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Effect of Peptizer in Mastication Process of Natural Rubber / Butadiene Rubber Blending: Rheological and Mechanical Properties

Ade Sholeh Hidayat*
Dewi Kusuma Arti*
Lies A. Wisojodharmo*
Muslim Efendi Harahap*
Herri Susanto*

Abstract

In our previous study, an investigation of different formulations with and without silica filler for passenger tire tread has been reported. The optimum formulation has been obtained, focusing on carbon black filled with natural rubber/butadiene blending. This study aims to extensively compare the optimal condition of mastication for three different types of peptizers. They were Vestenamer®, Aktiplast® 8 and Rhenosin® 145. The viscoelastic and mechanical properties of carbon black-filled with natural rubber/butadiene rubber blending from different types of peptizer were investigated and compared to find out the compound providing the highest compatibility for tire retread application. A wide variety of rheological properties were observed, such as payne effect and frequency sweep. The addition of Vestenamer® significantly increase the payne effect, hardness, rebound resilience and abrasion properties compared to the other two peptizers. However, the values of tensile strength and tear strength are still lower than Aktiplast® 8, but they have already fulfilled the requirement, 20 N/mm^2 and 200 N, for the tensile strength and tear strength, respectively. It is proved that Vestenamer® is the best peptizer to optimize the mastication process.

Keywords:

Rubber
Peptizer
Tyre tread
Mastication
Mechanical properties

Author correspondence:

Ade Sholeh Hidayat
Center for Materials Technology, Agency for the Assessment and Aplication of Technology,
Building 224, Pupspiptek Area, South Tangerang 15314, Indonesia
Email: ashhidayat@gmail.com

1. Introduction

Tire tread is a part of a tire that has the greatest impact on the trip and in its use. The performance of tire tread was measured by combination of "magic triangle properties". They are rolling resistance, traction and wear. The balance of those properties increases the quality of tire tread. To obtain high quality of tire tread, a good quality of rubber compound is needed.

Natural rubber (NR) has a wide application especially in tire tread since it has a wide hardness range, very strong and naturally self-reinforcing, good compression sets, good resistance to inorganic chemicals, and rebound resilience. However, it has some limitations such as lack of oil and organic fluids resistance,

* Center for Materials Technology, Agency for the Assessment and Aplication of Technology, Building 224, Pupspiptek Area, South Tangerang 15314, Indonesia

maximum temperature up to 75 - 100°C and poor ozone resistance. Cured Butadiene Rubber (BR) provides excellent abrasion resistance (good tread wear) and low rolling resistance (good fuel economy), due to its low glass transition temperature (Tg). In our previous research, the combination of NR-BR has been optimized [1].

Mastication process is very important step in compounding preparation. To obtain homogeneous compounding, mastication has to be prepared well. Mastication is a processing stage in an internal mixer or in an open mill, in which the viscosity of the rubber is reduced to a level that facilitates further processing, making processing more feasible. A useful additive for this process is peptizer. The peptizer has some important roles, including faster filler incorporation, better dispersion of compounding materials, better elastomeric blends, lower processing temperatures, improved flow properties and enhanced building tack. In some cases like natural rubber and synthetic rubber blending, it seems difficult to blend without a peptizer since they have different viscosities.

The benefits of peptizing agents are to accelerate peptization, reduce mixing time and power consumption, promote batch to batch uniformity, facilitate blending elastomers, reduce mixing costs, and improve dispersion [2].

The aim of this study is to compare the optimal condition of mastication for three different types of to find out the compound providing the highest compatibility for tire retread application. Three different peptizers were used in this research. They were Vestenamer®, Aktiplast® 8 and Rhenosin® 145. Selection of these types of peptizers was based on the popularity of them in the Indonesian market. Vestenamer® is a type of polyoctanamer, in specific it is trans-polyoctenylene. It consists of trans-double bond that improve not only mastication process but also vulcanization process. It has low melting point and low viscocity but it is the most reactive peptizer among all types that were used [3]. Aktiplast® consists of complex Zinc metal that works by reducing the molecular weight of rubber and decreasing rubber viscosity [4]. While Rhenosin® 145 is phenol formaldehyde which is usually used in synthetic rubber. It can decrease scorch time and curing time significantly [5].

Since a tire is a composite structure made of substances with various properties, each of these substances has to be chosen carefully. One of the substances which are important for blending different type of rubber is peptizer. The peptizer has significant role in mastication process and in decreasing viscosity. Therefore, the aim of this research is to improve mastication process by using different peptizers.

The systematics of writing this paper is as follows. Section 1 contains the introduction of the research which covers background and the aims of the research. Section 2 describes about the materials and methods that are used in the research. Section 3 explains the results of the research which are then followed by the discussion. And the last one, Section 4 contains the conclusion of the research.

2. Materials and Methods

Materials

Natural rubber (NR), Ribbed Smoked Sheet (RSS#1) with the density of 0.95 was provided by a local supplier in Indonesia. Butadiene rubber (BR) with the Mooney viscosity 40 and the density of 0.92 was obtained from Goodyear Chemical. Carbon black N 220 was purchased from Cabot. Three types of peptizers, Vestenamer® (V) from PT Evonik Indonesia, Aktiplast® 8 (A) and Rhenosin® 145 (R) from Lanxess, were used.

Preparation of rubber compound

A laboratory-sized kneader Moriyama DS3-10MWB-E was employed to prepare rubber compounds. The mixing was divided into two stages. In the first stage, the mixing condition was set at the temperature of 100°C and the velocity of 60 rpm. The mixing was started by mixing fixed amount of NR-BR at various compositions along with plasticizers for about 5 minutes, and followed by adding zinc oxide, stearic acid, carbon black, other additives and a half of oil for about 6 minutes. The remaining oil was then added into the kneader for about 2 minutes. The compound was passed on the two-roll mill at 70°C for 6 times. After the master batch was stored for a night to allow the rubber compound to rest, the batch then was mixed with curatives in the kneader. The temperature was set at 70°C and the velocity of 60 rpm for about 2 minutes. At the end of the mixing, the batch again was passed on the two-roll mill, cooled and stored for another 24 hours before it can be used for further analysis.

Three different formulations (samples) were designed which can be seen in the Table 1, i.e. FV, FR and FA. In all formulations the total of rubber (NR and BR) was kept at 100 phr. A fixed amount of 3 phr peptizer was also applied based on the previous research [6]. Cure characteristics were determined using an MDR 3000 MonTech. Delta torque is obtained by subtracting of maximum torque (MH) and minimum torque (ML). Scorch time (Ts2) is the time to reach 2 units above minimum torque (ML), and optimum cure time (T90) is the time to achieve 90% of delta torque above minimum. Sheets and test specimens were vulcanized by a compression molding. The experimental curing press was set at the temperature of 140ºC and the time of curing was based to T90, which was obtained from curing testing.

Rheological properties were measured using a RPA Flex TA Instrument. The loss tangent of the vulcanizates was determined using RPA at 60°C and strain 3.49% with varying sweep frequencies in the range of 0.5-50 Hz.

Table 1. Formulation design in phr

Components	**FO***	**FV**	**FR**	**FA**
RSS	85	85	85	85
BR	15	15	15	15
Rhenosin® 145	0	0	**3**	0
Aktiplast® 8	0	0	0	**3**
Vestenamer®	0	**3**	0	0
ZnO	5	5	5	5
Stearic acid	3	3	3	3
N220	50	50	50	50
Additives	8	8	8	8
Processing oil	6	6	6	6
Curatives	3	3	3	3

* FO is a formulation without addition of any peptizer.
It will be used as a benchmark for the other 3 samples

Testing of rubber vulcanizates

Tensile strength was determined according to ASTM D412 and DIN abrasion using DIN ISO 4649. While rebound resilience and hardness were based on the ASTM D2632 and ASTM D2240 respectively.

3. Results and Discussion

Mooney viscosity

The use of peptizers decreased the the mooney viscosity of compound. As shown in the Table 2, FR gave no signifficant effect to the decreasing mooney viscosity compared to FV and FA. In theory, the lowest mooney viscosity will give better dispersion and easier processing in further production [7].

Table 2. Mooney viscosity of the three different peptizers

Samples	**Mooney viscosity (MU)**
FO	56.76
FR	55.88
FV	52.45
FA	49.14

The decrease of compound viscosity when different types of peptizers were used implies an improvement of filler dispersion resulting in better compatibility. However, the compound viscosities can be affected by various factors including NR/BR blend incompatibility. Thus the presence of peptizers leads to the difference solubility and interfacial tension.

Rheological properties

Filler-filler interaction, as indicated by the Payne effect in the Figure 1, the filled compound with Vestenamer as peptizer showed higher shear modulus. And the data of the optimal cure time and scorch time of the samples can be seen in the Table 3.

Table 3. The optimal cure time and scorch time of the samples

Formulation	**Curing time t90 (minutes)**	**Scorch time ts2 (minutes)**
FO	14.02	2.44
FR	9.76	2.99
FV	10.81	2.53
FA	13.83	2.65

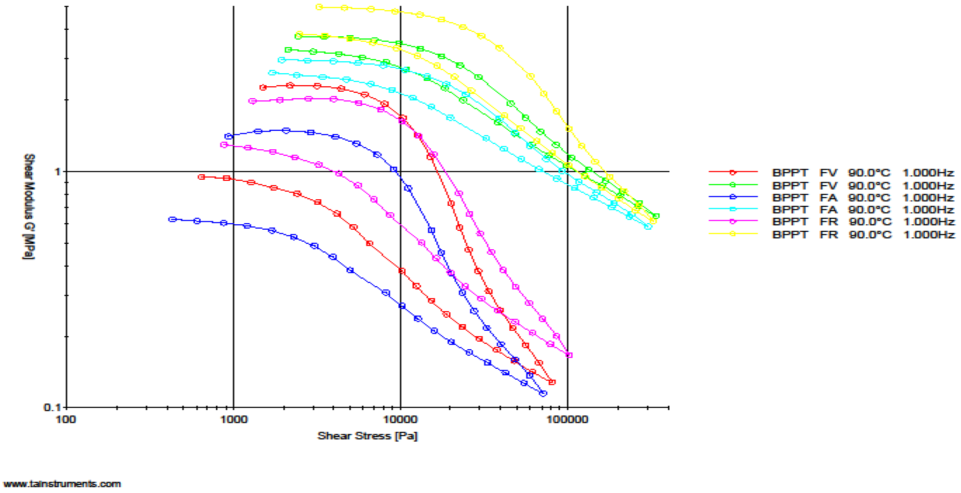

Figure 1. Payne effect back and forth of different types of peptizers

From the Figure 1 and Table 3 above, it can be seen that the addition of BR into the NR compound does not have a significant effect on altering curing time, scorch time or delta torque. There is no significant difference of curing characteristics between rubber compound and different peptizers.

Characterization of Vulcanized Rubber

a. Hardness

Hardness may be defined as a material's resistance to permanent indentation. The Shore A Hardness Scale measures the hardness of flexible mold rubbers that range in hardness from very soft and flexible, to medium and somewhat flexible, to hard with almost no flexibility at all.

It is expected that the addition of peptizer will have a significant effect on altering the hardness of rubber compound. In this research, the addition of peptizers has increased the hardness of rubber compound as presented in the Figure 2. The hardness of the rubber is influenced by the presence of cross-linking in the rubber compound and the amount of carbon black filler used. In this case, the amount of carbon black and sulfur used were similar for all compound formulations so it was not the factor that affects the outcome. The factor that can be said to affect the outcome is the peptizer used, wherein the peptizer is a material which can homogenize the dispersion of each additive mixed so as not to form too large aggregates in certain regions which may affect the interaction between polymer chains and polymer chain adsorption by carbon black impacts on the mechanical properties of the resulting compound. Hence, it can be interpreted that Vestenamer is a peptizer that can homogenize the mix well and does not cause large aggregate to accumulate in certain areas within the rubber compound, in other words interaction between polymer chain and polymer chain adsorption by carbon black occur optimum so that Van Der Waals which is formed stronger and can retain the shape of the rubber compound when given a force against it [8].

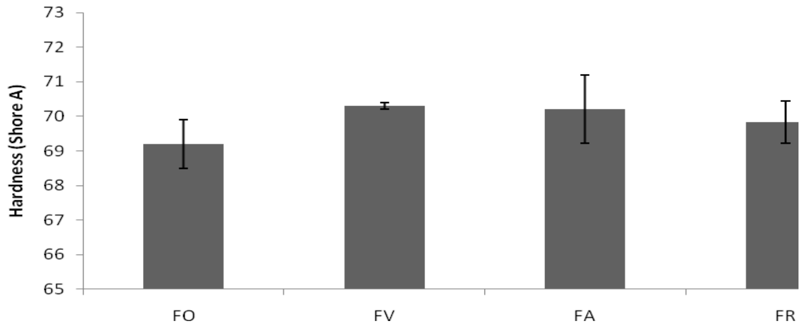

Figure 2. Compound hardness of the three types of peptizers (samples)

b. Tensile and Tear Strength

Tensile strength is the maximum tensile stress reached in stretching a test piece (either an O-ring or dumbbell). Tensile tests are used for controlling product quality and for determining the effect of chemical or thermal exposure or an elastomer. In the latter case, it is the retention of these physical properties, rather than the absolute values of the tensile stress, elongation or modulus, that is significant. Figure 3 shows the result of tensile strength measurement. The strength of rubber compound has reached the minimum requirement of tread tire, 20 N/mm^2.

Tear resistance (or tear strength) is a measure of how well a material can withstand the effects of tearing. In rubber, tear resistance measures how the test specimen resists the growth of any cuts when under tension. As well as, tensile strength, Figure 4 shows that the values of tear strength for each compound have fulfilled the requirement, 200-300 kN.

Unlike NR, BR does not have crystallization properties; therefore, the tensile strength of BR is very poor. When NR is blended with BR, the mastication process has an important role to improve the mechanical properties of mixing materials. Thus, those three peptizers, have been succeed to be the peptizing agent in this research.

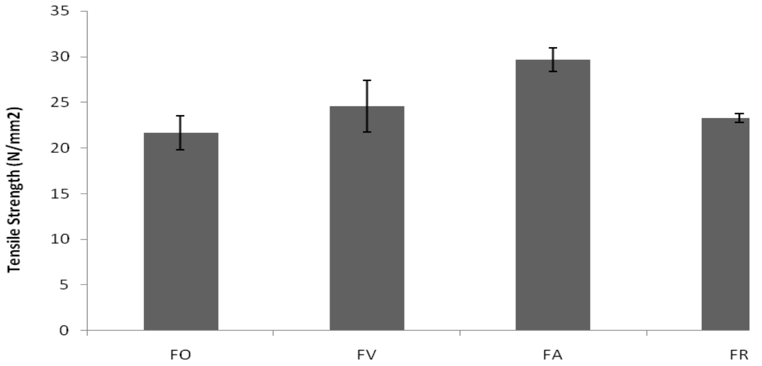

Figure 3. Tensile strength of compounds of the three types of peptizers (samples)

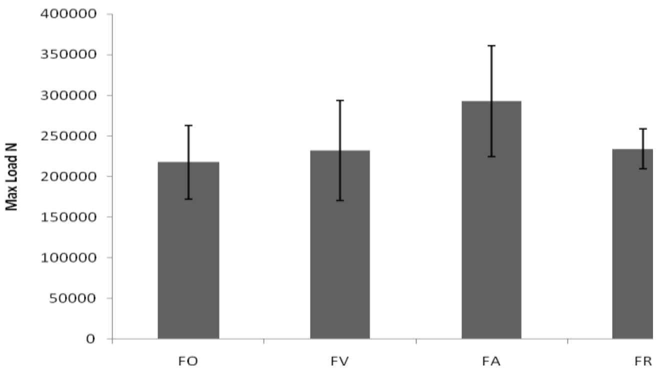

Figure 4. Tear strength of compounds of the three types of peptizers (samples)

c. Abrasion Resistance

Abrasion resistance is the ability of a material to resist mechanical action such as rubbing, scraping, or erosion that tends progressively to remove material from its surface. When a product has abrasion resistance, it will resist erosion caused by scraping, rubbing, and other types of mechanical wear. This allows the material to retain its integrity and hold its form. This can be important when the form of a material is critical to its function, as seen when moving parts are carefully machined for maximum efficiency. Abrasion resistant materials can be used for both moving and fixed parts in settings where wearing could become an issue.

Figure 5 shows that the properties of a vulcanized rubber can be significantly influenced by the composition of compounding. Practical materials will have difference abrasion resistences, in addition to the base polymer, fillers, antioxidants, cross-linking agents, accelerators etc. All of these can have an influence on the physical and chemical stability of the finished material. For example, rubber abrasion resistance can be related quantitatively to the frictional force and the crack growth characteristic of the rubber.

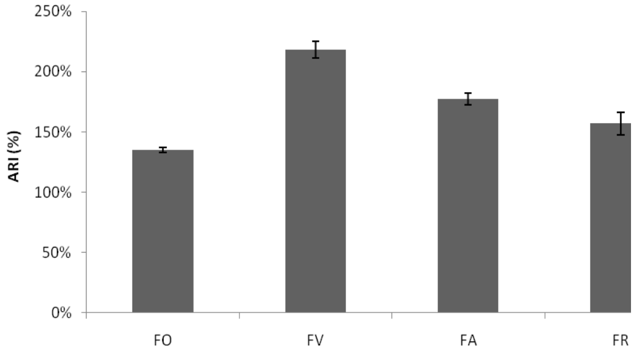

Figure 5. Abrasion resistance of compounds of the three types of peptizers (samples)

d. Rebound Resilience

Resilience of a rubber compound is a measurement of how elastic it is when exposed to various stresses. Resilience is the ratio of energy released in deformation recovery to the energy that caused the deformation. Measurement of rubber resilience can assist in choosing the right material for a given application, for example tread tire.

The adding of Vestenamer leads to resilience percentage improvement. It was in agreement with the increasing of abrasion resistance. Figure 6 shows rebound resilience using different types of peptizers.

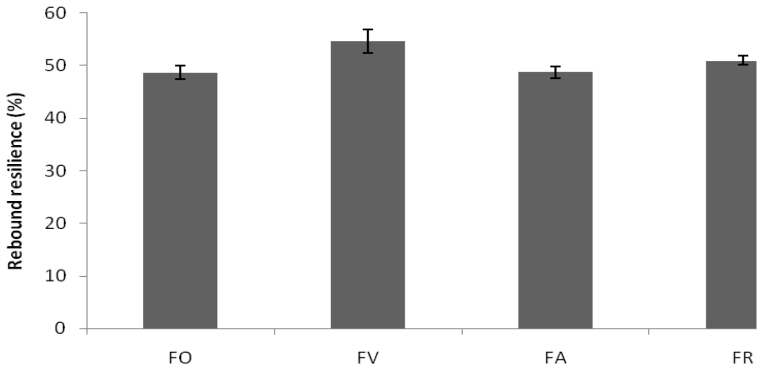

Figure 6. Rebound resilience of compounds of the three types of peptizers (samples)

Carbon Dispersion Tester

This analyzer is designed for the purpose of observing the dispersed situation of the carbon black in a mixing compound rubber. Carbon black as the main filler in this compound has an important role to determine the final compound characteristics. The carbon dispersion level is important to know because it will affect the properties of compound. In addition, the particle size of carbon black is very small and easy to agglomerate, so that the effects of colloid properties and compound will have poor behavior.

Carbon DisperTester MonTech takes the surface picture by shooting ray to the sample. The data from surface area are recorded and compared with the reference to interpret the carbon dispersion level. Figure 7 shows morphology of carbon dispersion level from the three samples (FR, FV and FA).

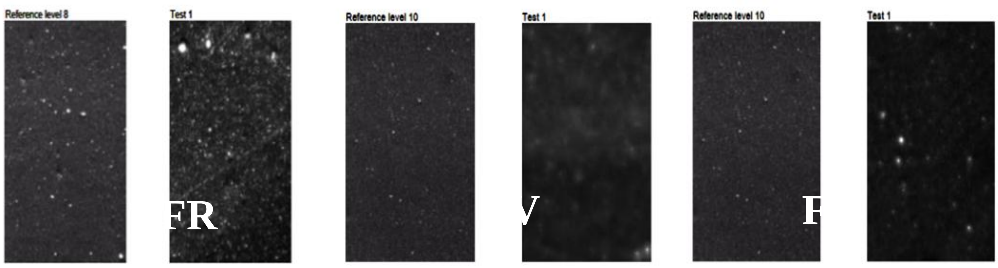

Figure 7. Carbon dispersion level of the three samples

Table 4. Data from carbon dispersion tester

Samples	Dispersion percentage (%)	Dispersion level
FR	90.09	8
FV	98.49	10
FA	99.32	10

Table 4 shows the percentage of carbon dispersion in each sample. Overall the level of dispersion in all samples was above 90%. Thus it can be labeled quite evenly. This dispersion value indicates that the distribution of carbon black filler in the FV and FA samples were the best which is inversely proportional to the amount of agglomeration.

The level of dispersion in the samples is strongly influenced by the mastication process which in this experiment used three different additives. Vestenamer® gives a good effect on the mixing that occurred. This is in accordance with research conducted by Rodges where Zn can capture the oxygen that will become the radical acceptor of the broken polymer chain [9]. Other ingredients present in the activator are unsaturated fatty acids which will help parafinic oil to decrease the internal viscosity of the molecule. In the study also mentioned that Zn is the best physics peptizer that can be used. While on the variation of FV used additives in the form of vestenamer which consists of polymers with low molecule weight polyoctenamer. According to Chang the viscosity of a raw rubber material can be decreased by adding polyoctenamer to the mixture [10], such as Rhenosin which contains aromatic hydrocarbon compounds.The mechanism of the decreasing viscosity in raw materials is not yet known exactly, however a research of Oter states that oil from aromatic hydrocarbons can reduce the viscosity in the sample efficiently [11].

4. Conclusion

Effect of peptizer for natural rubber (NR)/butadiene rubber (BR) blending in rheological properties is showed by comparing Payne effect diagram. Vestenamer shows higher shear modulus which indicates easier processing during preparation. However, curing time and scorch time of Rhenosin and Vestenamer compounding were not significantly different. The mechanical properties especially abrasion resistance and rebound resilience have been improved significantly by the addition of Vesternamer. These two mechanical properties are very impotant in tire tread characterization. Vestenamer as a peptizer for carbon black filler shows excellent mechanical properties of a tire tread formulation. Due to good properties of this blending, it can be recommended to apply this formulation in tire tread. But detail testing in order to fulfill the requirements of tread compound should be carried out in at more advanced level.

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