

Photochemical reduction of molecular weight and number of double bonds in natural rubber film

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Abstract—Natural rubber (NR) can be degraded depending on various factors such as heat, mechanical force, chemical reaction, and light. Light is a very interesting factor because it can cause the NR to degrade under low temperature and pressure. The photo-degradation of NR films was carried out to investigate the effects of the light and the temperature on the reduction of the weight-average molecular weight (M_w) and the double bonds in the NR films. The NR films, with and without catalysts, titanium dioxide (TiO₂), and potassium persulfate (K₂S₂O₈), were exposed to light from a mercury light bulb at 7,000 and 36,000 lux, and at the temperature of 25 °C and 80 °C for 192 hrs. After exposure, the M_w of the NR films was analyzed by gel permeation chromatography (GPC). Changes in the M_w were used to construct a kinetic model for the process, $(1/M_w) = (1/M_{w_0}) + (kt/2M_0)$ where k is the rate constant, and M₀ is the M_w of the monomer unit. The linear relationship between 1/M_w and time suggested pseudo first-order processes with random scission. The M_w distribution information from the GPC was used to calculate the number of double bonds in the NR films. The trend of the double bonds reduction curves was quite similar to the result obtained from the calculation from the FTIR spectra. This indicated that this calculation method might possibly be another alternative way to obtain the number of double bonds in the NR.

Key words: Photo-degradation, Natural Rubber, GPC, Titanium Dioxide, Potassium Persulfate

INTRODUCTION

Polymer degradation is a harmful process [1]. In order to stabilize the polymer, the mechanism of polymer degradation must be understood, the factors and stresses causing it must be identified, and the factors that affect polymer stability must be known. However, sometimes polymer degradation may be useful. Depolymerization leading to high purity monomers may be exploited for practical production of such materials.

There have been many research works devoted to photo-degradation of polymer in both aspects of how to stabilize and degrade it. Photo-degradation of various kinds of polymers, pure and blended, has been extensively investigated [2-7]. The decrease in double bonds and the formation of photoproducts are thoroughly reported. Stress is also found to accelerate the degradation in this process [8]. Moreover, it is a synergistic effect of increased UV radiation with other factors, such as temperature that would determine the extent of such reduction in service life [9].

Catalysts have been introduced into photo-degradation of polymers. TiO₂ is one of the photo-catalysts mostly used in many investigations of photo-degradation of organic materials [10-18], as well as of photo-degradation of polymers [19-21]. It is claimed that TiO₂ particles can absorb UV light ($\lambda < 387$ nm) to create mobile electrons (e⁻), and holes (h⁺) in the conduction band and valence band, respectively [21]. Adsorbed oxygen molecules can capture electrons, and produce O₂⁻, O, and O⁻ species. At the same time, photo-generated holes can be trapped by hydroxyl ions, or water adsorbed on the surface, producing hydroxyl radicals, •OH, which play important roles in photo-catalytic reactions, as displayed in the

following equations.



Some literature has reported the use of potassium persulfate (K₂S₂O₈) in the photo-degradation process [22]. It is revealed that photo-irradiation promotes surface oxidation of PE film with K₂S₂O₈. The kinetic aspect of the degradation process of some polymers has also been investigated [23]. A pseudo first-order rate equation [24] for random scission of a macromolecular chain was used to investigate the depolymerization of β -glucan.

Natural rubber is mainly composed of hydrocarbon substance, which can be cast into films that are usable for many purposes such as wrapping, decorative coating, protective covering, light screening or blocking, separating, and producing new types of materials or compounds. The NR can be degraded depending on various factors such as heat, mechanical force, chemical reaction, and light. Light is a very interesting factor because it can cause the NR to degrade under low temperature and pressure. When the NR is exposed to light, the energy transferred from the light will activate the NR into the excited state. In this state, there can be several kinds of reactions occurring, which change the properties of the polymer or produce new types of compounds. Photo-degradation is an attractive process used to improve or change the properties of NR because it can be held at low temperature and pressure. Furthermore, we can

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find the rate of photo-degradation of NR films in order to identify its lifetime. An example of NR application for engineering aspect is to use NR as a protective film for cellulosic construction materials. Bamboo trees are one of the cellulosic materials that are widely used in construction, such as houses and temples, because they can grow rapidly. But bamboo is easily attacked by insects, which can shorten its lifetime. One way to extend the bamboo's lifetime is to protect it with a coating, in which NR film is very interesting for this application. Due to the low T_g (glass transition temperature) at around -68°C of poly(*cis*-1,4-isoprene) [25], which is the main component of NR, NR film can still provide good flexibility at low temperature especially when used in cold countries. Also, with its good insulation property, it can help keep the temperature inside the building more stable. On the other hand, since NR is easy to be photo-degraded, more investigation on how to protect NR from the photo-degradation should be conducted.

In Thailand, a large quantity of NR can be produced. The authors would like to do research with the intention of finding new applications of NR. So it is very interesting to study the photo-degradation process of NR films to gain some knowledge in order to modify the rubber or to improve its properties, and also to make the products more valuable.

For the objectives of this present work, the NR films, with and without catalysts, were exposed to light in order to study the effects of catalysts (in some applications it may be useful to accelerate the degradation), light density, and temperature on the photo-degradation of the NR films, and to find the rate of change of NR Mw in the photo-degradation process. A calculation method was applied to calculate the number of double bonds contained in the NR films, and the results of calculation were compared to those in others' works, which were obtained from using the FTIR technique. A pseudo first-order rate equation was used to analyze the degradation kinetics.

EXPERIMENTAL SECTION

1. Preparation of NR Films

Usually, the NR latex from the rubber tree has approximately 30-40% of total solids content. But for convenience of transportation, the NR latex is centrifuged to eliminate some water to gain 60% DRC (dry rubber content) NR latex, which is a general com-

mercial standard. The 60% DRC NR latex was used in the experiments. The catalysts, TiO_2 (anatase, Aldrich), and $\text{K}_2\text{S}_2\text{O}_8$ (Carlo Erba), were dispersed, or dissolved in distilled water, in which the concentration was varied from 0.1-1.5 phr (parts per hundred of rubber). The solution was agitated until it was well mixed. Then, the NR latex was poured into the solution, and the mixture was stirred by using a magnetic stirrer until totally mixed. Two grams of the mixture, having 50% DRC, were transferred to a flat-bottomed plastic container, having a dimension of $5 \times 5 \times 1.5$ cm (W×L×H), and then dried at 40°C in an oven for 24 hours. A 0.4 mm thick NR film was finally obtained.

2. Apparatus

The experiments were performed in a $50 \times 52 \times 60$ cm chamber. A cooling bath made of zinc sheets, with an inside dimension of $28 \times 38 \times 15$ cm, and an outside dimension of $33 \times 44 \times 18$ cm, was placed in the chamber to control the temperature of the sample. A 400-watt mercury light bulb was installed at the front door of the chamber in a horizontal manner, 5 cm above the top of the cooling bath. The temperature of the sample was measured by placing a thermocouple on the surface of the sample.

3. Photo-degradation of NR Films

The NR films with and without catalysts were exposed to light, which had the density of 7,000 and 36,000 lux, at the temperatures of 25°C and 80°C for 192 hrs. The samples were collected at various intervals and were kept in a dry cool dark place.

4. Average Molecular Weight Analysis

The NR films, before and after exposure, were dissolved in the tetrahydrofuran (THF, HPLC grade), and filtered through 0.45- μm PTFE filters. The rubber solution with a concentration of 1 g/l was injected into the GPC system (Waters Corp.), which was composed of an isocratic HPLC pump that pumped THF at a flow rate of 1 ml/min, three Styragel columns with different sizes, and an online refractive index detector. The chromatograph of the sample injected into the GPC provided the signal intensity versus retention time, which was then converted into Mw.

5. Functional Groups Analysis

The NR films were dissolved in the toluene for 24 hrs. The solution obtained was cast on a sodium chloride cell and dried to get a thin film. Then the sodium chloride cell with the thin film was inserted into the FTIR (Thermo) to analyze the functional groups of

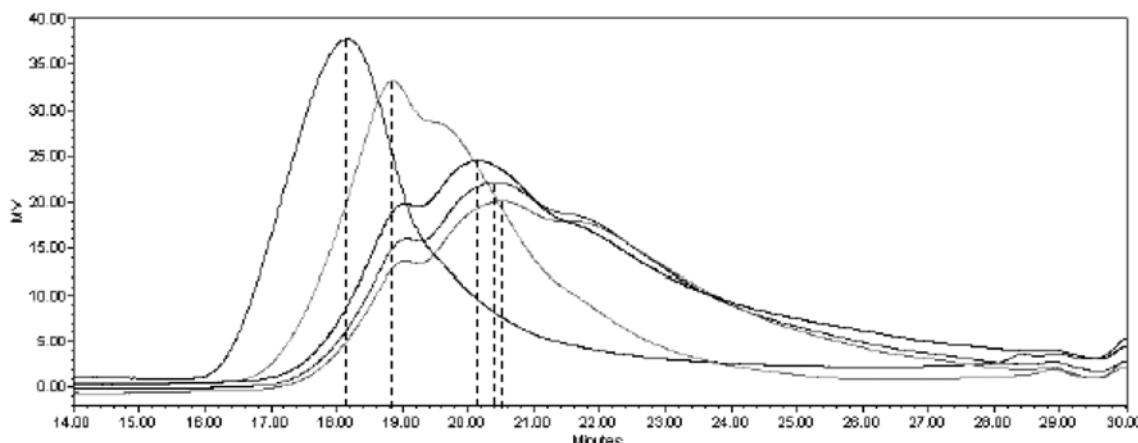


Fig. 1. GPC chromatograms of NR+ TiO_2 0.1 phr exposed to light for 0, 48, 96, 144, and 192 hrs from left to right, respectively.

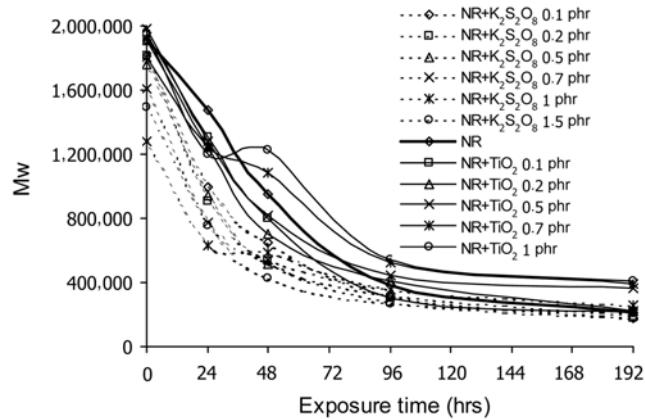


Fig. 2. Average molecular weight reduction of natural rubber films with and without catalysts, at 36,000 lux, 25 °C.

the NR.

RESULTS AND DISCUSSION

1. Effect of Types and Concentrations of Catalysts on Photo-degradation of NR Films

After being exposed to light at 36,000 lux, and at a temperature of 25 °C, the NR films were then characterized by GPC to find the Mw. Fig. 1 shows the GPC chromatograms obtained by injecting the NR samples, which were exposed to light for different periods of time. More retention time represents less Mw. From the relationship between the Mw and the exposure time in Fig. 2, the Mw of all NR samples decreases with time and seems to be constant after 96 hrs. Some cases where the Mw gets a little bit higher and then decreases again are probably due to the fluctuation of the experimental condition such as light instability, the position of the samples, the variation of the GPC results, etc. For the NR samples with TiO₂, all the curves have almost the same tendency, except those with TiO₂ 0.5-1 phr, which tend to have a little bit slower degradation rates than others. This is probably because the TiO₂ can also act as a stabilizer [26], as it can block the penetration of the light. So a greater concentration of TiO₂ can lead to a slower rate of photo-degradation of the NR. On the other hand, a greater concentration of K₂S₂O₈ tends to reduce more Mw since the films were not exposed. This is probably because K₂S₂O₈ can help promote oxidation on the NR films surface, for which K₂S₂O₈ is an oxidizing agent and usually used as a peptizer to reduce the viscosity of NR in the rubber industry. But this may not be acceptable from the aspect of stability because NR films should not degrade before being used. Therefore, the catalyst concentration chosen for further experiment was 0.1 phr.

Comparing the results tested at the same catalyst concentration of 0.1 phr in Fig. 3, it can be observed that the NR samples with and without catalysts, TiO₂ and K₂S₂O₈, give quite similar results. At 25 °C, the Mw of the sample with K₂S₂O₈ tends to reduce a little bit faster than others in the initial stage which may be due to the oxidizing property of K₂S₂O₈. But it gets to the same level as others at the end. Actually, the samples with catalysts, especially TiO₂, are expected to have a faster degradation rate than that without catalysts as shown in other works [19-21], which used TiO₂ as a photo-

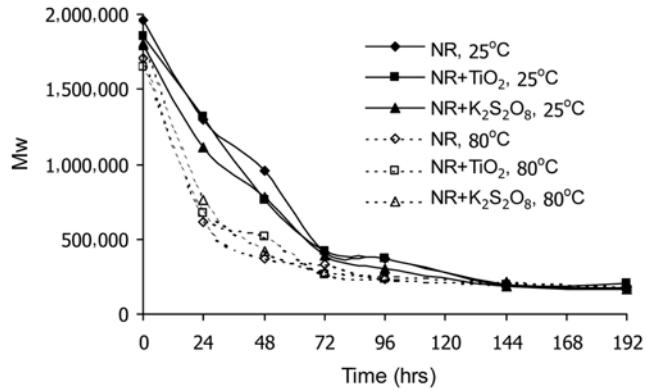


Fig. 3. Average molecular weight reduction of natural rubber films with and without catalysts 0.1 phr, at 36,000 lux, 25 °C and 80 °C.

catalyst in the photo-degradation process of some polymers. There may be several factors that make the results of each sample become the same, such as the thickness of the films, the experimental condition, and the types of polymers. Shang et al. [20] pursued the photo-degradation of polystyrene (PS) plastic with TiO₂ as a photo-catalyst. The PS plastic was made into thin films having a thickness of 35 μ m. The result showed that the PS-TiO₂ sample degraded more quickly than the PS sample. It was claimed that the degradation initially occurred over TiO₂ particles, followed by the diffusion reaction with the aid of reactive oxygen species generated on TiO₂ particle surfaces. Compared to Shang's work, the NR films (0.4 mm thick) used in the authors' work were much thicker than those of Shang's. Also naturally, there are some other components such as proteins, carbohydrates, sugars, etc. in the NR matrix which make it yellowish and turbid. Therefore, the thicker the film, the more opaque it becomes. This makes it difficult for the light to penetrate very deeply through the films. Thus, the degradation reaction occurred mainly on the surface of the films. In the Mw analysis, the NR films were cut into pieces, from the surface through the bottom, and the whole piece was dissolved in THF prior to the analysis. Therefore, the Mw obtained was the Mw of the whole piece of the NR sample. This probably makes the overall results become quite similar.

2. Effect of Temperature on Photo-degradation of NR Films

From the photo-degradation of NR films at the light density of 36,000 lux, and at the temperature of 25 °C and 80 °C, as shown in Fig. 3, it can be observed that the NR samples tested at 80 °C have a faster degradation rate than the ones tested at 25 °C. This is probably because the higher temperature provides more heat energy to excite the molecules, and that it gives more opportunities for many degradation reactions to occur at a faster rate. This is consistent with a study on degradation of polyethylene films [9]. The Mw reduction seems to stop at the exposure time of 144 hrs at 25 °C, and 96 hrs at 80 °C, respectively.

3. Effect of Light Density on Photo-degradation of NR Films

The photo-physical processes involved in photo-degradation include absorption of light by material, electronic excitation of the molecules, and deactivation by radiation or radiationless energy transitions, or by energy transfer to some acceptor [1]. When the lifetime of the excited state is sufficiently long, the species can participate

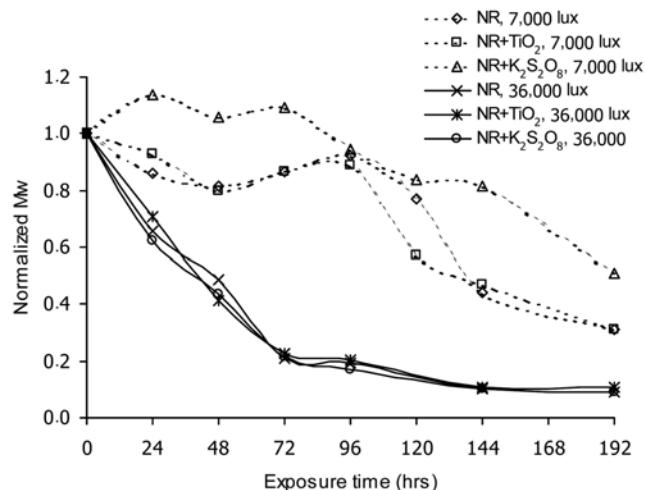


Fig. 4. Normalized Mw of natural rubber films with and without catalysts, at 7,000 and 36,000 lux, 25 °C.

in various chemical transformations. The absorption of light results in an electronic transition between two energy levels in the absorbing molecule; this absorbed energy is exactly equal to the energy of a light quantum:

$$E = nh\nu \quad (7)$$

where h is Planck's constant, ν is the frequency of the absorbed light, and n is the number of photons. More light density means more quantity of light, or greater number of photons, which leads to more energy. This is consistent with the results of the experiments in this section, which were carried out at 25 °C by placing two pieces of black cloth between the light bulb and the samples to reduce the light density. According to Fig. 4, the result shows the reduction of Mw with the exposure time. At this low light density condition, the result can fluctuate due to the unevenness of the light density on each sample position. It is shown that the rate of Mw reduction of the NR films exposed to light at 36,000 lux is much faster than that at 7,000 lux. Because more light density gives more energy to make the NR become more excited, more degradation reactions can occur.

4. Double Bonds Reduction in NR Films

Many researchers have studied the photo-degradation of polymers. One of their interests is the reduction of double bonds in the polymer chain, which is mostly studied by using IR technique. Adam et al. [2] investigated photo-oxidation of polyisoprene, and analyzed the products of degradation by using IR spectroscopy. As well as Adam, Santos et al. [6] pursued photo-degradation of synthetic and natural polyisoprenes at specific UV radiations. From the plots of the formation of photoproducts and consumption of double bonds versus time in Adam and Santos's works, the patterns of the reduction of double bonds in polyisoprenes are similar in that they do not decrease immediately, but they keep quite constant for some time before decreasing at a fast rate. The rate of reduction then becomes slower, and the reduction finally stops.

In this work, the number of double bonds was calculated from the information of the GPC distribution curve to see if it is possible to predict the number of double bonds from the known Mw. This would be useful if the Mw data has already been obtained from GPC

analysis, and we want to know the information about the double bonds reduction. Instead of using instrumental analysis again such as FTIR, we can then calculate the number of double bonds immediately from the known data. To make the calculation easier, it is supposed here that the degradation process only occurs at the double bonds, and the NR contains only polyisoprene chains. The calculation is started by slicing the GPC distribution curve into 100 pieces, in which each piece represents the weight (Wt) of NR having one Mw, and is done on the basis of 1 kg of NR. So the area under the curve is the weight fraction of 1 kg of NR. The number of molecules (n) of NR in each fraction (x) at time t is then calculated from

$$n_{x,t} = \frac{Wt_{x,t}}{Mw_{x,t}} \times 6.02 \times 10^{23} \quad (8)$$

where $Wt_{x,t}$ is the Wt of NR in each fraction at time t , and $Mw_{x,t}$ is the Mw of NR in each fraction at time t . The total number of molecules or the molecular chains of NR at time t ($n_{total,t}$) is the summation of the number of molecules of NR in each fraction.

$$n_{total,t} = \sum_{x=1}^{100} n_{x,t} \quad (9)$$

Imagine that we have one molecular chain of NR. If we break one double bond in the chain, we will get two chains of NR. If we break nine double bonds in the chain, we will get ten chains of NR. We can see that the total chains obtained are more than the broken bonds in the number of 1. From this idea, if $n_{total,t}$ is the number of molecules or the molecular chains obtained from breaking the double bonds, then it has a relationship with the broken double bonds at time t (B_t) as follows.

$$B_t = n_{total,t} - 1 \quad (10)$$

Since the number of molecules is very large compared to 1, Eq. (10) becomes

$$B_t = n_{total,t} \quad (11)$$

That is, the number of broken bonds is equal to the number of molecules.

Suppose that an ideal NR has only one long polyisoprene chain. Each isoprene unit contains one double bond. Therefore, the number of double bonds in the ideal NR (D_{ideal}) is equal to the number of isoprene units, which can be calculated as follows:

$$D_{ideal} = \frac{Wt_{NR}}{M_0} \times 6.02 \times 10^{23} \quad (12)$$

where Wt_{NR} is the weight of NR, and M_0 is the Mw of an isoprene unit.

Finally, we can obtain the number of double bonds in NR at time t (D_t) from

$$D_t = D_{ideal} - B_t \quad (13)$$

The results from the calculation using the equations above are plotted in Figs. 5 and 6. Fig. 5 shows the reduction of calculated double bonds in NR films with and without catalysts 0.1 phr, at the light density of 36,000 lux, and at the temperatures of 25 °C and 80 °C. The trends of all curves are quite similar, and are quite similar to the curves of Adam and Santos's works. It can be noticed that all curves have induction time from 0-48 hrs before they reduce at

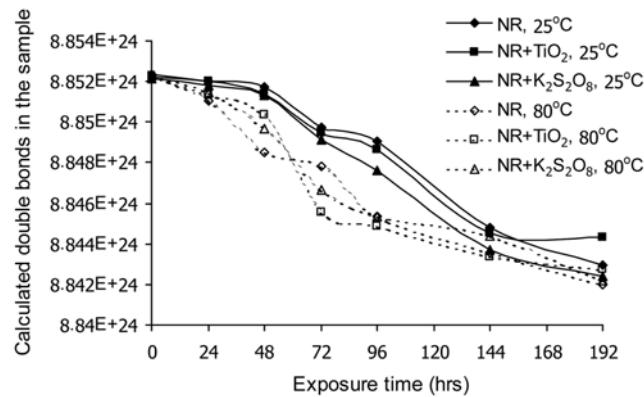


Fig. 5. Reduction of calculated double bonds in natural rubber films with and without catalysts 0.1 phr, at 36,000 lux, 25 °C and 80 °C.

a faster rate. This is probably because the NR molecules can still resist the degradation in the initial stage. The catalysts seem not to have much effect on the reduction of double bonds, but the high temperature has a significant effect in that it provides a faster rate of reduction of double bonds than the lower one does. When the light density is decreased to 7,000 lux, at 25 °C, the rate of reduction of double bonds is much slower than that at 36,000 lux, as shown in Fig. 6. This may be explained as that less light density gives less energy to excite the molecules. Thus, the NR samples can resist the degradation longer than those tested at higher light density.

In addition, the NR films photo-degraded at the light density of 36,000 lux, 80 °C, and exposure time of 0, 24, 48, 96, 192 hrs were analyzed by using FTIR. The FTIR spectra of the NR films are shown in Fig. 7. Refer to Santos's work, for *cis*-polyisoprene, the wave numbers of 1,665 and 837 cm⁻¹ represent C=C stretching and =C-H wagging modes, respectively. The positions of the peaks in the author's work are quite close to the wave numbers referred to in Santos's

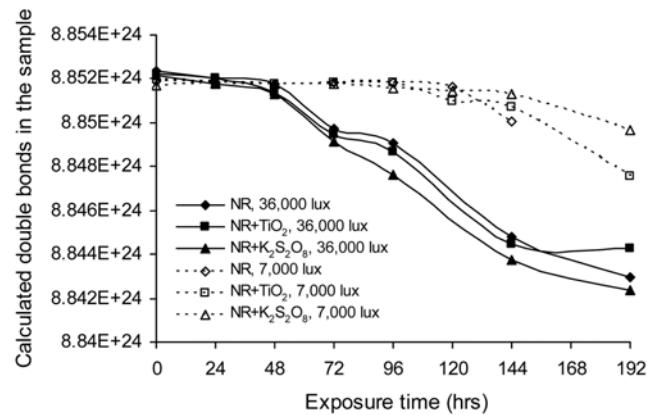


Fig. 6. Reduction of calculated double bonds in natural rubber films with and without catalysts 0.1 phr, at 7,000 and 36,000 lux, 25 °C.

work. Therefore, in this work, the peaks at 1,664 and 836 cm⁻¹ are assumed to be the peaks of C=C stretching and =C-H wagging modes, respectively. It is mentioned in Santos's work that =C-H wagging modes are used as references to monitor the consumption of C=C bonds. This is because the C=C stretching absorption band can overlap with the C=O stretching band in which they are very close to each other. Therefore, the larger peaks at 836 cm⁻¹ are selected to represent the double bonds in the NR films. The reduction of double bonds calculated from the FTIR spectra is shown in Fig. 8. The curve has nearly the same trend as those obtained from the calculation from the GPC results. The comparable patterns of all curves exhibit that the calculation of the amount of double bonds in this work may possibly be used.

5. Kinetic Aspect of the Photo-degradation of NR Films

The photo-degradation of NR films was followed experimentally by determination of the Mw as a function of time, using GPC

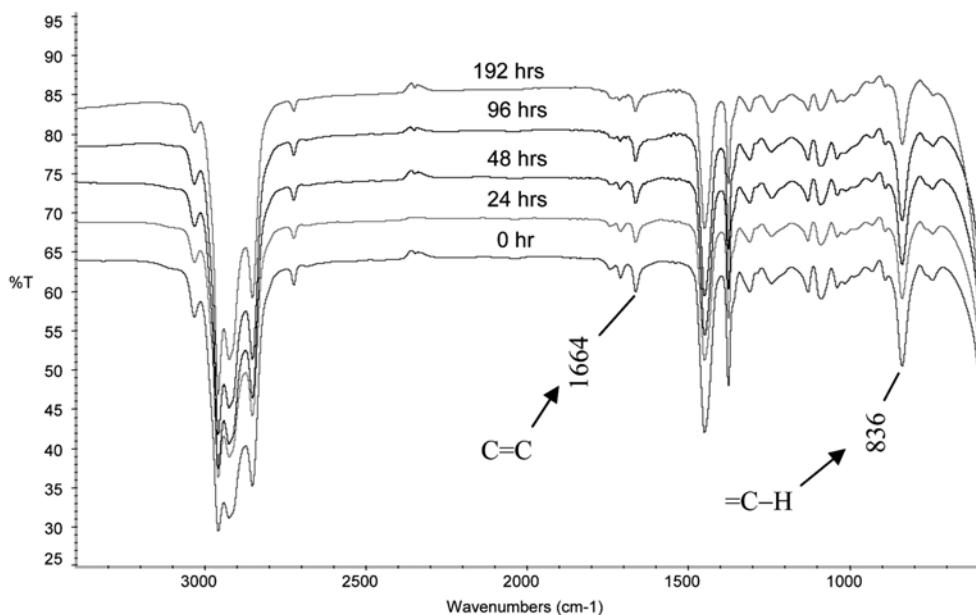


Fig. 7. FTIR spectra of the natural rubber films photo-degraded at different exposure time.

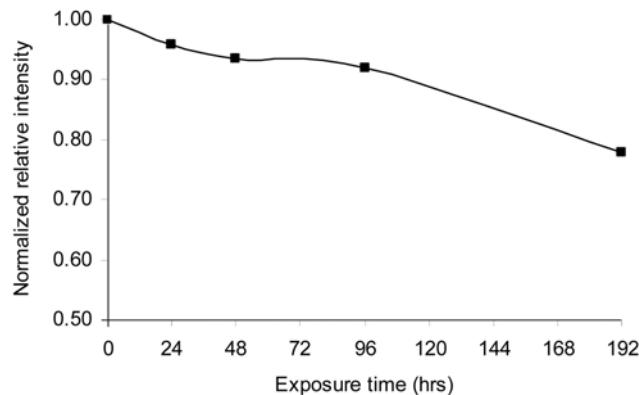


Fig. 8. The reduction of double bonds in the natural rubber films without catalysts at 36,000 lux, 25 °C, calculated from FTIR spectra.

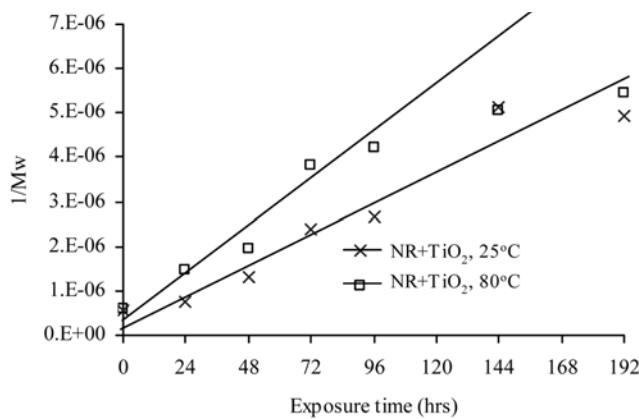


Fig. 9. Reciprocal of Mw of NR films with TiO_2 0.1 phr plotted as a function of degradation time (at 36,000 lux).

technique. This technique can be applied only as long as the Mw remains large, i.e., in terms of the number of bonds broken, which involves a study of the initial stages of the reaction only [24]. A first-order rate equation for random scission of a macromolecule was used here:

$$\frac{1}{Mw} = \frac{1}{Mw_0} + \frac{kt}{2M_0} \quad (14)$$

where Mw_0 is the Mw of NR at $t=0$, M_0 is the Mw of the monomer or an isoprene unit, and k is the pseudo first-order rate constant for breaking double bonds of NR chain. If the plot of $1/Mw$ versus time of the initial stage of the degradation is linear, it demonstrates a first-order reaction. The plots of $1/Mw$ versus the exposure time of the NR films with TiO_2 0.1 phr at the light density of 36,000 lux, and at the temperatures of 25 °C and 80 °C are shown in Fig. 9. The linear plots of the initial stages of the degradation exhibit the pseudo first-order reactions. Even though it is claimed in Santos's work [6] that cross linking and polymer reticulation can also occur in the photo-degradation process, but from the linear plots, it is quite obvious that photo-degradation of NR films in the present work is the pseudo first-order reaction, which the random chain scission reaction occurs preferentially. The calculated rate constants are shown in Table 1. The rate of the reaction at 80 °C is faster than that at 25 °C. The same

Table 1. Rate constants calculated at the initial stages of degradation (0-96 hrs) of NR films with and without catalysts 0.1 phr, at 36,000 lux

	k (hr^{-1})	
	25 °C	80 °C
NR	2.72E-06	5.44E-06
NR+ TiO_2	2.72E-06	5.44E-06
NR+ $\text{K}_2\text{S}_2\text{O}_8$	4.08E-06	5.44E-06

tendency is obtained for the pure NR films and the ones with $\text{K}_2\text{S}_2\text{O}_8$ 0.1 phr, which demonstrates that these degradation processes are pseudo first-order reactions with random chain scission. Normally, if there are not any catalysts or any conditions that can accelerate the reaction, the rate of reaction depends on the temperature of the reaction. At 25 °C, the NR films with $\text{K}_2\text{S}_2\text{O}_8$ 0.1 phr have a faster rate of reaction than the other two which have the same rate. As stated before, this is probably because $\text{K}_2\text{S}_2\text{O}_8$ can help promote oxidation on the NR films' surface. The rates of the reaction at 80 °C are all the same because at this high temperature, $\text{K}_2\text{S}_2\text{O}_8$ can decompose (it decomposes completely at 100 °C) so that only light and temperature mainly have an effect on the degradation of the NR films.

CONCLUSION

The photo-degradation of NR films was obtained by exposing the NR films with and without catalysts, TiO_2 , and $\text{K}_2\text{S}_2\text{O}_8$, to light at 7,000 and 36,000 lux, and at 25 °C and 80 °C. The results show that types of catalysts do not have significant effects on the photo-degradation process of NR films. Higher concentrations of catalysts do not help increase Mw reduction of NR films or provide faster rates of degradation. But higher concentration of TiO_2 decreases Mw reduction of NR films, because it can prevent the penetration of the light through the films. High temperature makes the NR films degrade more rapidly. More light density also provides faster photo-degradation rates. The calculation of double bonds in NR films from the information of the GPC distribution curves gives the same tendency of the double bonds reduction as the result obtained from the FTIR technique. From using the first-order rate equation for random scission, the linear plots of the photo-degradation of NR films suggest that the degradation processes in this work are first-order reactions with random chain scission.

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NOMENCLATURE

- B_t : number of broken double bonds at time t
- D_{ideal} : number of double bonds in the ideal natural rubber
- D_t : number of double bonds in natural rubber at time t
- k : pseudo first-order rate constant [hr^{-1}]
- M_0 : molecular weight of an isoprene unit

M_w : weight-average molecular weight [g/mole]
 M_{w_0} : weight-average of natural rubber at $t=0$
 $M_{w_{x,t}}$: weight-average molecular weight of natural rubber in each fraction at time t [g/mole]
 n : number of molecules of natural rubber
 $n_{total,t}$: total number of molecules of natural rubber at time t
 t : GPC elution time (min) or degradation time [hr]
 W_t : weight of natural rubber [g]
 $W_{t_{NR}}$: weight of natural rubber [g]
 $W_{x,t}$: weight of natural rubber in each fraction at time t [g]
 x : weight fraction of natural rubber

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