The effect of antioxidant concentration of N-isopropyl-N-phenyl-p-phenylenediamine, and 2,2,4-trimethyl-1,2-dihydroquinoline and mixing time of physical properties, thermal properties, mechanical properties and microstructure on natural rubber compound

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The Effect of Antioxidant Concentration of N-isopropyl-N-phenyl-p-phenylenediamine, and 2,2,4-trimethyl-1,2-dihydroquinoline and Mixing Time of Physical Properties, Thermal Properties, Mechanical Properties and Microstructure on Natural Rubber Compound

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Abstract. Study the influence of high concentrations of antioxidants N-isopropyl-N-phenyl-p-phenylenediamine (IPPD) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) and the mixing time of the vulcanization physical properties, thermal properties, mechanical properties and structure micro on natural rubber compound has been done. The purpose of this study is to compare the effect of anti-oxidants types IPPD and TMQ and mixing time of vulcanization of the physical properties, mechanical properties, microstructure and elemental composition of the synthesis of natural rubber compound. Processes of vulcanization with variations in the concentration of antioxidant IPPD and TMQ: 2, 3, and 4 grams and mixing time: 20, 30, and 40 minutes. Analysis characterization of physical properties and mechanical properties of natural rubber compound showed that the maturity value 0,499Nm (TMQ) and 0.489 Nm (IPPD), Mooney viscosity value of 26.7 (TMQ) and 20.8 (IPPD), the value of the elongation at break 583.75 % (IPPD), and 552.63% (TMQ) as well as the value of tensile strength of 28.108 M.Pa (TMQ), and 27.986 M.Pa (IPPD). Analysis of thermal properties of natural rubber compound antioxidant IPPD with DTA shows there are three endothermic peak on the curve that is temperature 405ºC, 550ºC and 660ºC and tested by TGA showed that the curve of the total reduction in the sample are 81.745% and compound rubber antioxidant TMQ with the analysis of DTA also contained 3 endothermic peak at a temperature 397,21ºC, 514,02ºC, and 610,27ºC and TGA analysis shows the curve of the total sample of 82.356% reduction. Gsi fun group analysis rubber-antioxidant compound IPPD / TMQ with FTIR spectrophotometer shows some typical infrared absorption peak at the wave number (1 / λ) 833-895 cm-1 for cluster / CH bonds, 1,313 cm-1 for group / single bond Si-O, 1368 cm-1 to g ugus / single bond CC, 1507 cm-1, for cluster / bond C = C, 1665 cm-1For cluster / bond-C = O, 2128 cm-1 is the group / bond CN single, 3371cm-1 for group-OH, 3506 cm-1 for cluster / CH3 bond and 3585 cm-1 showed the presence of vibration in the cluster / bond-NH. The results of morphological observation with SEM produces uneven surface (homogeneous) and are compatible at 2000 times magnification, as well as the test composition by EDX spectroscopy showed that the biggest element in the rubber compound is carbon and Zn, S, Ca, Si, Mg, Al, N. This shows that the natural rubber compound antioxidant IPPD / TMQ meet the standard of "Mechanical Properties of Industrial Tyre rubber Compounds".

INTRODUCTION

Indonesia is the second largest rubber producer in the world after Thailand, therefore the natural rubber has an important role in Indonesia's exports. Rubber plant widely spread in all parts of Indonesia, particularly in Sumatra and Java are cultivated both by the state plantation, private as well as the people. The consumption of natural rubber will have a very significant increase from 9.23 million tons in 2006, and is predicted to be 11.9 million tons in 2020. Therefore, improving the quality of rubber products is needed, especially in the manufacturing process. The biggest influence happens to the rubber is caused by the oxidation process, resulting in chain termination rubber molecules.

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Therefore, to ensure that damage does not occur rapidly, then the vulcanization ingredients need to be added antioxidants or antiozonation.

Natural rubber monomer has the general formula is (C5H8)n where N is the degree of polymerization or number that indicates the number of monomers in the polymer chain. Values in natural rubber ranges from 3000-15000. The main form of natural rubber is composed of 97% cis 1,4 isoprene. [1,2]

Antioxidants are substances that can prevent the oxidation (prevent reaction with oxygen). These substances have the aim of preventing the rubber goods become damaged. The addition of anti-oxidants in the rubber compound will inhibit damage to the rubber for the air (O_2), sunlight and ozone. Rubber without anti-oxidants will easily oxidized to become sticky and soft then eventually become hard and cracked (aging). Antioxidants IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine) with the molecular formula $C_{15}H_{18}N_2$ is an antioxidant that is commonly used in the manufacture of tires or as components of pneumatic tires, solid tires, belts, hoses, cables, general mechanical products that require protection from ozonation, and has a strong antioxidant properties with high temperature resistance good. While antioxidant TMQ (2,2,4-trimethyl-1,2-dihydroquinoline) with molecular formula $(C_{12}H_{15})_n$ is an antioxidant that is soluble in benzene, chloroform and acetone, insoluble in water, but little soluble in petroleum hydrocarbon.

Analysis of maturity of the compound is usually done before the vulcanization process and compound said to mature when the rubber produced films have a maximum dropout voltage. [3]

Vulcanization process is a chemical reaction that makes the rubber molecules are shaped linearly to form a cross-reaction thus continued primer molecules into three-dimensional circuits. This reaction causes the rubber that originally had the plasticity (soft) and the weak becomes elastic, hard and strong. [5]

The existence of these bonds makes the rubber polymer molecules become not move freely again. This means that the rubber turned more rigid or strength and elasticity increases. Therefore, natural rubber with a medium molecular weight can provide a meeting point between the energy-efficient with superior physical properties. The degree of cross linking high molecular chains expressed more cross linking reaction (cross linking reaction) that occurs, thereby increasing the value of Mooney viscosity natural rubber. [6.7]. Manurung (2010) used a mixture of phenol as an antioxidant with sulfur and peroxide vulcanization concluded that the test results obtained maximum tensile namely SIR 20 with vulcanization benzoyl peroxide with a value of 5562.27 KN /m^2. PO value and maximum PRI with vulcanization sulfur with a value of 92% and FTIR results show that there are changes in the functional groups and chemical interactions. [4.8]

The purposes of this study are to analyze the influence of the synthesis and use of antioxidants IPPD and antioxidant TMQ and mixing time on the synthesis vulcanized natural rubber compound on the physical properties, mechanical properties, thermal properties, the nature of the functional group, and surface morphology and chemical composition. The results of the research will be used as a modification and innovation of raw materials in the manufacture of vulcanized rubber for car tires.

RESEARCH METHODOLOGY

Materials and Tools

Material

Natural rubber, antioxidant IPPD (N-isopropyl-N-phenyl-p-phenylene diamine) and TMQ (2,2,4-trimethyl-1,2-dihydroquinoline), carbon powder fillers, ZnO, sulfur, a substance activists, accelerator, softening agent.

Tools

Machine roll full level controlled by temperature, Tensometer 2000 (instrument tensile test), Roorless rheometer RLR-3 (test equipment maturity), Mooney viscometer (test equipment suppleness and moisture), Stage cutter (mixer compound), Scanning Electron Microscope (SEM) for observation of surface morphology and structure of the micro-Energy X-ray Disversive Spectroscopy (EDXS) to measure the chemical composition, to test its thermal properties by TGA and DTA, for testing of functional groups by FTIR spectrophotometer.

Methods

Making natural rubber compound sample-antioxidant IPPD and TMQ using vulcanization method, and physical properties testing was conducted at the Laboratory Bridgstone, Bekasi, West Java. Several stages of research as follows. [4.8]

- Preparing the materials needed to make natural rubber compound, namely natural rubber, sulfur, filler, antioxidant, accelerator and activator, composition see Table 1.
- Doing sample preparation in three stages, namely the manufacture of sheet (slab), curring, and cutting the sheet into a specimen.
- Heat up the engine 10 Inch Roll for preparation of compounds with the amount of the planned temperature.
- Making process begins by weighing the rubber compound and antioxidant IPPD and TMQ, grinding natural rubber to natural rubber are mature enough to be given other chemicals. after mature, natural rubber other chemicals slowly. This process is based on the time variation of mixing vulcanized predetermined i.e 20 minutes, 30 minutes, and 40 minutes.
- Once the rubber compound antioxidant IPPD and TMQ created, printed and tested quality compound with a maturity test and Mooney viscosity. For tensile testing and analysis of FTIR and SEM-EDX and TGA / DTA rubber compound needs to be cooked in advance (curring) with the engine first stage cutter. This curring process takes 30 minutes at a temperature of 145 °C.
- Testers thermal properties by TGA and DTA, SEM-EDXS, FTIR spectrophotometer performed at Forensic Laboratory Jakarta Police Headquarters.

TABLE 1. Formulation samples with variations Antioxidants (IPPD and TMQ)

No.	Name of Material	Concentration (PHR)						Concentration (Gram)					
1	Natural Rubber	100						300					
2	Sulfur	2.5						7.5					
3	Carbon Black	30						90					
4	Stearic acid	2						6					
5	ZnO	5						15					
6	Softener	5						15					
7	Tackfier	2						6					
8	Accelerator	0.3						0.09					
9	Antioxidants	IPPD			TMQ			IPPD			TMQ		
		0.7	1	1.3	0.7	1	1.3	2	3	4	2	3	4

RESULT AND DISCUSSION

From the research that has been done, the data showed the influence of the concentration of antioxidant IPPD and TMQ and mixing time of vulcanization compound to maturity, viscosity Mooney, and tensile strength (modulus of elasticity, elongation at break, and tensile strength at break) can be seen in Figure 1 and Figure 7.

Analysis of maturity, Mooney Viscosity and Tensile Strength as effect of IPPD and TMQ

From the test results of the maturity of the concentration of antioxidant IPPD and TMQ are presented in Fig.1 a-c.

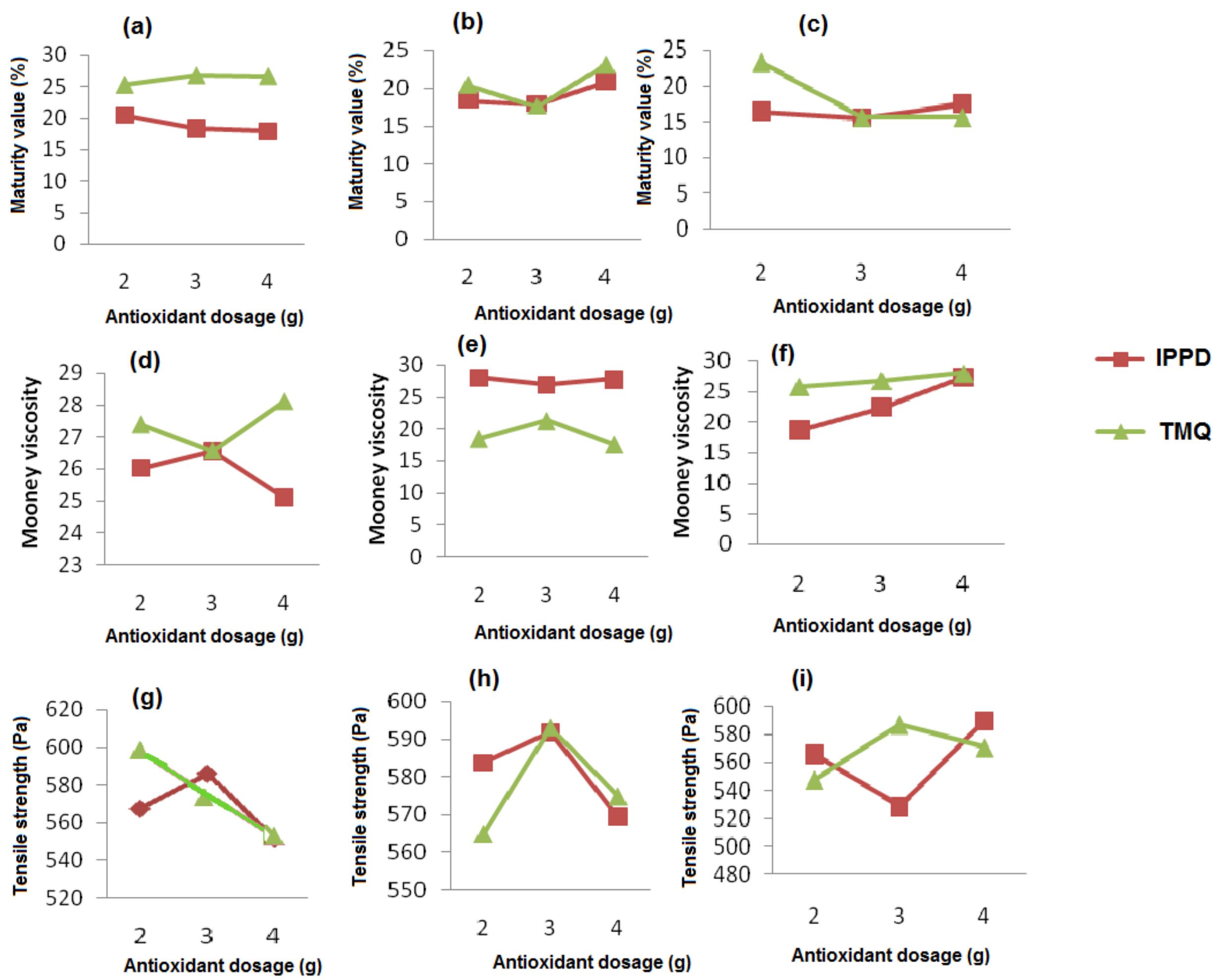


FIGURE 1. Effect of IPPD and TMQ antioxidants dosage on (a)-(c) maturity values, (d-f) Mooney viscosity and (g-i) tensile strength varied time; 20 minutes, 30 minutes, and 40 minutes respectively.

Fig. 1a-c show that the greater the concentration, the smaller the maturity value of the rubber compound antioxidant IPPD and TMQ and within mixing vulcanized varied. After statistical analysis ANOVA was the same, namely the concentration of antioxidant IPPD and TMQ does not affect the value of maturity on natural rubber compound (price P-value> 0.05, and $F_{arithmetic} < F_{crit./table}$).

Mooney viscosity of the test results on the concentration of antioxidant IPPD and TMQ can be seen Fig. 1 (d-f). Mooney viscosity analysis carried out to analyze the level of resilience and resistance to the flow of rubber compounds-antioxidants IPPD and TMQ. From the figures, it is found that the higher the concentration of antioxidant IPPD and the longer mixing time tends to value the greater the viscosity. This suggests that if a high molecular weight, the viscosity will be higher and the molecular chains are getting longer and the higher resistance to flow so that the rubber becomes harder and the energy required to pulverize the rubber will be even greater. Conversely, if the value of the low viscosity, the chain will be more short-term plans will facilitate the processing of rubber so it does not require great energy, but less good mechanical properties. Therefore been rubber with medium viscosity to obtain good mechanical properties and the less energy required.

From the effect on tensile strength, it is found that the rubber compound with antioxidant TMQ highest value of 28.108 MPa tensile strength at a concentration of 4 grams and mixing time of 20 minutes. While the value of the minimum tensile strength of 17.619 MPa. Furthermore rubber compound with antioxidant IPPD concentration of 4 grams and mixing time of 30 minutes at the highest tensile strength value and the value of 27.986 MPa minimum tensile strength at 18.620 MPa at a concentration of 2 grams and a mixing time of 40 minutes. For that the rubber compound with antioxidant or antioxidant TMQ IPPD has the greatest tensile strength values, the tensile strength when the big break, so that the rubber will be more elastic. Wherein the strengthening effect in the form of the tensile strength of the rubber compound has been studied or researched some decade last and spawned several modeling the interactions that occur between the carbon powder and chain poly isropena. One model *molecular slippage* has been found by previous researchers,[12] because the carbon powder has a high surface energy derived from unsaturated poly aromatic structure and its functional groups. This structure makes the carbon powder particles can adsorb strongly polymer chains. So that the tensile strength is greater because it is supported by the interaction between polymer chains with a carbon powder. Impairment on the tensile strength of rubber compounds (figure 3a and 3b) is due to the antioxidant IPPD and TMQ, it can make inter phase area becomes weak and the strength of the natural rubber compound material products decreased. At concentrations of antioxidant IPPD and TMQ resulted in lower tensile strength decreased.

Analysis elongation at break of the rubber compound-IPPD and TMQ

Effect of antioxidants on elongation at break are presented in Fig.2.

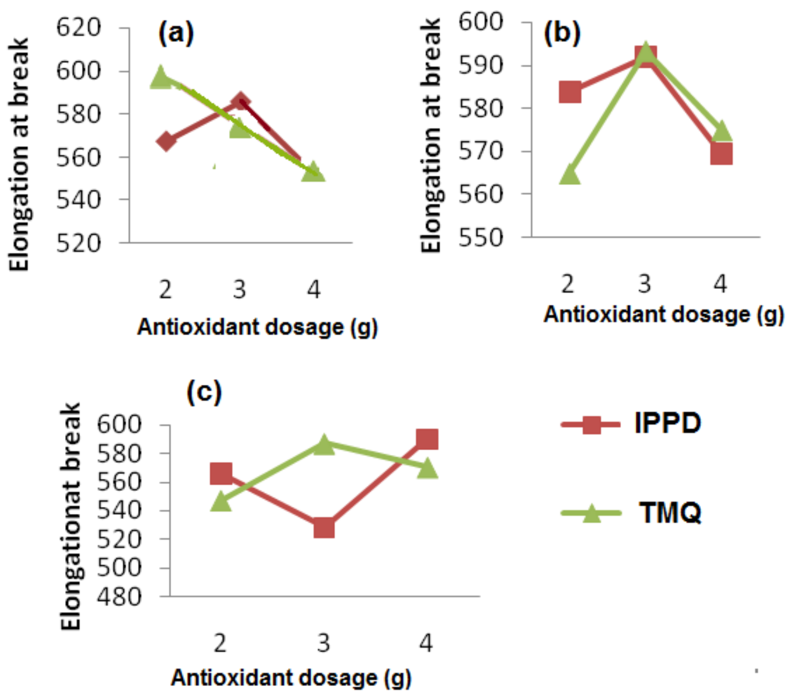


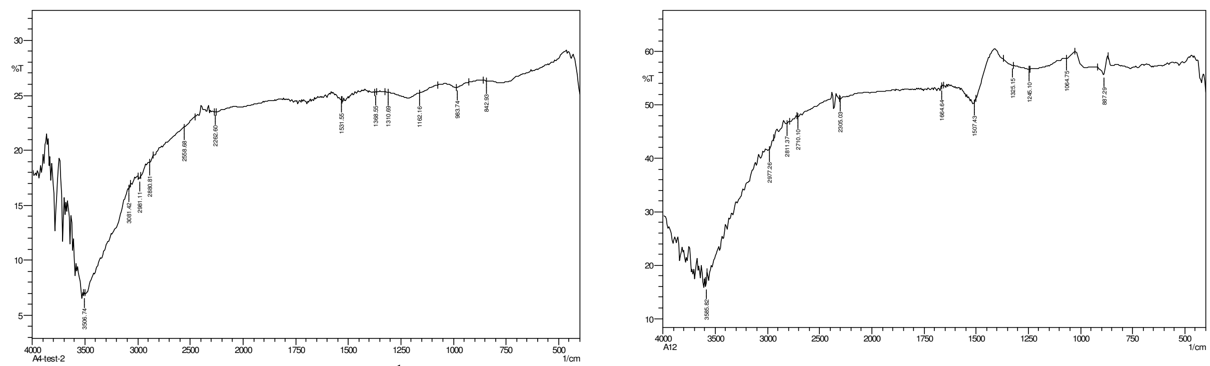
FIGURE 2. Graph relationship IPPD and TMQ antioxidant concentration of the elongation at break at the time of mixing vulcanization (a) 20 minutes, (b) 30 minutes, and (c) 40 minutes.

From Fig.2, it is seen in that the compound with antioxidant IPPD mixing time variation of vulcanization 20, 30, and 40 minutes elongation at break of the highest value there is the concentration of 3 grams and 30 minutes is 591.88%, and the elongation at break is lowest at a concentration of 3 grams and vulcanization mixing time 40 minutes is 528.13%.

While in the compound with antioxidant TMQ, elongation at break value is highest at a concentration of 2 grams and vulcanization mixing time 20 minutes is 597.50%, and the elongation at break is lowest at a concentration of 2 grams and a time of 40 minutes is 547.13%. This is due to the elongation at break will decrease, because the resulting filler clots (agglomeration). These clots will reduce the surface area and so will weaken the interaction between filler and matrix, resulting in a decrease in the physical properties of polymeric materials. The increase and decrease in elongation at break is occurred due to the increase filler resulting decrease in the deformation ability inter phase filler and matrix samples[10-12]. This is reinforced Anova statistical analysis that the concentration of antioxidant IPPD and TMQ on the synthesis of rubber compounds do not affect the value of the elongation at break (price P-value> 0.05, and $F_{arithmetic} < F_{crit./table}$) Compound Rubber - antioxidant IPPD and TMQ with elongation at break of the greatest value, then the rubber compound will not be easily damaged / torn.

Analysis of functional groups cluster in rubber compounds-antioxidants IPPD and TMQ

From the test results of functional groups by FTIR spectrophotometer on rubber- antioxidant compound IPPD and TMQ can be seen Fig.3. and the lists of spectra are presente in Table 2.



Wavelength (cm $^{-1}$)
(a)

Wavelength (cm $^{-1}$)
(b)

FIGURE 3. Curve infrared absorption spectra of compound rubber- antioxidants a.IPPD, and b.TMQ

Analysis of infrared spectra FTIR spectrophotometer to analyze the characteristics of rubber compound with a functional group of antioxidants IPPD and antioxidant TMQ.

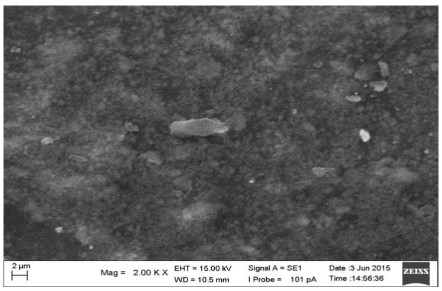
TABLE 2. Infra Red absorption spectra of rubber compounds-antioxidants IPPD and TMQ

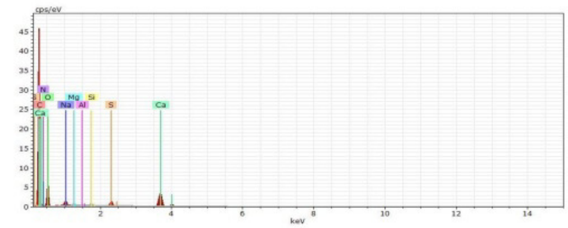
Wavelength (cm $^{-1}$)	Analysis of Functions Cluster
833-895	CH
1050-1300	CO
1300-1350	Si-O
1360-1375	CH_3
1450-1600	C = C
1640-1700	CC
2100-2300	CN
3000-3030	CH group (C-CH_3 and CH_2)
3100-3390	OH
3506-3600	NH

The test sample by FTIR spectrophotometer is taken from optimum rubber compound -Antioxidant IPPD with a concentration of 2 grams and *mixing* time vulcanization 30 minutes, as well as the antioxidant TMQ rubber compound concentration of 4 grams and vulcanization mixing time of 20 minutes.
From the figure 5a and 5b, visible infrared absorption spectra of rubber antioxidant IPPD and TMQ there are peaks of infrared analysis results indicate that the compound natural rubber (isoprene) with a ntioksidan IPPD and TMQ antioxidant proven at 833-895 cm^{-1} wave number for groups / bond CH, 1313 cm^{-1} for group / single bond Si-O, 1368 cm^{-1} for groups / C-C single bond, 1507 cm^{-1} for groups / C = C double bond, 1665 cm^{-1} for groups / bond-C = O, 2128 cm^{-1} for groups / single bond CN, 3371 cm^{-1} for group-OH, 3506 cm^{-1} for groups / CH_3 bond and wave numbers 3585 cm^{-1} showed the presence of vibration in the cluster / bond-NH.

Analysis a morphology and chemical composition of the rubber compounds-antioxidants IPPD and antioxidant TMQ.

The observation on surface morphology of compounds by using SEM-EDXS can be seen Fig.4.

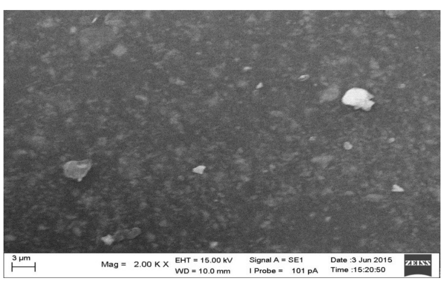


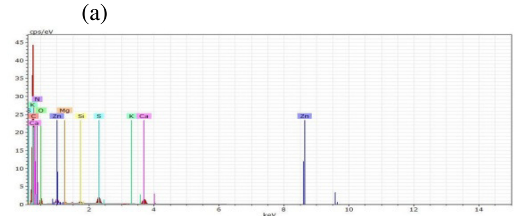


Spectrum: Acquisition

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Carbon	K-series	66.11	66.11	75.04	7.40
Oxygen	K-series	24.08	24.08	20.51	3.13
Sodium	K-series	0.93	0.93	0.55	0.09
Magnesium	K-series	0.28	0.28	0.15	0.04
Aluminium	K-series	0.16	0.16	0.08	0.04
Silicon	K-series	0.28	0.28	0.14	0.04
Sulfur	K-series	0.91	0.91	0.39	0.06
Calcium	K-series	6.20	6.20	2.11	0.22
Nitrogen	K-series	1.06	1.06	1.03	0.38
	Total:	100.00	100.00	100.00	

(a)





Spectrum: Acquisition

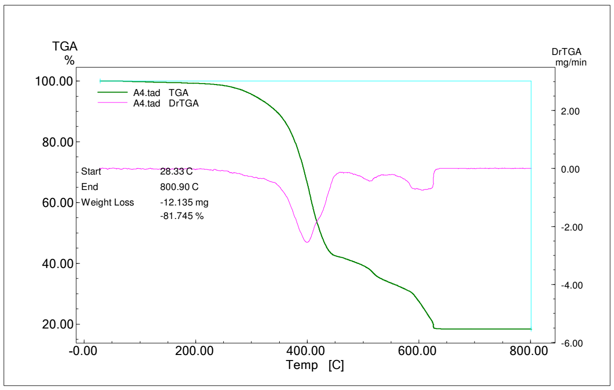
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Carbon	K-series	81.85	81.85	89.60	9.12
Oxygen	K-series	9.36	9.36	7.69	1.45
Zinc	K-series	3.31	3.31	0.67	0.19
Sulfur	K-series	1.78	1.78	0.73	0.09
Calcium	K-series	3.03	3.03	0.99	0.12
Silicon	K-series	0.32	0.32	0.15	0.04
Magnesium	K-series	0.22	0.22	0.12	0.04
Potassium	K-series	0.12	0.12	0.04	0.03
Nitrogen	K-series	0.00	0.00	0.00	0.00
	Total:	100.00	100.00	100.00	

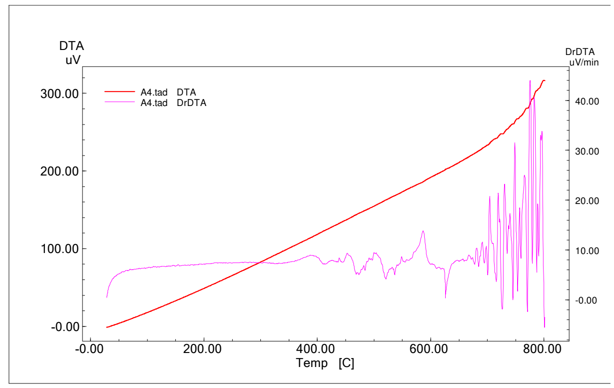
(b)

FIGURE 4. SEM profile and EDX profile of of rubber- antioxidant compound (a). IPPD, b. TMQ

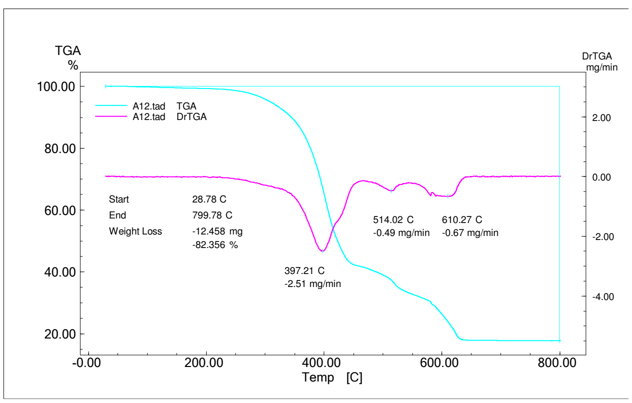
Analysis by SEM on a rubber compound was conducted to determine the distribution or distribution IPPD and TMQ antioxidant found in natural rubber compound. Fig.4a shows the distribution of the rubber antioxidant IPPD at a concentration of 2 grams and mixing time 30 minutes, 2000x magnification. Fig.4b shows the distribution of the rubber antioxidant TMQ at a concentration of 4 grams and mixing time of 20 minutes, 2000x magnification. From the micrographs show that the addition of antioxidant IPPD and TMQ visible aggregate particles evenly dispersed in rubber compounds, thus making rubber compounds-antioxidants and IPPD and TMQ be elastic and strong. Chemical composition by EDX Spectroscopy in the rubber compound antioxidant IPPD indicated that the composition of the total of carbon with a percentage of 66.11% and oxygen with a percentage of 24.08% and the remaining metal content of Na, Mg, Al, Si, S, Ca, and N, while chemical composition by EDX spectroscopy in rubber compounds-antioxidants TMQ, it appears that the composition of the total of carbon with a percentage of 61.85% and oxygen with a percentage of 9.38%, and the remaining content metal Zn, S, Ca, Si, Mg, K and N.

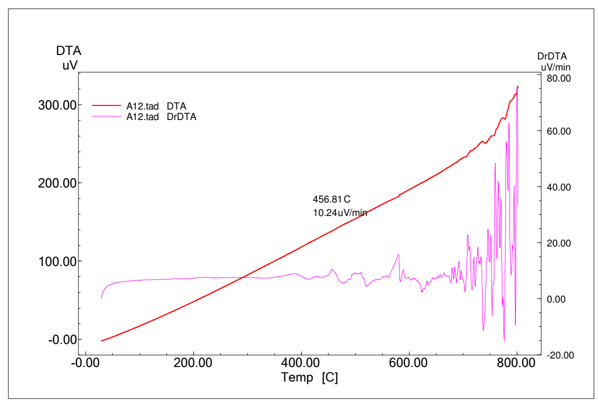
Resistance to heat a rubber compound products is highly dependent on the number of crosslinks formed[13]. The high energy required to break the glass of an elastomer indicates the elastomer material has good heat resistance. In this study, factors which became focus of the inquiry is the effect of the heat resistance of the concentration and the *mixing* time in the vulcanization of rubber compounds-antioxidants IPPD and TMQ.





(a) (b)





(c) (d)

FIGURE 5. Thermogram curve of rubber compounds-antioxidants and mixing time of 30min, a. TGA(IPPD), b. DTA (IPPD), c. TGA (TMQ), and d. DTA (TMQ).

Fig.5 shows TGA curves to analyze the thermal resistance of the rubber- antioxidant IPPD compound in a concentration of 2 grams and mixing time 30 minutes, where there are three, namely endothermic peak temperature of 405ºC, 550ºC and 660ºC. This is supported by DTA thermogram curve (Fig. 5b) showing the total reduction to decompose the polymer sample or isoprene is 81 745%.

Fig.5c shows calorimetry TGA curves of rubber compounds - antioxidants TMQ with a concentration of 4 grams and mixing time of 20 minutes there are three endothermic peak at a temperature 397.21ºC, 514.02ºC, and 610.27ºC. This is supported by DTA thermogram curve (Fig.5) decompose the polymer of isoprene or total sample of 82 356% reduction.

CONCLUSION

From the calculation and analysis of research-rubber compound and antioxidant TMQ IPPD antioxidants can be summed up as follows, namely:

1. Rubber compound -Antioxidant IPPD optimum concentration of 2 grams and time mixing vulcanization 30 minutes with a maturity test result value is 0.489 Nm; Mooney viscosity of 20, 8; stronger tensile value of 27.986 M P a; the value of elongation at break of 583.75%, and heat endurance 400 ℃. And compound rubber-antioxidant TMQ optimum with a concentration of 4 grams and vulcanization mixing time 20 minutes the test results, a value maturity: 0.499 Nm; Viscosity 26.7; Tensile strength: 29.108 MPa; the value of the elongation at break: 552.63%, and Heat resistance: 400 ℃
2. The results of FTIR analysis of rubber compounds-antioxidants IPPD and TMQ seen their infrared absorption spectra that shows the functional groups / bonding in wave numbers certain. In the 833-895 cm^{-1} wave numbers for groups / bond CH, 1313 cm^{-1} for group / single bond Si-O, 1368 cm^{-1} for the cluster / CC single bond, 1507 cm^{-1} for the cluster / C = C double bond, 1665 cm^{-1} for the force / bond-C = O, 2128 cm^{-1} is group / single bond CN, 3371 cm^{-1} for the group-OH, 3506 cm^{-1} for the cluster / CH_3 bond and numbers wave of 3585 cm^{-1} showed the presence of vibration in the cluster / bond-NH
3. The results of morphological analysis by SEM showed aggregate particles are evenly distributed throughout the magnification 2000x, both on the antioxidant IPPD and TMQ. Carbon composition with a percentage of 66.11% (on IPPD) and oxygen with a percentage of 24.08% and the remaining metal content of Na, Mg, Al, Si, S, Ca, and N. While rubber-TMQ antioxidant, carbon composition with a percentage of 61.85% and oxygen with a percentage of 9.38% and the remaining metal content Zn, S, Ca, Si, Mg, K and N.
4. The results of the analysis of TGA / DTA, the compound rubber- same antioxidant IPPD and TMQ there are three endothermic peak, but the different temperature curves DTA thermogram (at IPPD) at a temperature of 405ºC, 550ºC, and 660ºC, while the temperature TMQ 397.21ºC, 514.02ºC, and 610.27ºC. In contrast to the curves calorimetry TGA shows the total sample of 81.745% reduction (IPPD) and 82.356% (for TMQ).

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