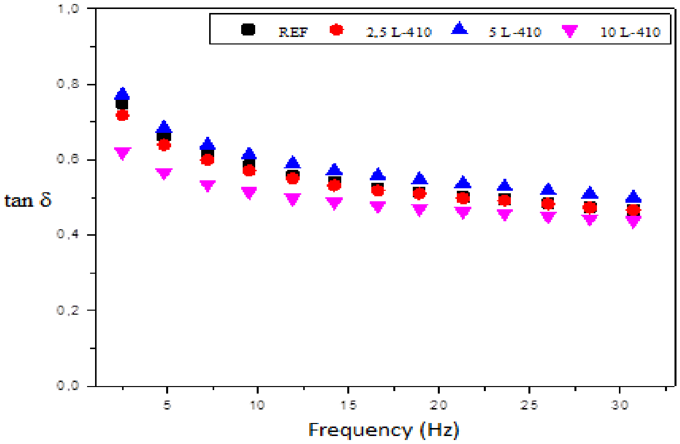


Fig. 7. Frequency sweep of uncured LIR410

As seen in the results Fig. 7, it was observed that the processability values of 2.5 phr mixtures improved in both liquid rubber additions. With increasing liquid rubber amounts, a decrease was observed in the processability properties compared to the reference mixing. There is a rheological relationship between temperature sweep and frequency sweep tests. Increasing frequency values are theoretically proportional to decreasing temperature data [10]. The low tan δ value of the vulcanizates emphasizes that the elastic property of the material is better. All of the L-403 liquid rubber added mixtures exhibited lower tan δ values than the reference mixing after curing.

It is a desired feature that the elastic properties are constant or at a lower level at increasing frequency values. In the light of the data obtained from the Lee-Pawloski-Coran crosslink density calculation, it was expected that the mixtures containing 2.5 L-403 and 2.5 L-410 would show better elastic properties. It provided better elastic properties with 2.5 L-403 and close to reference with 2.5 L-410.

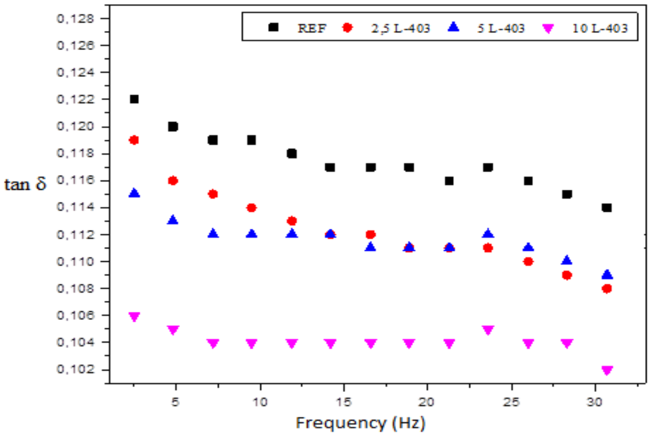


Figure 8. Frequency sweep of cured LIR403

3.4. H Adhesion Results

The H adhesion changes between polyester fiber and all compound was evaluated for 30 and 150 minutes and at 150 °C. The adhesion is decreased with increasing liquid rubber loading for short time cured compound as against reference compound. The reason for this is that when the curing characteristics at 150°C are examined, it is thought that 30 minutes of curing time is not enough for liquid rubbers to reach 100% crosslinking level. According to the results of the H-adhesion test after aging for 72 hours at 75°C for compound of cured for 30 minutes, it is seen that there is a decrease in the adhesion strength with the addition of liquid rubber compared to the reference vulcanizate as before aging. With the aging process, the bond strength is measured at lower levels than the unaged vulcanizates, since chain shears occur in the vulcanizates and the cord-rubber interface with the effect of temperature.

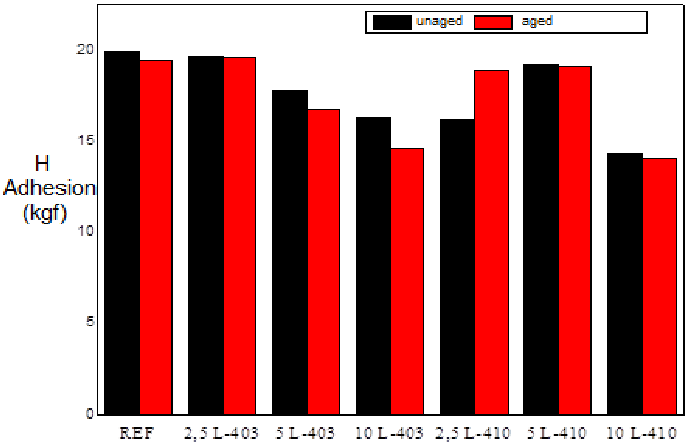


Figure 9. H adhesion results for 30 minutes

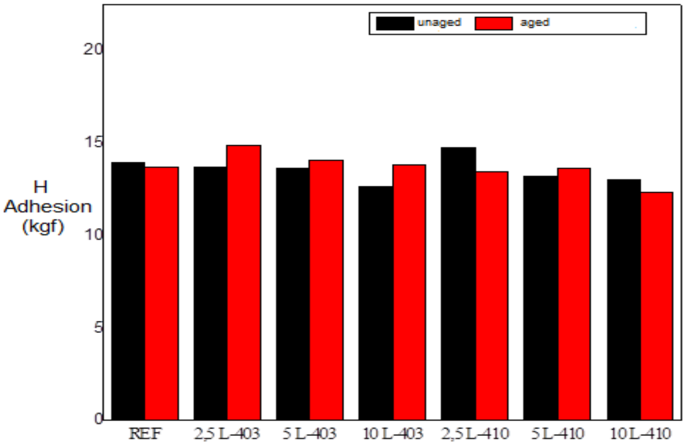


Fig. 10. H adhesion results for 150 minutes

It is observed that the adhesion strength of all compounds curing for 150 minutes decreased significantly (Fig. 10). The fact that the reversion effect of the reference compound at high curing times can be reduced by the addition of liquid rubber indicates that it is very beneficial to prefer liquid rubbers for long-term curing processes, as is the case with tires with a thick profile. Reversion reduces the bond strength as it reduces the chemical interaction in both the rubber matrix and the cord-rubber interface [11]. For this reason, It was observed that compounds with heat stability and reversion strength with the addition of liquid rubber exhibited better adhesion strength than the reference compound. In addition, compounds prepared with liquid rubbers, it is observed that the adhesion improves with aging, unlike the reference compound, except for minor deviations. This is because, during aging, liquid rubbers are thought to still continue crosslinking reactions (post-cure).

4. Discussion

In both liquid rubber types, it was observed that the viscosity decreased as expected with increasing liquid rubber ratios. This means that the rubber material will have easier processability properties in the presence of liquid rubber. Again, similar to viscosity, a significant decrease was observed in the ML values of liquid rubber added materials. However, the reason why the processability values of 5 and 10 phr mixtures with lower viscosity are lower than the reference and 2.5 phr mixtures is attributed to the high amount of liquid rubber loading and the increase in the tendency of chain entanglement in the material and the agglomeration of fillers like previous studies. As a result of these results, it was concluded that the raw processability properties of rubber mixtures improved and the fillers (carbon black-silica) in the recipe could be better dispersed in the presence of liquid rubber with the optimum amount. When the rheological properties of the mixtures were examined, it was observed that the amount of crosslinking decreased with the addition of liquid rubber. It was observed that the curing amplitude values of the mixtures decreased systematically with increasing liquid rubber ratio. These results have been demonstrated by the tests performed, where similar results were obtained with the calculation of the crosslink density of rubber materials measured using the Lee-Pawlowski-Coran approach. In the light of the rheological results, it was concluded that the 2.5 phr mixtures gave the closest results to the reference compound and the physical crosslink density gave better results than all the other mixtures, with the improvement of the above-mentioned disperse properties and the improvement of the secondary interactions of the rubber chains while they were in the raw state. In the light of this results, while maximum 421 kmol/m^3 high crosslink density can be obtained for L-403 compounds obtained by Lee-Pawlowski-Coran approach; this value is at most 437 kmol/m^3 for L-410 compounds. This value remained 405 kmol/m^3 in the reference compound. However, it has been observed with increasing amount of liquid rubber that liquid rubber has a definite negative effect on chemical crosslinking. In addition, when the rheological results were examined, a decrease in the curing rate index (CRI) values was observed in proportion to the amount of addition in all liquid rubber added mixtures. The low value of this value is seen as an important improvement in terms of wetting the cord in coating compounds.

As a result of the H tests, there was no finding that the liquid rubber clearly affected the adhesion of the polyester cord. However, liquid rubbers are thought to be preferable for long-term curing. The reason for this is that the reversion effect of the reference compound is higher than the compound with the addition of liquid rubber at high curing times. In addition, the results obtained show that, after aging, the adhesion strength of vulcanizates containing liquid rubber is higher than the reference. The reason for this is thought to positively affect the adhesion performance due to the extra crosslinking (post-cure) formation of liquid rubber added vulcanizates with aging.

Conclusions

Long curing times are preferred due to the dimensional (wall and tread thickness) properties of industrial rubber compounds. It is predicted that it can be an alternative rubber type by determining the optimum ratios for industrial tire production, since liquid rubber compounds exhibit better adhesion performance at high curing times and there is no negative effect on rheological and processability data.

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