Interaksi Karet Alam/High Cis Butadiene *Rubber*-Bahan Pengisi Dan Sifat Reologi Pada Kompon *Rubber Airbag*

Natural Rubber/High Cis Butadiene Rubber-Filler Interactions And Rheological Properties In Rubber Airbag Compounding Formulation

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Abstract

The rheological properties of rubber compound in general application and especially rubber airbag compounding is very important to predict the mechanical properties of rubber products, as well as useful for obtaining optimum formulations in the research and development of a product. The viscoelastic properties of the rubber compound are strongly influenced by the type of rubber and the filler used. The purpose of this research is to investigate the rheological properties of rubber airbag compounding using natural rubber (NR) and high cis butadiene rubber (BR) materials with various compositions of carbon black N220 filler. The mixing of NR and BR with 90/10 phr ratio was performed in a kneader, with carbon black N220 filler variation: 35, 45, 50 phr, named as BD1, BD2 and BD3, respectively. Rheology and viscosity properties were tested using Rubber Process Analyser (RPA) 2000 Alpha Technology. The test was performed with strain sweep at 70 C and comparing 1% strain and 10% strain to indicate dispersion and homogenity. Frequency sweep was performed at 100 C at 6 cpm and 7% strain. High strain sweep was also done as well as strain sweep after cure (ASTM D6601) which material were cured at 180^0 C and strain sweep was applied at 1%, 2%, 5%, 10% and 20% to determine the mechanical properties of compound. The result showed that 35 phr of carbon black N220 (BD1) was the optimum formulation since compounds BD3 and BD2 have higher elastic torque (S') peaks and may be harder to process as a result. The results for Tan (Delta) from all compounds in the high strain sweep verify that compounds BD3 and BD2 have lower Tan(Delta) values and therefore will probably have more difficulty in processing. The highest peak of modulus values at low strain indicates the carbon black with the highest reinforcement or the worst dispersion. BD3 and BD2 have high peak modulus value which is show the worse dispersion compared to BD1.

Keywords: *rheology, rubber airbag, filler, RPA*

Abstrak

Sifat reologi pada kompon karet untuk aplikasi karet teknik terutama kompon *rubber airbag* sangat penting untuk memprediksi sifat mekanik dari produk karet, serta memperoleh formulasi yang optimal dalam penelitian dan pengembangan suatu produk. Sifat viskoelastis dari kompon karet sangat dipengaruhi oleh jenis karet dan bahan pengisi yang digunakan. Tujuan penelitian ini adalah untuk mengetahui sifat rheologi kompon *rubber airbag* menggunakan bahan karet alam (NR) dan karet sintetik high-cis butadiene rubber (BR) dengan berbagai komposisi bahan pengisi carbon black N220. Pencampuran NR dan BR dengan rasio 90/10 phr dilakukan dengan kneader, dengan variasi bahan pengisi carbon black N220: 35, 45, 50 phr, dinamakan masing-masing sebagai BD1, BD2 dan BD3. Sifat rheologi dan viskositas diuji menggunakan Rubber Process Analyzer (RPA) 2000 Alpha Technology. Pengujian dilakukan dengan *strain sweep* pada 70^0C dan membandingkan strain 1% dan strain 10% untuk menunjukkan dispersi dan homogenitas. *Frequency sweep* dilakukan pada 100^0C pada 6 cpm dan 7% regangan. *Strain sweep* tinggi juga dilakukan dan juga *strain sweep* setelah matang (ASTM D6601) dimana kompon dimatangkan pada 180^0 C dan *strain sweep* diaplikasikan pada 1%, 2%, 5%, 10% dan 20% untuk menentukan sifat mekanik dari kompon. Hasilnya menunjukkan bahwa 35 phr carbon black N220 (BD1) adalah formulasi optimum karena kompon BD3 dan BD2 memiliki puncak torsi elastis (S') yang lebih tinggi dan mungkin lebih sulit untuk diproses sebagai hasilnya. Hasil untuk Tan (Delta) dari semua kompon dalam *high strain* memverifikasi bahwa senyawa BD3 dan BD2 memiliki nilai Tan (Delta) yang lebih rendah dan oleh karena itu akan lebih sulit dalam pengolahan. Puncak tertinggi nilai modulus pada regangan rendah menunjukkan carbon black dengan *reinforcement* tertinggi atau dispersi terburuk. BD3 dan BD2 memiliki nilai modulus puncak tinggi yang menunjukkan dispersi yang lebih buruk dibandingkan dengan BD1.

INTRODUCTION

Although longitudinal ship launching is a conventional launching technique, Chinese shipyards have adopted and become proficient in a new launching technique that uses ship launching airbags (hereinafter referred to as airbags) instead of a slipway. This so-called “soft launching” technique was invented in the 1980s and became popular at small- and medium-scale domestic shipyards because of its low cost and environmental friendliness. In 2010, a 70,000-ton bulk carrier was safely launched using airbags in Zhejiang province with the launching weight approached 13,000 tons. However, with increasing launch weight, it becomes necessary to focus more on the overloading of the airbags as well as on the possibility of permanent deformation to the ship bottom. Based on the accumulated experience of launching by ship-airbags, several national and international standards have been established for ensuring the success of the launching process [1].

One of the challenge in production of ship launcher is the quality of rubber compounding material. In this study, rheological review and viscoelastic becomes the main focus because they are very important to predict mechanical properties of rubber products, as well as useful for obtain the optimum formulation in the study and the development of a product. Before preparing the samples in the laboratory scale that will be spent more material and takes time the longer, optimization of the formulation with perform rheological and viscoelastic properties testing expected to be more efficient method [2].

The purpose of the study was to determine the nature viscoelastic and rheology of rubber airbag compounds using natural rubber base material (NR) and high-cis butadiene rubber (BR) with variations in the composition of fillers carbon black [3]. This development is necessary in the process of rubber airbag preparation in Indonesia considering the Indonesia in maritime country that needs large application of this product to launch the ship as one of main transportation.

MATERIALS AND METHODS

Natural rubber type RSS III that used in this research was obtained from local supplier, and butadiene rubber (BR) from Goodyear Company. Carbon black N220 from Cabot and highly dispersible Silica from Jebsen and Jessen were used as filler. The formulation for each variable is shown as Table 1.

The RPA 2000 is a Dynamic Rheological Tester. The RPA applies a strain to a polymer sample using a sinusoidal amplitude. The number of these cycles per minute can be programmed. In addition, the temperature of the test can vary from room temperature to 230 ^{0}C. The customer asked for the capabilities of the RPA with their mixed stocks.

Table 1. Formulation.

Materials	**Formulation (phr)**			
	BD1	**BD2**	**BD3**	**BDS**
RSS III	90	90	90	100
BR	10	10	10	0
CB N220	35	45	50	35
Silica	5	5	5	5
Additives	26.5	26.5	26.5	26.5

Accelerator	1	1	1	1
Curative	2	2	2	2

For the purposes of this study, the RPA 2000 ran the following tests on all of the materials. Each test was run twice to verify repeatability the tests and possibly the homogeneity of the compounds. The four tests are as follows in order of possible importance. Firstly, strain Sweep at 70 ^{0}C – Low strain region indicates dispersion of compounds. The strain softening characteristic of the compound can be quantified by comparing the results at 1% strain and 10% strain. This can also indicate the dispersion of the mix by running the test at 70 ^{0}C. The second, frequency Sweep at 100 ^{0}C – Crossover point of G' and G" can indicate the relative Molecular Weight (MW) and Molecular Weight Distribution (MWD) of the mixed polymer if the formulations are similar. The Tan (Delta) results at 6 cpm and 7% strain can indicate potential processing issues if the values are near or less than 0.500. Third, high Strain Sweep at 100 ^{0}C – Helps characterize raw elastomers or mixed compounds. Materials with peaks at high strains are often more difficult to process. The last, strain Sweep After Cure (D6601) – Materials were cured at 180 ^{0}C [4]. The Automatic End of Cure was selected so that the test would stop when the cure curve reached a plateau. With this feature, there was no need to run a test just to determine the cure time. After cure, a strain sweep was applied at 1%, 2%, 5%, 10% and 20% to determine the mechanical properties of the compound.

RESULTS AND DISCUSSION

Figure 1 shows the elastic shear modulus G' versus strain on all four compounds. This test includes the lowest strains that the RPA is capable of reaching. The results at these low strains indicate the polymer / filler interaction and the quality of the mix. There are two tests for each compound. The results were very repeatable. The materials had peak modulus values at low strains with the following rankings:

BD3 > BD2 > BDS > BD1

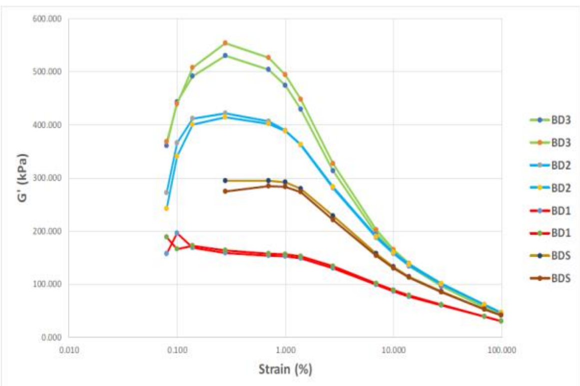

Figure 1. G' versus strain at 0.1 Hz and 70 C on all mixed compounds. Repeatability is very good. Results indicate different levels of reinforcement in each of the compounds by comparing results at low strains as well as different amounts of strain softening or the Payne effect as seen in the reduction of G' with increasing strain.

Repeatability is also very good. Results indicate different levels of potential heat build up during processing. Higher G" values will produce higher heat build up [5].

The highest peak may indicate either the carbon black with the highest reinforcement or the worst dispersion or highest level of carbon black or combinations of all three depending on the formulation and mixing procedure. Figure 2 shows that G" has similar shapes. Figure 3 shows the results for Tan(Delta). All of the compounds have values around 0.800. This is a range where processing is often easy [6].

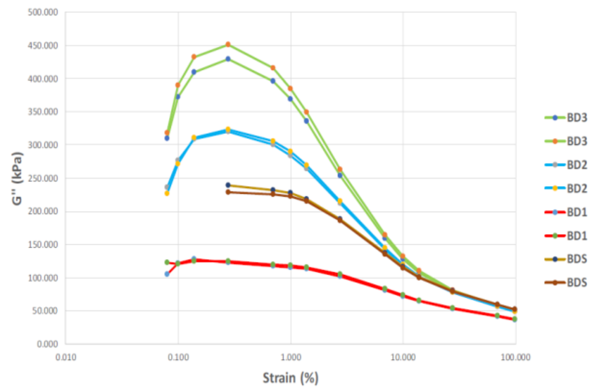

Figure 2. G'' versus strain at 0.1 Hz and 70 C on all mixed compounds.

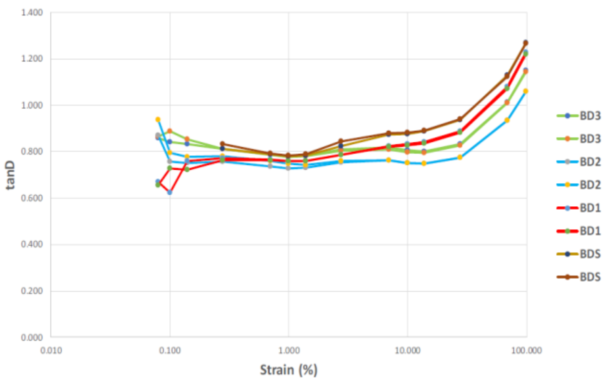

Figure 3. Tan(Delta) versus strain at 0.1 Hz and 70 C on all mixed compounds. Repeatability is very good. Results are similar for all compounds. Tan(Delta) values often indicate processability of uncured mixed compounds. The values here which are around 0.800 indicate that there should be no problem in processing. Problems can occur if the values approach 0.500.

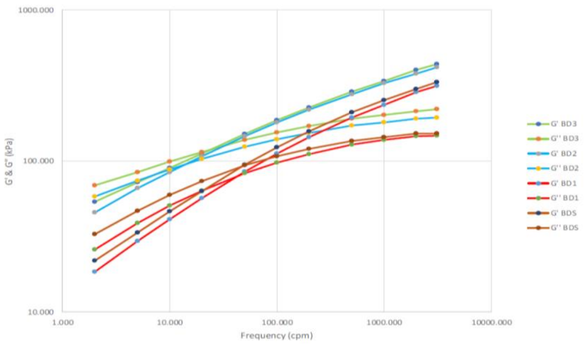

Figure 4. Frequency sweeps at 100 C from all four mixed compounds. Both G' and G" from each compound are plotted versus oscillation frequency. Each compound uses its line own color for both G' and G". but different markers. Each compound has a crossover point which can indicate the molecular nature of linear elastomers.

Figure 4 shows a frequency sweep on the four compounds at 100 C and 7% strain. There is only one set of curves from each compound. For each compound, both G' and G" are plotted. The crossover point of G' and G" can indicate the MW and MWD differences among similar compounds using the same linear elastomers and the same amount of filler [7]. Figure 4 also shows that compounds BD3 and BD2 are similar. BD2 does appear to have a broader MWD and a higher MW. Compounds BD1 and BDS are also similar. This suggests that they have similar elastomers. BD1 appears to have a broader MWD. These observations apply only if all four materials were made with the same linear elastomers and contained the same amount and type of fillers [8].

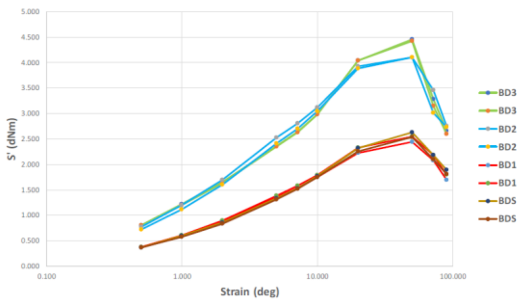

Figure 5. S' versus strain from a high strain sweep. The four compounds appear to form two distinct shapes. Peaks in S' at high strain often indicate materials with processing issues.

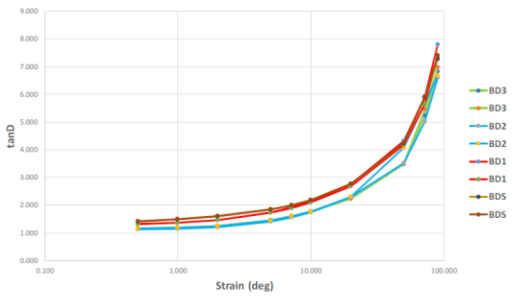

Figure 6. Tan(Delta) versus strain from a high strain sweep. The four compounds appear to form two distinct shapes.

Figure 5 shows S' versus strain from a high strain sweep on all four compounds. Figures 1 to 3 show the results from strains of 0.07% to 100%. Figure 5 has strains of 7% to 1256%. All of the compounds have distinct S' peaks. Typically, S' peaks indicate compounds with difficulty in processing. Compounds BD3 and BD2 have higher peaks and may be harder to process as a result. Figure 6 shows the results for Tan(Delta) from all compounds in the high strain sweep. The results verify that compounds BD3 and BD2 have lower Tan(Delta) values and therefore will probably have more difficulty in processing.

Materials with lower Tan(Delta) values at high strains such as BD2 and BD3 often have processing issues [9].

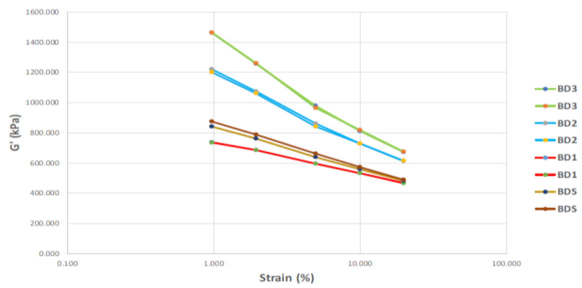

***Figure 7**.* G' versus strain at 100 C after cure. BD3 has the highest stiffness and BD1 is the softest.

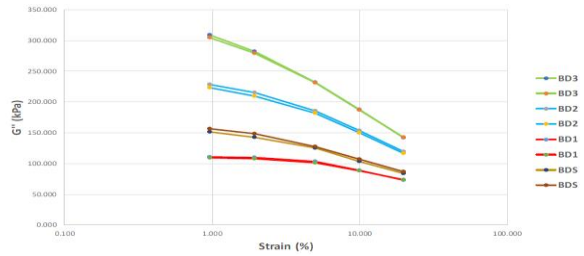

***Figure 8**.* G" versus strain at 100 C after cure. Higher G" values produce more heat during deformation and can produce more damping.

Figure 7 shows G' versus strain after cure at 100 C. The G' value after cure indicates the durometer of the cured compound [10] with the ranking as follows:

BD3 > BD2 > BDS >BD1

The steeper slopes indicate more strain softening and probably more reinforcement from the carbon black used. Figure 8 shows a similar plot for G". Higher G" values indicate more heat build up when deforming these cured compounds [11].

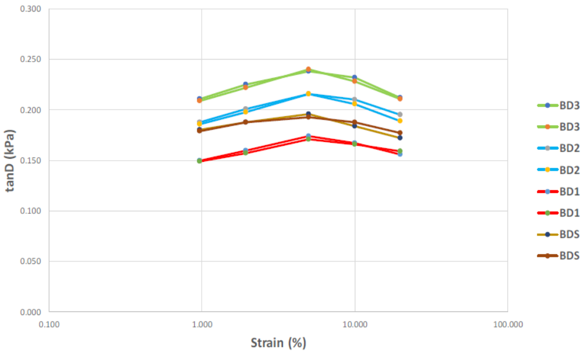

Figure 9. Tan(Delta) versus strain at 100 C after cure. Results show that BD3 has best mechanical damping while BD1 has the least.

Figure 9 shows the Tan(Delta) versus strain for all cured compounds. The results show that BD3 has the best dampening of all compounds. BD1 has the least amount of dampening.

CONCLUSIONS

Four compounds were tested on an RPA. Samples were tested with strain sweeps and frequency sweeps before cure. Low strain sweeps were able to clearly characterize all four compounds. Frequency sweeps showed that the materials could be put into two groups with molecular differences in their polymer structure. High strain sweeps also showed that the materials belonged in two groups. After the materials were cured, a strain sweep showed that the stiffness of the cured materials were all different. The tan(Delta) values after cure showed four different levels of damping present in the cured materials. The result showed that 35 phr of carbon black N220 (BD1) was the optimum formulation since compounds BD3 and BD2 have higher elastic torque (S') peaks and may be harder to process as a result.

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REFERENCES

[1] Yu, L., Li, Y., Xia, L., Dinga, J., Yang, Q. (2015) Research on mechanics of ship-launching airbags I—Material constitutive relations by numerical and experimental approaches. *Applied .Ocean Research*, 52: 222–233.

[2] Wisojodharmo, L.A., Fidyaningsih, R., Fitriani, D.A., Arti, D.K., Indriasari, and Susanto, H. (2017). The Influence of Natural Rubber – Butadiene Rubber and Carbon Black Type on the Mechanical Properties of Tread Compound. *IOP Conf. Series: Materials Science and Engineering*, 223: 012013.

[3] Hofmann, W. (1989). Rubber Technology Handbook, Oxford Univ. Press, New York.

[4] ASTM D6601-15, Standard Test Method for Rubber Properties—Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer, ASTM International, West Conshohocken, PA, 2015.

[5] NA (2017) Evonik presents new solutions for improved rubber compounds. *Additives for Polymers*. 4: 4-5.

[6] D.G Lloyd. (1991). Additives in rubber processing. *Materials & Design*. 12 (3): 139-146.

[7] Wisojodharmo, L.A., Indriasari, and Arti, D.K. (2015). The Influence of Natural Rubber-Butadiene Rubber and Type of Carbon Black Particle as the Filler on the Mechanical Properties of Track. *Proceeding The International Conference on the Innovation in Polymer Science and Technology 2013*. 48-57.

[8] Sengloyluan, K., Sahakaro, K, Dierkes, W.K., and Noordermeer, J.W.M. (2104). Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber. *European Polymer Journal*. 51: 69-79.

[9] Rodges, B. (2016). Rubber Compounding Chemistry and Application, CRC Press, Florida.

[10] Chang,W.Y, Shin,Y.S. Chun, H. dan Nah, Y. (1999). Effects of trans-Polyoctylene Rubber (TOR) on the Properties of NR/EPDM Blends , *Journal of Applied Polymer Science*,. 73: 749–756.

[11] Oter ,M., Karagenac, B. Deniz,V., and Koracel. (2011). Substitution of Aromatic Prosessing Oil in Rubber Compound. *Journal KGK*, 09032011:1-5.