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Oxidation Degradation Analysis Of Cyclic Natural Rubber (Resiprene-35) Due To Storage, Heating And Ultraviolet Rays

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Abstract

Research on analysis oxidative degradation and stabilization of cyclic natural rubber (resipren-35) using wax commercial antioxidants, BHT, and Wingstay has been conducted. Properties of physics as a result of treatment of storaging, heating and irradiating by ultraviolet rays was studied. Structural analysis of functional groups was studied using FTIR, thermal properties using DSC and TGA analysis, crystallinity by XRD and test of the solubility and viscosity of cyclic natural rubber (CNR) before and after the occurrence of oxidative degradation. Research results indicate that the analysis of cyclical natural rubber (resipren-35) very easily degraded due to crosslinking and oxidized due to reaction with air (oxygen and ozone) in storaging, heating and irradiating by ultraviolet rays. Antioxidants can inhibit the oxidation degradation rate with the effectiveness is Wingstay> BHT> wax though not very significant. Samples Resipren-35 compared to rubber cyclically-450 Alpex more easily degraded due to differences in the degree of cyclization or the number of C = C double bond in Resipren-35. The measurement results are expected to provide input technologically cyclic preservation of natural rubber products which are resistant to storage, heating and exposure to UV rays.

Keywords: Cyclic Natural Rubber, antioxidants, Polymer Degradation, Stabilizer, and Chain Breaking

1. Introduction

Materials such as elastomer or diene derivative compounds are very sensitive to oxidative degradation. Study of oxidation degradation of the material was first made by Henry (1911). Henry (1911) reported that the degradation of natural rubber when irradiated directly is proportional to the length and intensity of the ultraviolet light. In the last four decades of study of the degradation of natural rubber more intensively developed as oengaruh thermal (Schenacel, 1981), ozonolisis (Lacoste *et al,* 1994), ultrasonic (Yashin and Isayev, 1999), a photo-oxidation (Gonon, 2002), and elongation (Wattrisse, Caborgan, Muracciole, Sabatier, and Chrysochoos, 2013). Cylic natural rubber (CNR) is a material derived from natural rubber into superior products as a downstream rubber industry in Indonesia. CNR is one of the natural rubber modified chemically by the method of cyclization. CNR has considerable potential to be used as raw material for adhesives, ink manufacturing and also as a raw materials in coating industry (paint), especially the anti-corrosion paint. This is due to the CNR physical properties are typical, that is lightweight, rigid and resistant to abrasion (friction power) and has a good adhesion to metal, wood, rubber, leather, textiles and paper (Departemen Perindustrian, 2009). Natural rubber is a polymer of isoprene with the chemical name cis 1,4 polyisoprane. The general formula of natural rubber monomer is $(C_5H_8)_n$ is the degree of polymerization that is a number that indicates the number of monomers in the polymer chain. The value of n in the natural rubber ranged 3000-15000 (Surya, 2006).

Natural rubber is a hydrocarbon compound which is macro-molecules polyisoprene $(C_5H_8)_n$ and join for bonding head to tail. The polyisoprane chain to form the cis configuration with a regular arrangement of space, so that the chemical formula cis 1,4 polyisoprane. The elastic properties related to viscosity or plasticity (Morton, 1987). Natural rubber in the world 70% generated from Indonesia, Malaysia and Thailand. Indonesia is a natural rubber producer second largest in the world after Thailand (Departemen Perindustrian, 2009), which in 2005 has been producing natural rubber in 2.271 million tons, consisting of production of farmers as much as 1.893 million tonnes (81%) state plantations (PT. Perkebunan Nusantara) as 210 thousand tons (9%), and private estates as much as 222 thousand tons (10%), involving more than 10 million farmers (Gema Industri Kecil. Edisi XXI, 2008).

Rubber cyclically *(cyclised rebber)* is a product obtained from the cyclization of natural rubber, including modifications to the group of type 1, due to the modification took place without the inclusion of other compounds to the rubber molecules (Alfa, 2007). Another event which also included the modification of type 1 is an event depolymerization of natural rubber is the shortening of molecular chains of natural rubber up to the molecular weight down, and event changes the molecular structure of natural rubber from cis to trans isomer state. Fisher and Mc Colm (1927) added that if the natural rubber is mixed with sulfuric acid or p-sulfonic acid in the mill then heated then heated it will produce cyclo rubber. According to Janssen (1956) addition of sulfuric acid can also be performed on latex gardens, where after clot rubber milled so tangible sheet, then heated.

Another method of making rubber cyclo is by dissolving the rubber in the first rubber solvent, then heated together with an acidic catalyst (Edward, 1955). Coomarasamy *et al.* (1981) adds that the appearance and properties of rubber in made cyclical depending on the method and type of acid. Cyclical rubber made of solid rubber, usually only appropriate used as reinforcing material, because the solution high viscosity and poorly soluble in the solvent rubber.

This rubber solution cyclization technology has advantages because the process to avoid the influence of oxidation and able to produce cyclic rubber soluble in the solvent rubber, but the processing cost is very high. Cyclization processing fee covers the cost of processing a rubber solution of solid rubber from latex rubber plantation dense, solid rubber dissolution costs and the use of a solvent and an acid catalyst in large quantities (Coomarasamy *et al.* (1981)). Cyclical rubber can be prepared by treating the rubber with an acidic catalyst at a temperature between 500 C-1500 C. acid used is sulfuric acid, the toluence sulfonic acid and hydrochloric sulfonif. The principle of this method is heating the rubber which has added a number of acid at a temperature of 1250C-1450C for 1 – 4 hours. A mixture of concentrated latex with sulfuric origin resulted in the emergence of a lot of heat. During the cyclization reaction mixture needs to be cooled for preventing clots or even composing *(charring).* According Veersen (1951), cyclical rubber processing (cyclization) of the base material in the form of natural rubber is generally done using *electrophil agent* or heat. Cyclization of natural rubber from the base material in the form of a latex with *electrophil* type of *agent* used is sulfuric acid (H_2SO_4). Into 134 g of concentrated latex which has been consolidated with a blistering 2.0% surfactant, added 161 g of concentrated H_2SO_4. Latex is heated at a temperature of 1200C for 2 hours. The reaction mixture was be diluted with water for 3 times the volume of the reaction mixture. Dispersion obtained is filtered, washed and then dried (Veersen, 1951). Achievement degree of cyclization of the products affected by the cyclization method or type of feedstock and type of catalyst used (Alfa and Syamsu, 2004). With the reaction mechanism as Fig. 1.

2. Methods

The Cyclic natural rubber used in this research are Resiprene-45, Wingstay-L and BHT. CNR sample was prepared in laboratory scale which is made by the same method used by the CNR of PTPN 3 North Sumatra. For a variety of products with a degree of cyclization and different molecular weight, sample SIR 20 is reacted first through chain termination reaction difenilbenzena presence and oxygen. CNR sample submersionwith antioxidant (BHT) before exposing treatment. After sampling is completedsubmersion, the samples then analyzed and characterized by solubility and crystallinity (XRD) test and also analyze its Thermal (DSA / DSC) and Chemical Structure (FTIR).

3. Results and Discussion

From Fig. 2 FTIR spectra showed absorption at some numbers as shown in Table 1 the wave numbers 2929, 1594, 1453, 1371, 1020, and 747 before exposed. FTIR spectra of resipren-35 before exposed, as in Figure 1 can be found for absorption at 1594 wave numbers that indicate the presence of double bonds that owned the sample. Once exposed turns at 1594 wave numbers not found (lost), but it appears the new absorption in 1704. The presence of the absorption peak at 1594 local gives resipren-35 has a C = C double bond in the carbon chain structure.

From Fig. 3 it can be seen that there is a new absorption at wave number 1704 which shows a typical absorption of carbonyl (C = O). The longer the exposure given the higher intensity of carbonyl absorption. This can be explained as a result of the oxidation reaction of C = C double bond produce carbonyl group. It can be confirmed from absorption intensity at 1594 wave numbers (uptake typical C = C) which decreases as the length of the sample was given warming.

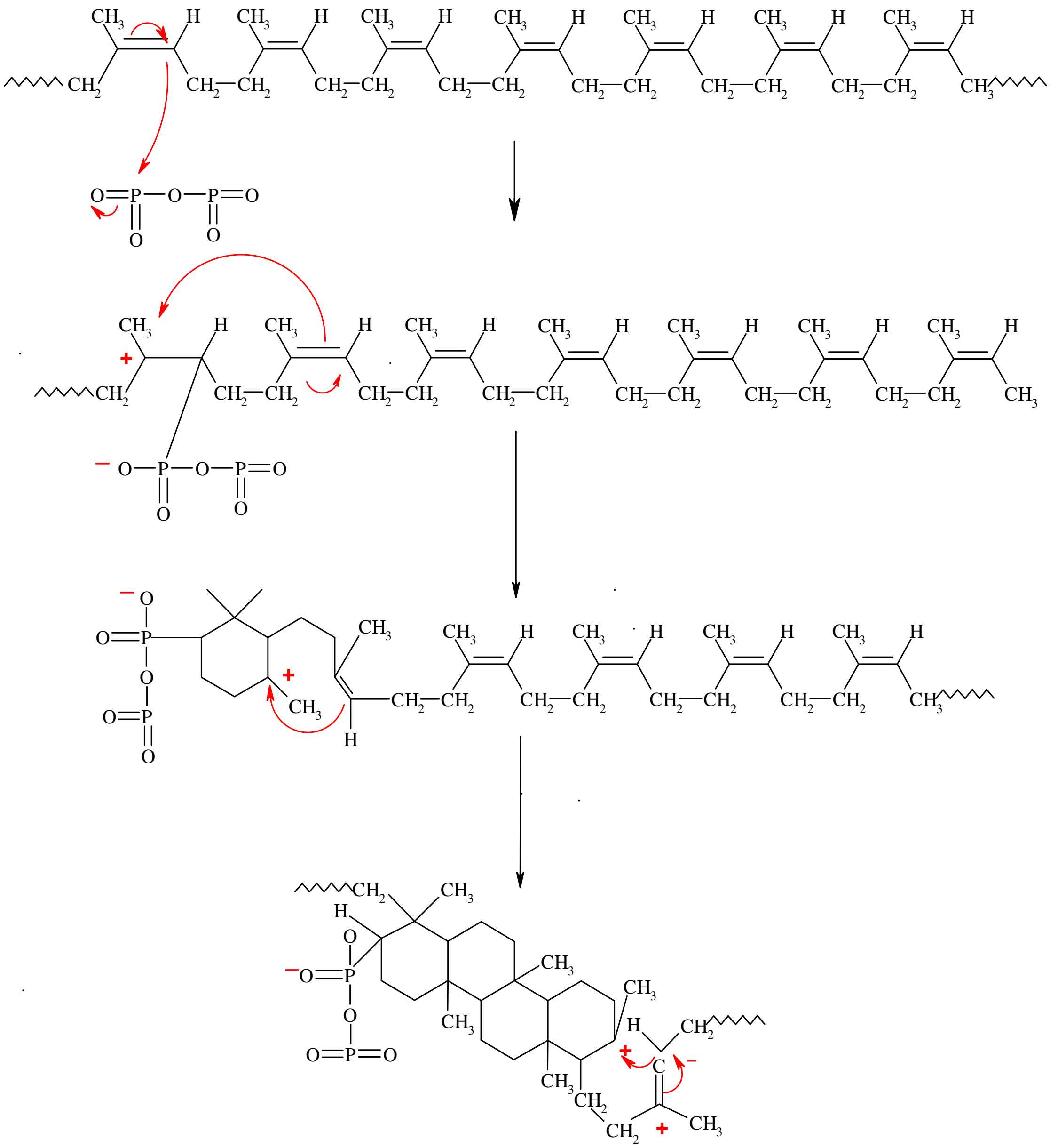
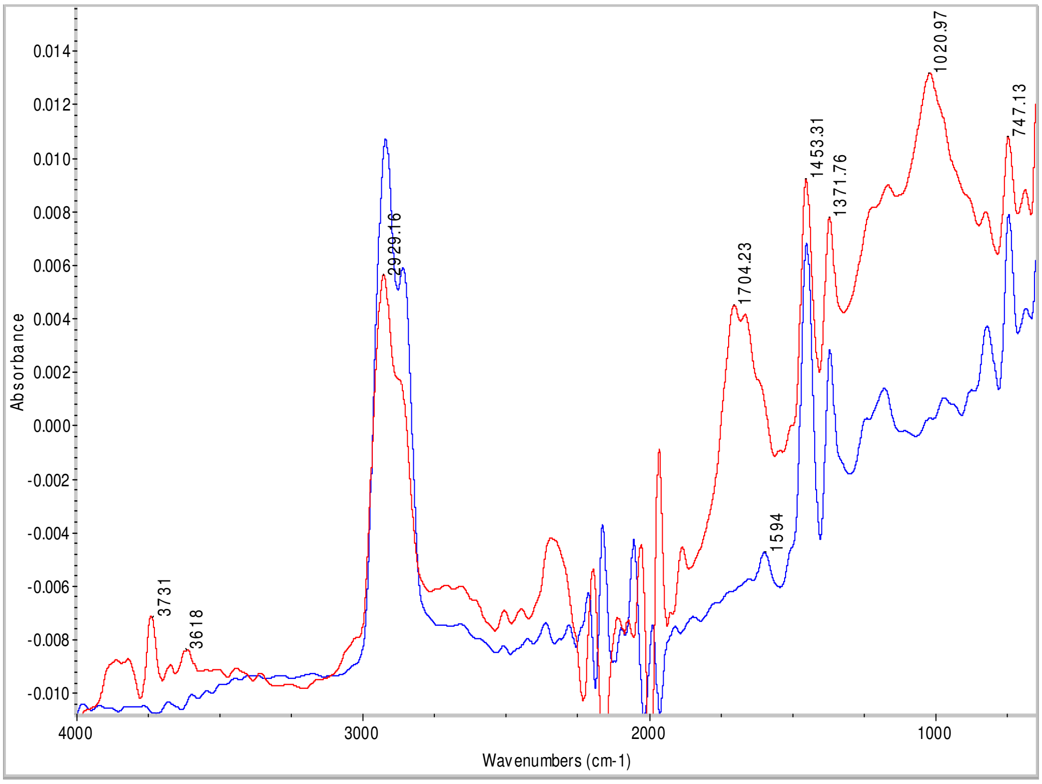


Figure 1. The reaction mechanism of CNR



Source: Siregar (2014)

Figure 2. FTIR spectra for Resipren-35.

Omnic software determine the amount of carbonyl index on FTIR spectra of samples as shown in Fig. 4. Typical uptake increasing carbonyl shown of carbonyl index increased due to heating after 3, 6, and 9 days as in Figure3. Besides exposure is done by heating the samples were also given treatment with radiation (UV). Typical carbonyl absorptions were also observed in the FTIR spectra of the samples are getting radiation (UV), as shown in Fig. 5. The longer radiation (UV) were given turned out to increase the intensity of the absorption at wave number 1707 cm^{-1}.

Heating and radiation (UV) in the sample resipren-35 showed oxidative degradation. Heat and light exposure resulted in many resipren-35 degraded as indicated by the increasing of absorption intensity at wave number around 1700 cm-1 are thought to have come from the oxidation reaction involving a double bond C = C on chain structure resipren-35. Increased absorption intensity associated with an increased rate of oxidative degradation in resipren-35. This indicates the occurrence of damage to the sample resipren-35. As an industrial product that demonstrates the weakness of the product which of course must be overcome. One recommended method to overcome the degradation of the polymer by using antioxidants.

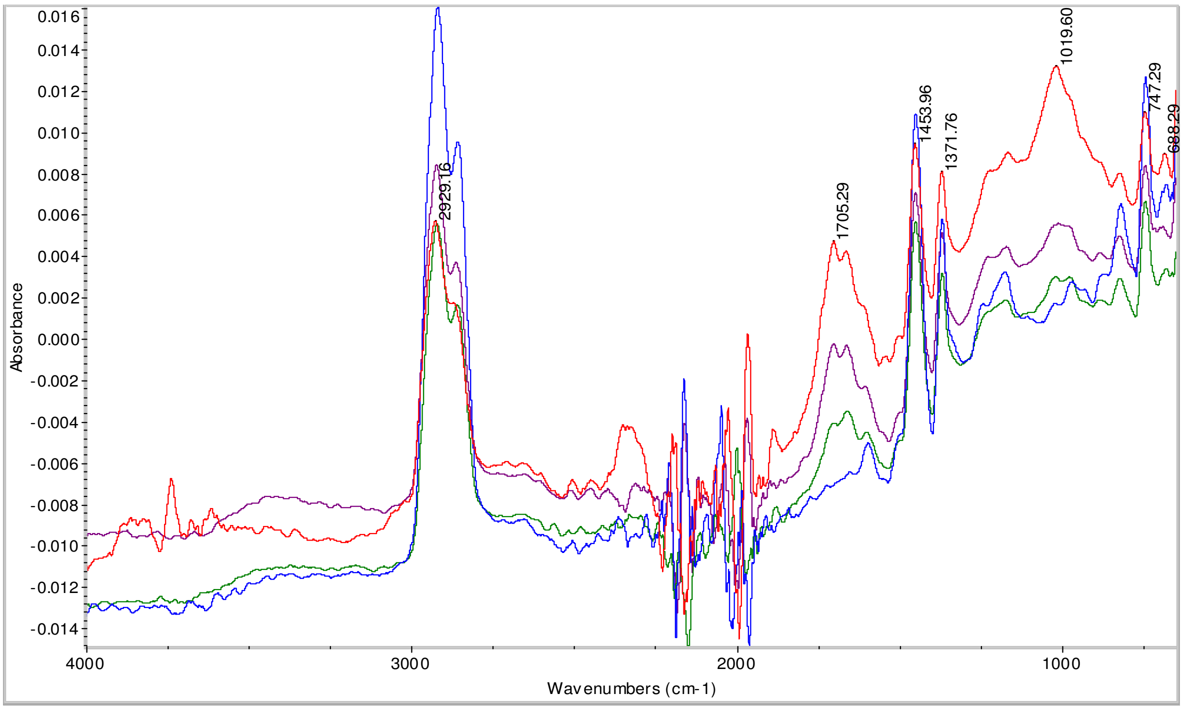
Fig. 5 shows the increasing of absorption intensity after the sample is irradiated for 3, 6, and 9 days. Carbonyl index value was increased in line with the duration of heating.

Table 1. Identification of Functional Groups of Spectrum CNR

Sample	Figure	Peak (cm^{-1}) Before expose	Peak (cm^{-1}) After expose	Intensity	Fungsional Group
CNR	1	2929	2929	Very strong	$\upsilon(CH_2,CH_3)$
			1704	Strong	$\upsilon(C=O)$
		1594		Medium	$\upsilon(C=C)$
		1453	1453	Strong	$\delta(CH_3)$
		1371	1371	Strong	$\delta(CH_2)$
		1020	1020	Strong	$\tau(CH_3)$
		747	747	Very Strong	$\rho(CH_2)$

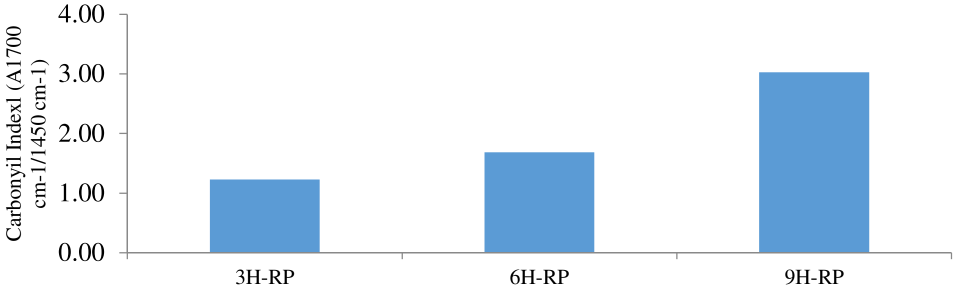
Remark: υ = stretching, δ = bending, τ = twisting, ϖ = wagging, ρ = rocking

Source: Siregar (2014)



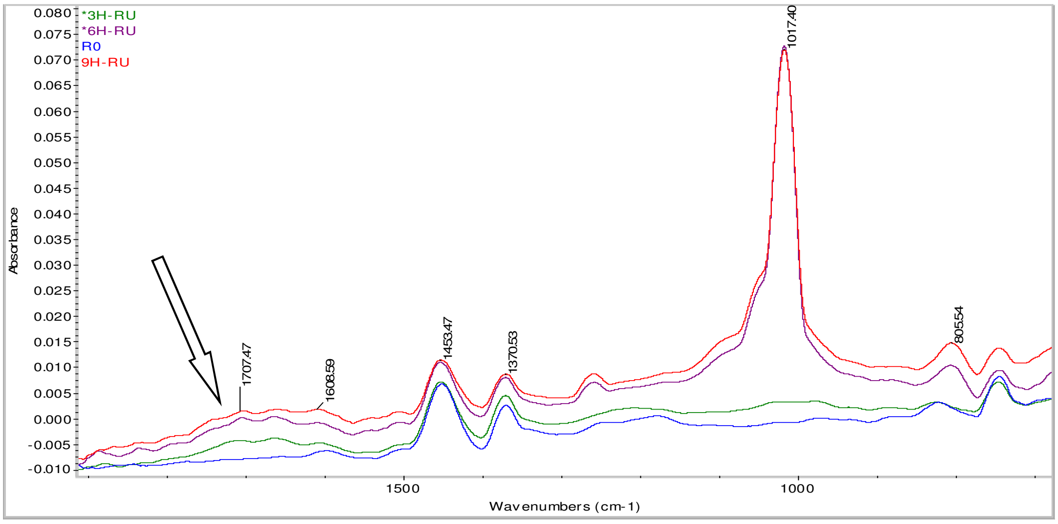
Source: Siregar (2014)

Figure 3. FTIR spectra for Resipren-35 before and after heating after 3, 6 and 9 days.



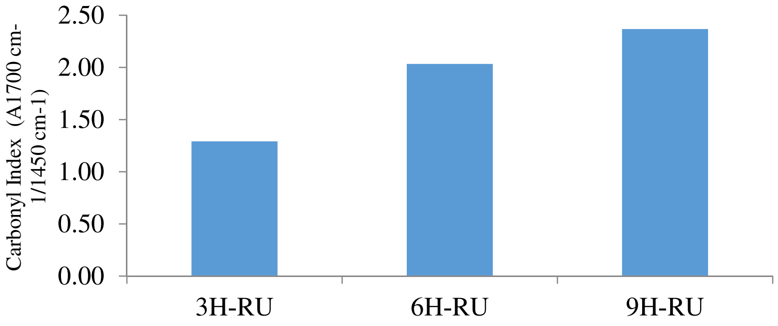
Source: Siregar (2014)

Figure 4. Carbonyl index of Resipren-35 for 3, 6 and 9 days.



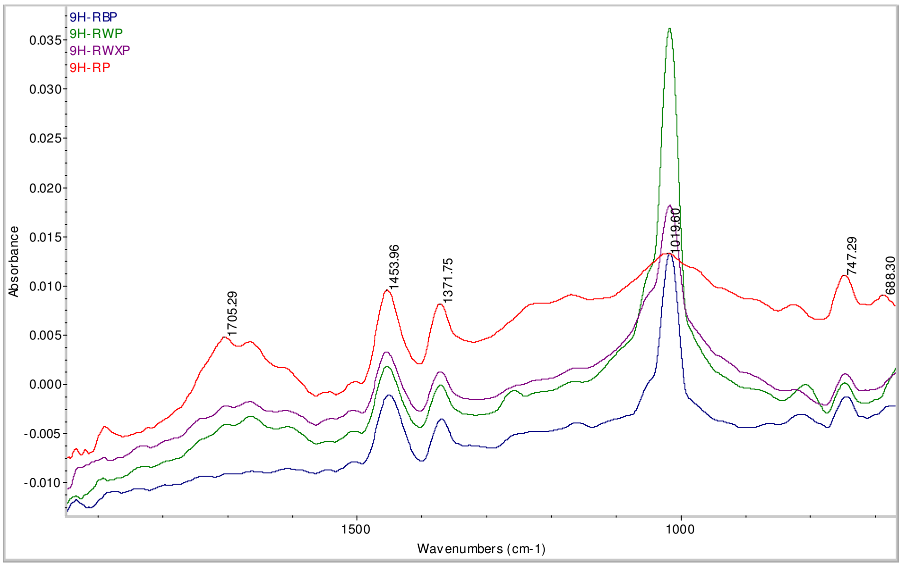
Source: Siregar (2014)

Figure 5. FTIR spectrum of Resipren-35 after exposing UV for 0, 3, 6 dan 9 days.



Source: Siregar (2014)

Figure 6. Index carbonyl heating resipren-35 for 3, 6 and 9 days.

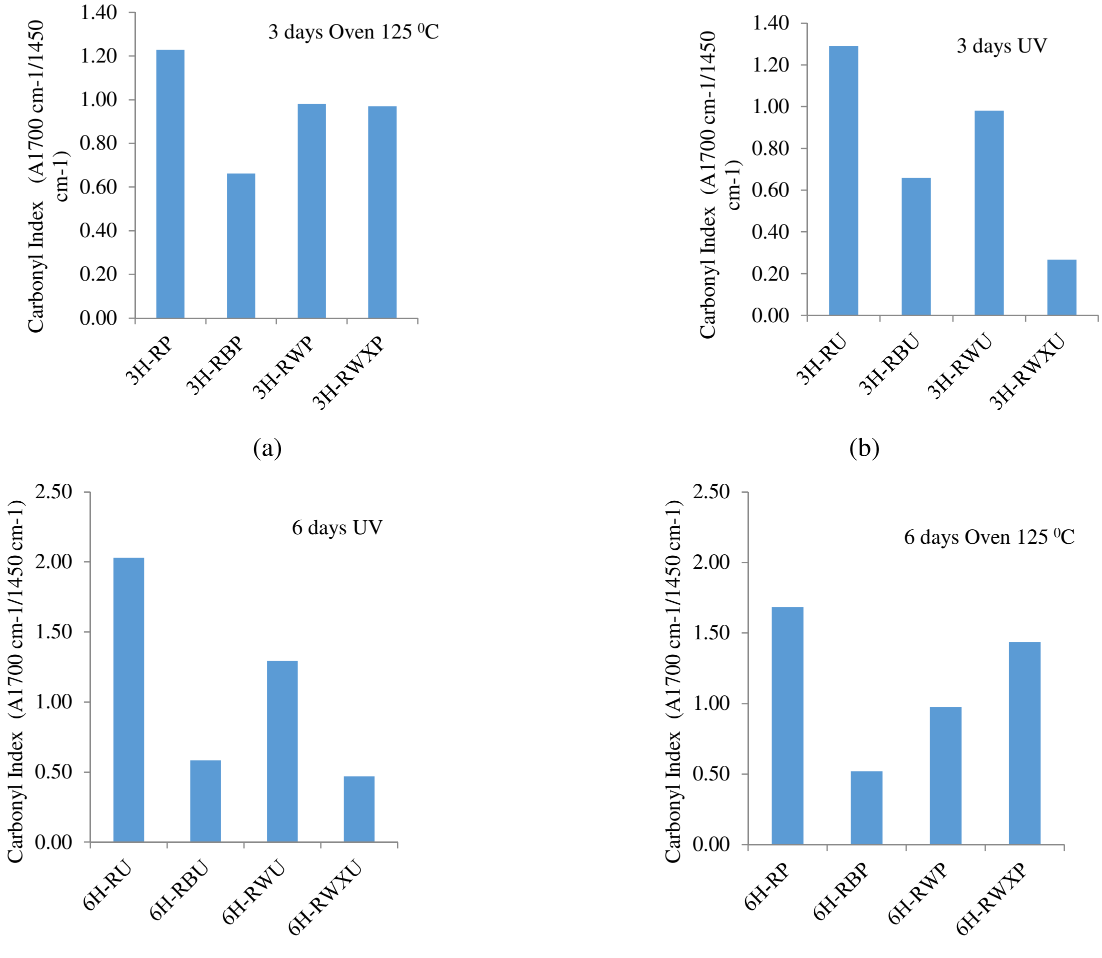


Source: Siregar (2014)

Figure 7. FTIR spectra of Resipren-35 with and without antioxidants on heating for 9 days.

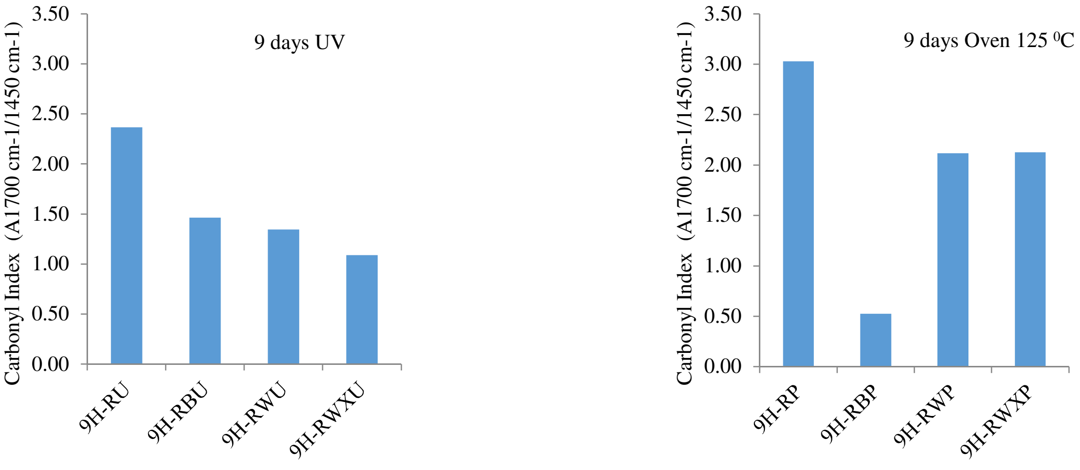
The use of antioxidants showed a decrease in the intensity of FTIR absorption spectra. A decrease in the intensity of the absorption can also be confirmed by the appearance of absorption at 1705 cm -1 numbers. Fig. 8, Fig. 9, and Fig. 10 shows the ability of resipren-35 and resipren added with antioxidants to radiation (UV) and heating. Based carbonyl index, resipren-35 were added with antioxidants consistently having carbonyl indexes were lower when compared to resipren-35 or in comparison with the addition of other antioxidants against radiation (UV). On the other hand, the addition of antioxidant BHT shows the index value of carbonyl low when compared to resipren-35 and with the addition of other antioxidants. Although the wax carbonyl index value is lower when compared with other antioxidants, but the carbonyl index value continues to increase. Radiation (UV) to the wax showed that carbonyl index value increased after irradiation for 3, 6, and 9 days.

Fig. 11 shows the change in the thermal capability resipren-35 after experiencing heating 9 days. Resipren-35 were heated for 9 days showed higher thermal capability. It allegedly associated with the degradation resipren-35 the reaction of C = C double bond produce carbonyl. In this case the possibility of connective cross that causes increased molecular weight.



(a) (b)

(c) (d)

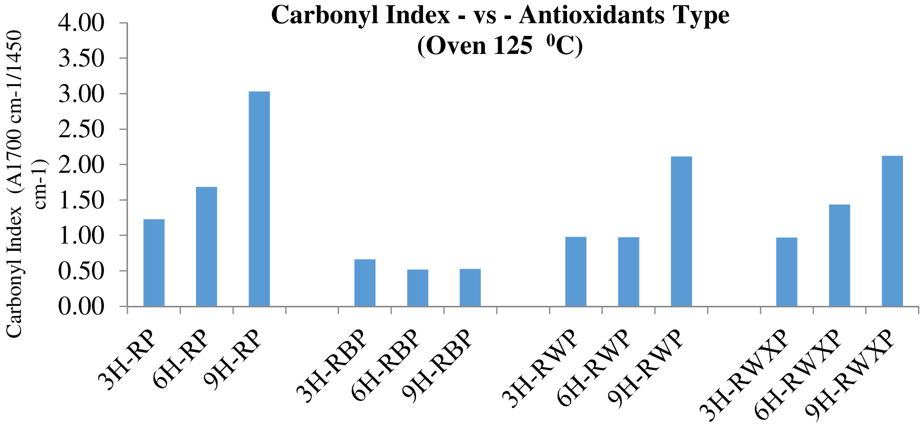


(e) (f)

Source: Siregar (2014)

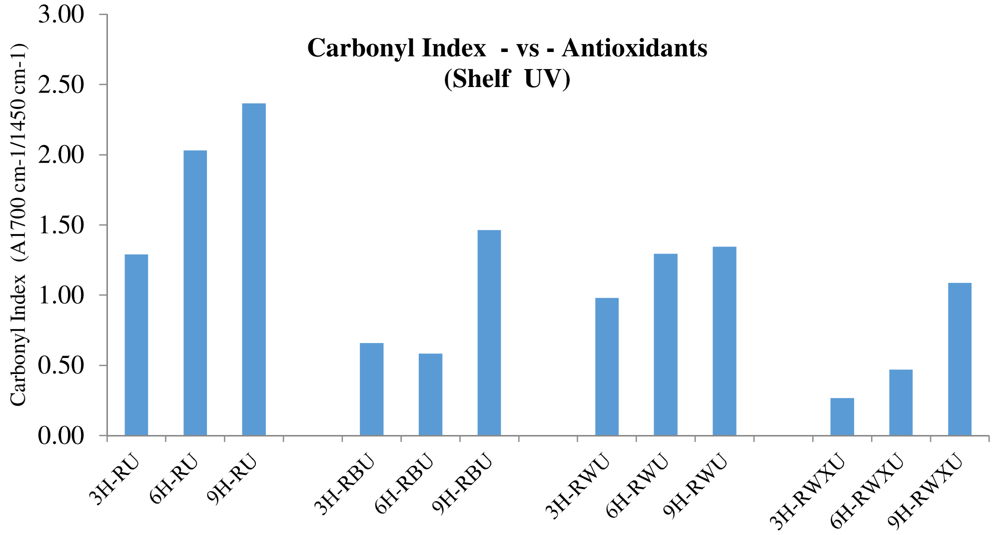
Figure 8. Samples carbonyl index after exposing with heating and UV for 3, 6, and 9 days.

Explanation for oxidative degradation using FTIR and TGA analysis showed degradation oxydation of resipren-35. Support of data analysis is then performed using XRD instrument. XRD work on the basis of interference wave files of X-rays (X-rays) at a wavelength, approximately 1.54060 A^0, which is diffracted by the crystal lattice. Hence, even when the arrangement of the crystal lattice perfectly arranged will deliver the intensity of the interference pattern (XRD pattern) are very sharp. Imperfections or amorphous forms would soon be known by the intensity of the interference pattern of diffraction. XRD data showed the highest peak at 2 theta value of 14.6400, 16.8000, and 18.3600 indicates that the material tested is not a pure crystal, but containing crystalline part and amorphous part. This pattern leads to the diffraction pattern of a polymer which has a crystalline structure and amorphous.



Source: Siregar (2014)

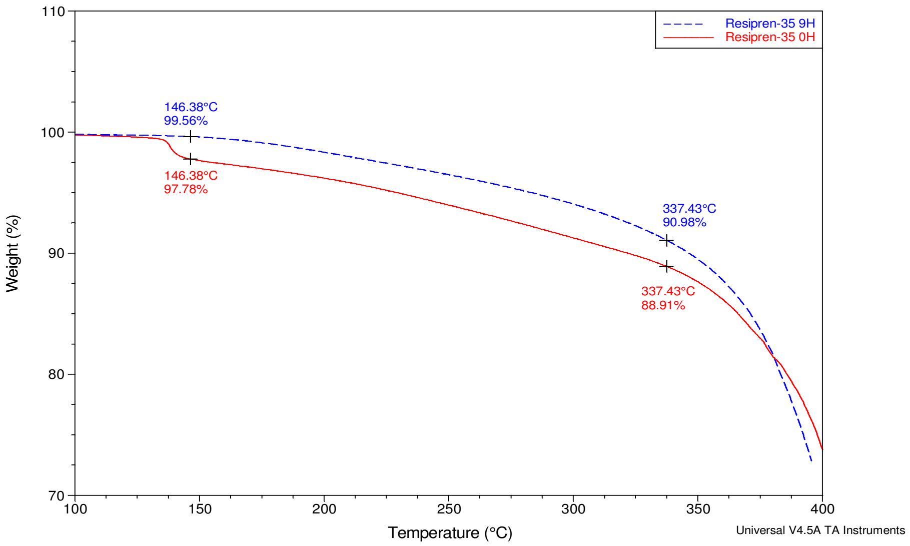
Figure 9. Carbonyl index of samples with and without antioxidants on heating.



Source: Siregar (2014)

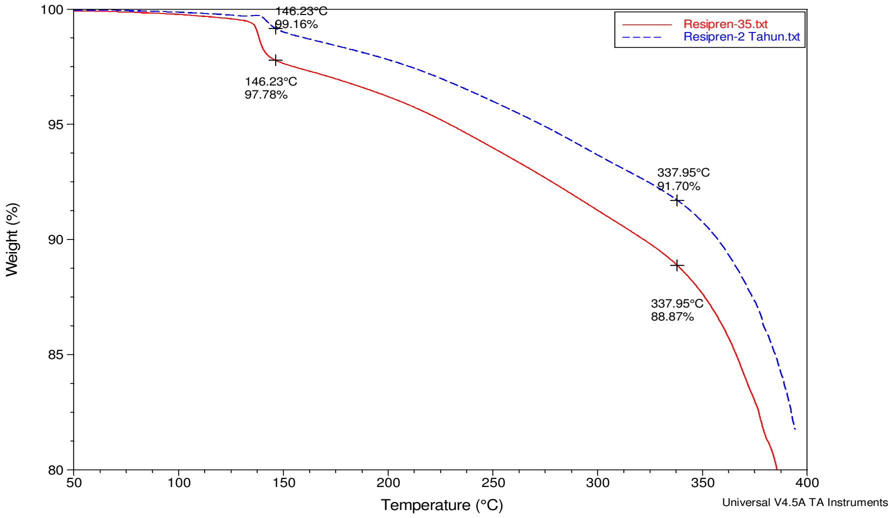
Figure 10. Carbonyl index of samples with antioxidants on exposure to UV.

The data in Table 2 shows that the highest intensity is owned by CNR-Pure samples indicating that CNR-Pure has a number of crystals are more when compared to other samples. On the other hand the sample CNR-Wax has a crystal structure with a lattice spacing of adjacent more when compared to other samples based on the value of the Full Wave at High Maximum (FWHM). Samples CNR-Wax also has a crystal lattice spacing smaller.



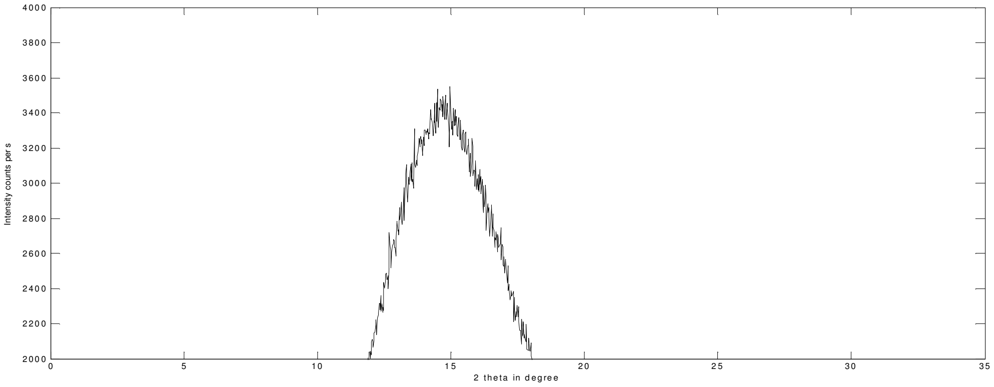
Source: Siregar (2014)

Figure 11. TGA of resipren-35 without exposure to heat and heat exposure for 9 days.



Source: Siregar (2014)

Figure 12. TGA of resipren-35 without exposure to heat and stored for 2 years.



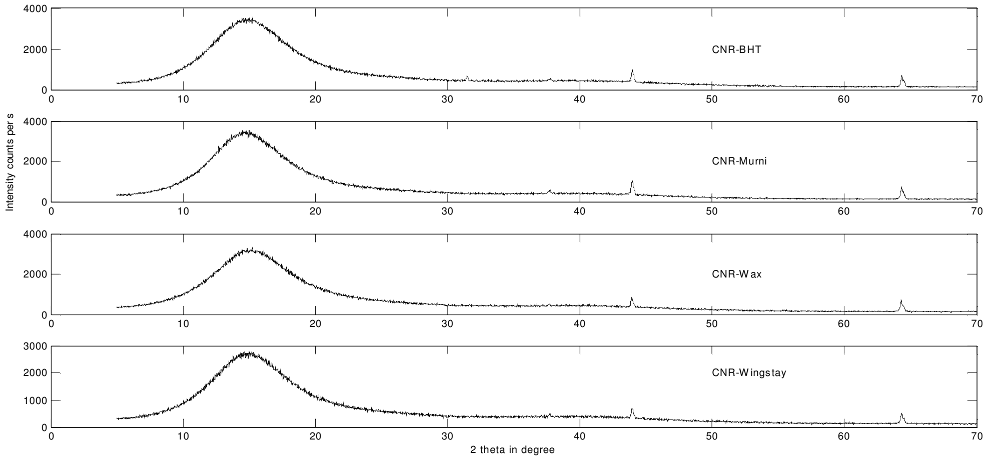
Source: Siregar (2014)

Figure 13. Peak of the highest intensity at the CNR-Pure.

Table 2. Summary of data on the highest peak

No	Samples	Corner (2θ)	The Highest Intensity	FWHM	*d_Spacing*
1	CNR Pure	14,6400	1576	4,9964	6,04580
2	CNR-BHT	14,7800	1551	5,30220	5,98884
3	CNR-Wax	15,1844	1381	5,63110	5,83024
4	CNR-Wingstay	15,0148	1181	5,62170	5,89571

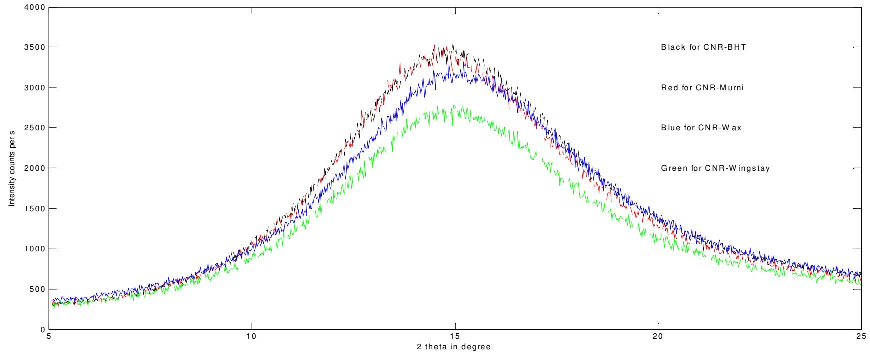
Source: Siregar (2014)



Source: Siregar (2014)

Figure 14. Overlay intensity pattern for the entire sample

Fig. 14 and Fig. 15 are an overlay pattern XRD intensity for the entire sample. Visually not so noticeable differences from each intensity pattern exists. However, when sampled at 2 theta values between 5 to 25, were apparent differences.



Source: Siregar (2014)

Figure 15. Overlay profile intensity pattern to the highest peak

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