e-Jurnal Sains Nuklear Malaysia, 2021, Vol. 33: 1 – 10
eISSN: 2232-0946

EFFECT OF ANTIOXIDANTS ON MECHANICAL, PHYSICAL AND AGING PROPERTIES OF HYBRID RADIATION-PEROXIDE VULCANIZED LATEX

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ABSTRACT

Oxidative aging of a rubber-based product occurs stepwise throughout its operating life; during the manufacturing processes *and even during* storage. *Exposure to oxidation causes chemical, mechanical and physical changes resulting in declining functional performance. In order to inhibit the oxidation rate, this study is looking at the usage of antioxidant which was added into the radiation-peroxide vulcanized latex to trap or deactivate the free radicals. All the physical properties of the latex films were in compliance to the standard specifications. The addition indicated that 2.5 pphr of Aquanox Lp antioxidant offered superior effect compared to Irganox 1520 in slowing down the oxidative aging process of the hybrid RVNRL-peroxide latex films. The values of tensile stress, modulus at 500 % and modulus at 700 % were compared before and after accelerated aging test for 22 hours at 100 °C and showed major drop of 1.3 %, 42.2 % and 46.3 % respectively. Prolong aging via 7 days accelerated aging test at 70 °C also showed that the values of the tensile stress, modulus at 500 % and modulus at 700 % dropped at 6.8 %, 33.4 % and 41.9 % respectively.*

Keywords: radiation-peroxide; vulcanized latex, oxidative aging; vulcanization, antioxidant

INTRODUCTION

During late nineteen century, natural rubber was the only elastomeric polymer available for commercial use. However, there is one major problem with products made from rubber; where they have poor weathering resistance and have the tendency to become soft and tacky with the function of time, and finally experienced deteriorating performance. Many researchers discovered that the cause of degradation and pre-mature failure of rubber products was due to reaction with oxygen in the atmosphere and it can occurs at every stage of life of the products such as during the manufacturing processes, storage and usage (Akrochem, 2020; Chai, 2009). This oxidative aging can cause molecular and structural chain changes, affecting the chain length which then resulted in reduction in molecular weight (Figure 1). Rubber-based products generally undergo chemical, mechanical and physical changes and encounter a decline in their performances upon oxidation (Hong, 2004).

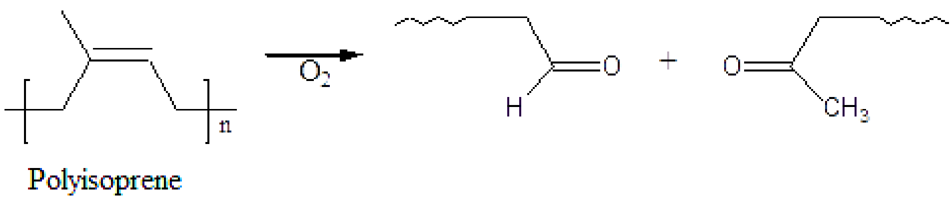

Figure 1: Oxidation reaction on polyisoprene upon contact with oxygen

Beside oxygen, oxidation can also be initiated by several other factors such as exposure to heat, light and ozone. Thus, researchers have been intensively researched for materials that would extend the service life of a rubber latex product to slow down the oxidation process. Some findings indicated that by incorporating certain phenols, hydroxylamine derivatives and secondary aromatic amine derivatives into the compounded rubber latex during mixing helps to retard the degradative effects of oxygen. These chemicals are popular by their generic names called "antioxidant". Antioxidant can inhibit or slow down the oxidation rate of finished rubber latex products by trapping or deactivating radicals during storage, transport and service life of the products.

The evolution of antioxidant becomes trendy and at present there are a lots of commercial antioxidants available and widely used by the latex industries. However, for radiation prevulcanized natural rubber latex (RVNRL), it is common to use only Irganox 1520 and Aquanox Lp antioxidants which are more suitable to slow down the aging process without sacrificing the strength. Irganox and Aquanox Lp were selected as the main antioxidants in this study as suggested by previous researches (Ma'zam & Wan Manshol et al., 1996; Shukri et al., 1990; Sofian et al., 2018a & 2018b; Wan Manshol et al., 1996. The quantities of Irganox 1520 and Aquanox Lp have been set at 1.0 part per hundred rubber (pphr) and 2.5 pphr, respectively. Effectiveness of both antioxidants to slow down the aging effects of the hybrid RVNRL-peroxide samples was observed, recorded and compared.

MATERIALS AND METHODS

Materials

The latex utilized in this work was hybrid RVNRL-peroxide latex without antioxidant (52.5 % total solid content, TSC) provided by RAYMINTEX Plant, Malaysian Nuclear Agency, Malaysia. The antioxidants used were Aquanox Lp (45 % TSC) supplied by Aquaspersion (M) Sdn. Bhd., Malaysia and Irganox 1520 (40 % TSC) supplied by Ciba Speciality Chemicals, Switzerland. These materials were used as received.

Sample preparation

The hybrid RVNRL-peroxide samples were prepared using three different compounding formulations, each containing 1 kg of rubber latex. The first sample contained no antioxidant and it served as control sample. The second and third compounding formulations comprised of 2.5 pphr of Aquanox Lp and 1.0 pphr of irganox 1520 antioxidants, respectively with the amount added following Equation 1 and tabulated as shown in Table 1. The mixtures were stirred separately for 12 h at ambient temperature using a magnetic stirrer.

$$m_1 = \frac{TSC_1}{100} \times \frac{x}{100} \times \frac{100}{TSC_2} \text{ x } m_0 \qquad \text{(Eq.1)}$$

m_0 mass of hybrid RVNRL-peroxide, g
m_1 mass of antioxidant in the hybrid RVNRL-peroxide, g
x fraction in part per hundred rubber (pphr) of antioxidant in the hybrid RVNRL-peroxide
TSC_1 total solid content of hybrid RVNRL-peroxide, %
TSC_2 total solid content of antioxidant, %

Table 1: Amount of antioxidant in the hybrid RVNRL-peroxide

Type of Antioxidant (AO)	Amount of AO, pphr
Aquanox Lp	2.5
Irganox 1520	1.0

Accelerated aging test and measurement of mechanical properties

Testing on the aging resistance of hybrid RVNRL-peroxide films was performed in accordance to the (Standard Test Method for Rubber-Deterioration in an Air Oven) (ASTM D573-4, 2004). The hybrid RVNRL-peroxide film samples of the control, 2.5 phr Aquanox Lp and Irganox 1520 were prepared using the coagulant dipping method, where a glass plate was immersed in the coagulant and then placed in an oven at 100 °C to partially dry the coagulant prior to immersion in the latex compound for 20 s. The wet gel was allowed to consolidate at 100 °C for 1 min, and then leached in distilled water at 50 °C. The latex film was finally dried at 100 °C and then cut into dumbbell shape test pieces (ten pieces per sample) as shown in Figure 2.

Two aging analysis parameters were conducted to all the dumbbell shape specimens from each three samples. The first aging analysis parameter was performed by exposing five dumbbell shape test pieces from each samples to hot air in the oven at 70 ºC for 7 days, while the second aging analysis parameter was performed with exposing five dumbbell shape test pieces from each samples to hot air in the oven at 100 ºC for 22 h. Subsequently, mechanical properties such tensile strength, modulus at 500 % and modulus at 700 % were determined using Universal Testing Machine Instron 5564 following the procedures in ASTM D412 (2016) (median value was taken as the final result) in order to study its aging properties.

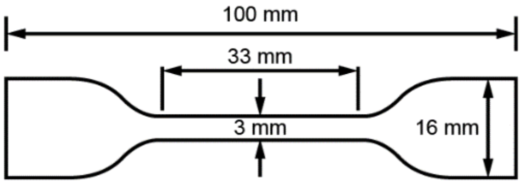

Figure 2: Dimension of dumbbell cut sample

Determination of total solid content (TSC)

Total solids content (TSC) is the percentage by weight of latex which is non-volatile at a definite temperature. The standard method of determination is as described in ISO 124 (2014). In this method, 2.0 g ± 0.5 g of latex was weighed in a petri dish to the nearest 0.1 mg. The petri dish was then placed in an oven and heated at 70 ºC ± 2 ºC for 16 h or at 105 ºC ± 5 ºC for 2 h until the whiteness of the tested portion disappeared. The petri dish is weighed again and the mass of dry latex was recorded. The TSC was calculated using Equation 2:

$$\text{Total solid content, } \% = \frac{m_1}{m_o} \text{ x } 100 \qquad \text{(Eq. 2)}$$

m_0 and m_1 are the weight (g) of the wet and dried latex, respectively.

Determination of alkalinity

The alkalinity of the latex samples was determined using referred procedures in the ISO 125 (2011). About 5 g of latex was poured into 500 cm^3 beaker followed by 200 cm^3 of water. The mixture was then stirred thoroughly. An electrode of the pH meter was let to insert in the mixture. Hydrochloric acid solution (HCl) was added slowly into the mixture until the pH dropped to pH 6.00 $\pm$ 0.05.

The alkalinity of the latex was calculated using Equation 3:

$$\text{Alkalinity } = \frac{1.7cV}{m} \qquad \text{(Eq. 3)}$$

c actual concentration of HCl used, g/dm^3
V volume of acid used, cm^3; and
m mass of latex sample, g

Determination of mechanical stability

The latex samples were subjected to mechanical stability (MST) testing using Klaxon MK3 machine in accordance to ISO 35 (2004) standard requirement, where 80.0 g ± 0.5 g of the latex was first added into MST machine container. The container was then positioned in the Klaxon MK3 MST machine and stirred at 14000 ± 200 rpm until the end-point was achieved. The detection of the end-point was preceded by a marked decrease in the depth of the vortex around the stirring shaft, loss of turbulence and change in the sound of stirring action. The end-point which was the first appearance of flocculum was determined by removing a drop of the sample with a clean glass rod at an interval of 15 s and the sample was gently spread on a suitable surface; in this study, the palm of the hand.

Viscosity measurement

Viscosity of the latex samples was measured at temperature range of 25–29 ^oC in accordance to MS 281 standard requirement. The viscometer used in this study was Brookfield model DV-II +. About 200 g of latex sample was weighed into a 250 ml capacity beaker. Spindle #2 was inserted into the latex sample until the mark and the machine was set at 60 rpm frequency. The viscosity was attained after 20 to 30 s at steady-state.

RESULTS AND DISCUSSION

At present, antioxidants commonly use to prevent or slow down the chain reaction due to degradation/oxidation of RVNRL are antioxidants consist of phenolic groups, secondary alkyl and diarylamine (Makuuchi et al., 1993). The mechanism of the oxidation reaction and the effect of antioxidant addition on the natural rubber latex is as shown in Figure 3 (Makuuchi, 2003). Bonding mechanism of oxygen to the natural rubber radical, R· is as suggested in step (2). The ROO· radical formed in step (2) will then removed the hydrogen from the nearest natural rubber molecule and formed the peroxide and re-generated the R· radical. The peroxide then decomposed and formed the RO·, ROO· and ·OH radicals through the side chain reaction as shown in steps (2) to step (6). The final products for oxidation of natural latex are alcohol, esters, carboxylic acids, ketones and a number of other chemical products. A radical acceptor (AH) type of antioxidant contains phenolic groups as its main component which deactivates natural rubber radicals, R· and ROO· through the reaction shown in steps (9) to (11).

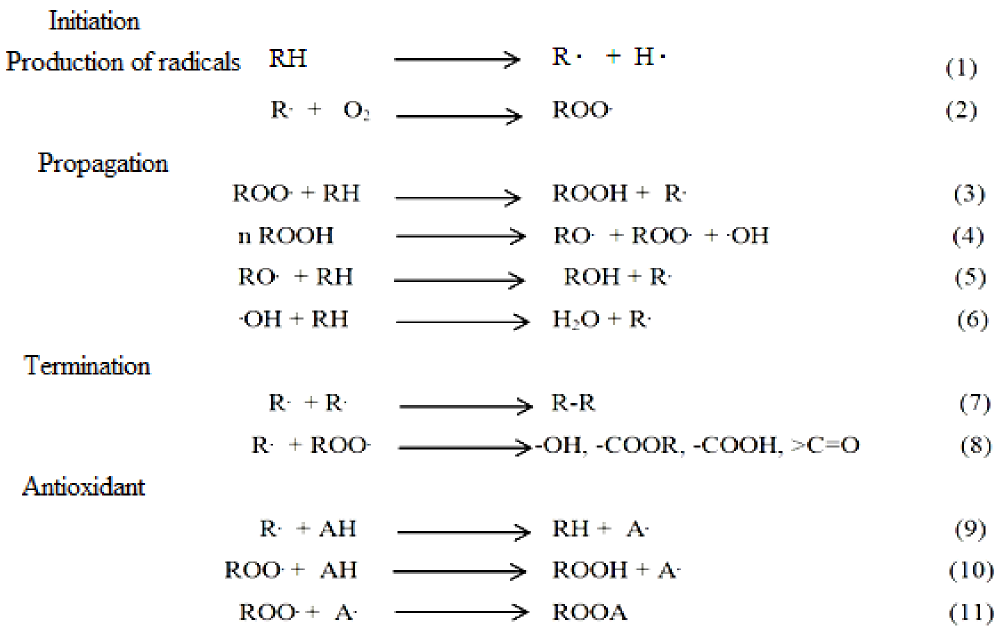

Figure 3: Mechanism of oxidation reaction and reaction of antioxidant on RVNRL

The addition of 1.0 pphr of Irganox 1520 and 2.5 pphr of Aquanox Lp antioxidants respectively into the hybrid RVNRL-peroxide compounding formulations resulted in different physical and mechanical properties to the samples.

Physical properties

Experimental data obtained for the physical observations are as shown in Table 2. The TSC of each hybrid RVNRL-peroxide compounding formulation containing both antioxidants did not significantly change compared to the control sample and still complied with the standard set by RAYMINTEX plant (minimum TSC 52 %). This finding is very important since the purpose of the TSC measurement is to determine the fraction of rubber (hydrocarbon) and non-rubber compounds in the latex. Latex with low TSC is not suitable for the production of thick rubber latex products due to lower content of rubber molecules (Akademi Hevea Malaysia, 2012).

Besides TSC, measurement of alkalinity of the latex is also very important. Alkalinity means indicates the free alkali content in latex and is usually expressed as the percentage of ammonia in the latex. The alkaline content for prevulcanized latex should be within the range of 0.3 to 0.7 %. Under alkaline condition, fatty acids and proteins will be ionized to produce negative charges on the rubber particles surface. The presence of these charges will provide colloid stability of the latex where the electrostatic repulsion between two neighbouring particles (having the same negative charge) will prevent them from coming into close contact with each other. When alkalinity goes lower than 0.3 %, it will create a suitable environment for the bacterial to break down protein in latex and spoiling it. On the other hand, when the alkalinity goes more than 0.7 %, the ammonia will affect the production process of dipping-product where formation of thin latex gelatine lining in the industrial production line is made impossible (Abu Bakar & Rosley, 1994; Chai, 2009; Nocil Limited, 2010). This study showed that the addition of both antioxidants has no significant effect on the alkalinity of all hybrid RVNRL-peroxide compounding formulations compared to control latex.

Table 2: Physical properties of hybrid RVNRL-peroxide with and without antioxidants

Antioxidants	TSC, %	Alkalinity, %	MST, s	Viscosity, cps
0 (Control)	52.85±0.04	0.42±0.01	892±5.31	29.5±0.41
1.0 pphr Irganox 1520	53.40±0.02	0.40±0.01	935±8.16	40.2±0.12
2.5 pphr Aquanox Lp	53.10±0.04	0.41±0.02	989±5.00	31.0±0.47

MST test is for investigating the latex resistance and stability towards mechanical agitation. Besides, it can also be defined as the time in seconds required for the coalescence of rubber particles to be initiated when the latex is subjected to high speed stirring under closely defined (Akademi Hevea Malaysia, 2012). In the production of latex dipping-products, the minimum requirement for the MST of the prevulcanized latex is 650 s (ISO 35, 2004). Latex with lower MST can easily form lumps in the dipping tank at production lines, and even during storage. This will cause defect to produced products. Table 2 exhibited that addition of Irganox 1520 and Aquanox Lp antioxidants into the hybrid RVNRL-peroxide compounding formulations help to improve the stability of the latex towards mechanical agitation and exceeded the minimum requirement for MST. This can be explained by referring to mechanisms in steps (9) to (11) in Figure 2, where the final result from the antioxidant reaction is ROOH and ROOA and the subsequent decomposition of these compounds by hydrolysis produced water and oxygen as by-products. Blackley (1997) and Roshanie (2010) suggested that oxygen promotes hydrolysis of proteins and phospholipids to polypeptides and amino acids and subsequently to various substances such as glycerol, fatty acid anions and phosphate anions. These compounds are then absorbed to the surface of the rubber particles and thus enhance latex stability; directly contributes to the increase in the value of MST.

Viscosity of the hybrid RVNRL-peroxide compounding formulations on the other hand, is also important to manufacturers of latex dipping-products. The viscosity of the prevulcanized latex has to be controlled at a certain viscosity range so that the end products are within the specified thickness range. Usually, the viscosity range set by the manufacturer is between 30 to 40 cps. Table 2 showed that viscosity of the latex samples increased upon inclusion of the antioxidants. A significant increment occurred when 1.0 pphr of Irganox 1520 antioxidant was added into the hybrid RVNRL-peroxide compounding formulation. This may be due to the presence of certain chemical compounds in the antioxidant that becomes interference to the stability of rubber particles in the latex. However, this issue can be overcome by adding in a small amount of stabilizer in the hybrid RVNRL-peroxide compounding formulations.

Mechanical properties

Our findings and analysis on the experimental data discovered that the addition of Irganox 1520 and Aquanox Lp antioxidants into the hybrid RVNRL-peroxide compounding formulations did not affect the tensile strength, modulus at 500 % and modulus at 700 % significantly as shown in Table 3.

However, the real effect of these antioxidants on the mechanical properties of the latex films can only be observed when samples undergone accelerated aging test.

Table 3: Mechanical properties of the hybrid RVNRL-peroxide with and without antioxidants

Samples	Tensile properties		
	Tensile strength, MPa	Modulus at 500 %, MPa	Modulus at 700 % MPa
0 (Control)	26.1	4.0	13.3
1.0 pphr irganox 1520	26.1	4.1	13.4
2.5 pphr Aquanox Lp	26.5	4.1	13.3

Accelerated aging

One of the major concerns for manufacturers of rubber and latex products is the shelf life of their products. This is because in challenging environmental conditions, in terms of temperature, humidity and sunlight, the properties of end products start to decline slowly at storage stage until the operation stage. In order to study the effect of extreme environment on the latex films, ASTM D 573-04 (2004) standard has been referred for accelerated aging test.

This standard include factors such as heat, pressure, humidity, oxygen and vibration in order to replicate the normal aging process. Through this controlled test method, the long-term effects of all these parameters on the products can be determined and predicted in the short period. For example, the mechanical properties of latex films undergoing 7 days aging at 70 ^{o}C are similar to latex films stored for 6 months at room temperature (ASTM D573-4, 2004; Wan Manshol et al., 1996). In other words, product life expectancy can be estimated faster when real life data is not available.

The accelerated aging analysis results is summarised in Table 4. These results were compared to the data obtained for hybrid RVNRL-peroxide prepared with and without antioxidant before accelerated aging (Table 3). The reduction in the mechanical properties of the latex was calculated using Eq. 4:

$$\% \text{ of decrement} = \frac{\text{Mechanical property before aging} - \text{Mechanical property after aging}}{\text{Mechanical property before aging}} \times 100$$

(Eq. 4)

Physical observations made onto all samples discovered that the control sample changed to a yellowish colour and melts. Therefore, the determination of mechanical properties using Instron universal machines is not possible and was omitted for the control samples. On the contrary to the control sample, the addition of 1.0 pphr of irganox 1520 antioxidant into the hybrid RVNRL-peroxide compounding formulation has successfully slowed down the aging effect on the films. Comparison of tensile strength, modulus at 500 % and modulus at 700 % before and after accelerated aging test for 22 hours at 100 ^{o}C (Table 3 and Table 4) showed 17.2 %, 36.8 % and 35.4 % decrement on tensile strength, modulus at 500 % and modulus at 700 % respectively. Meanwhile, for the 7 days accelerated aging at 70 ^{o}C, tensile strength, modulus at 500 % and modulus at 700 % showed 11.0 %, 43.9 % and 43.7 % decrement respectively.

Table 4: Tensile properties of hybrid RVNRL-peroxide with and without antioxidants upon accelerated aging test

Samples	Aging for 22 h at 100 °C			Aging for 7 days at 70 °C		
	Tensile strength, MPa	Modulus at 500 %, MPa	Modulus at 700 %, MPa	Tensile strength, MPa	Modulus at 500 %, MPa MPa	Modulus at 700 %, MPa
0 (Control)	melt	melt	melt	melt	melt	melt
1.0 pphr irganox 1520	21.6	2.6	8.7	23.2	2.3	7.6
2.5 pphr Aquanox Lp	25.7	2.3	7.2	24.3	2.7	7.7

As for the hybrid RVNRL-peroxide compounding formulation with Aquanox Lp antioxidant, the aging effect on the sample films was slower than Irganox 1520. Comparison of tensile strength, modulus at 500 % and modulus at 700 % before and after accelerated aging test for 22 hours at 100 °C (Table 3 and Table 4) showed 1.3 %, 42.2 % and 46.3 % decrement on tensile strength, modulus at 500 % and modulus at 700 % respectively. Lastly, as for the 7 days accelerated aging at 70 °C, the tensile strength, modulus at 500 % and modulus at 700 % showed 6.8 %, 33.4 % and 41.9 % decrement respectively.

CONCLUSION

Aquanox Lp antioxidant at loading amount of 2.5 phr showed better potential as the dominant antioxidant compared to Irganox 1520 at 1.0 phr loading amount due to its effectiveness in slowing down the oxidation stage of the hybrid RVNRL-peroxide latex films. In addition, Aquanox Lp did not influence or made any significant changes to physical properties of the samples. Moreover, the hybrid RVNRL-peroxide compounding formulations have successfully complied to all the standard requirements. An optimization on Aquanox Lp antioxidant concentration has been intensively studied to get the best hybrid RVNRL-peroxide compounding formulation with excellent mechanical properties and superior oxidative aging resistivity.

ACKNOWLEDGEMENTS

The authors would like to express their deepest appreciation to Revertex (M) Sdn. Bhd., Malaysia for supplying HA latex to be used in this research and RAYMINTEX Plant, Malaysian Nuclear Agency for financial and technical supports of this work. The process of publishing this work was supported through the project grant No. GGP-2019-021.

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