

Controlled Degradation of Cured Natural Rubber by Encapsulated Benzophenone as a Photosensitizer

Sa-ad Riyajan,¹ Jitladda Tangpakdee Sakdapipanich,^{1,2} Yasuyuki Tanaka^{1,2}

¹Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

²Institute of Science and Technology for Research and Development, Mahidol University, Salaya Campus, Nakornprathom 73170, Thailand

Received 29 May 2002; accepted 13 January 2003

ABSTRACT: The photodegradation of raw natural rubber and natural rubber compound film were studied using an artificial solar energy simulator. The properties of degraded rubber sheets containing benzophenone (BP) were determined by solution viscosity, ¹H-NMR, and FTIR analyses. In the case of rubber compounds containing BP, the changes of tensile strength and crosslinking density were determined. It was found that BP could amply accelerate the photodegradation of rubber. To control the release rate of BP, it was necessary to encapsulate BP with urea–formaldehyde as a matrix. The encapsulated BP or capsule was formed by an interfacial polycondensation reaction between formalde-

hyde and urea. The kinetic of release rate of BP from urea–formaldehyde capsule was markedly observed within 15 days of release time; after that the rate of BP released from urea–formaldehyde microcapsule was very slow. At the same concentration of BP, the degradation rate of rubber compound by adding BP directly was faster than that of the rubber containing encapsulated BP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 297–305, 2003

Key words: encapsulation; photosensitizer; photodegradation; natural rubber; cured natural rubber

INTRODUCTION

Natural rubber (NR) vulcanizates show high tensile strength over a wide range of hardness, which is attributed to the crystallization of polymer chains at high strain. Furthermore, natural rubber shows high tear resistance, high resilience, high abrasion resistance and low compression properties. Natural rubber is often used in many applications requiring low heat build up.¹ Cured natural rubber products are manufactured in a way to strengthen the rubber properties. Some examples of these products are gloves, condoms, and balloons. These are disposable and generate a large amount of cured natural rubber waste products, which are highly resistant to environmental degradation. Disposal of these wastes from homes, offices, hospitals, and factories has been a major problem in big cities. There are several possible processes for the disposal of solid wastes, such as incineration, pyrolysis, composting, biodegradation, and recovery of the base materials.^{2–7} A major disadvantage is that incomplete incineration can produce carcinogens such

as dioxins. Another possibility may be to considerably decrease the stability or aging properties, in a controlled manner, of such cured natural rubber products. If the polymer chains are photochemically decomposable, the physical properties will degrade and the product will become brittle and finally decompose into small pieces by natural erosion, rain, and wind. They eventually can form a powder and pass into the soil, which then is attacked by microorganisms, and reenter the biocycle.⁸

A photosensitizer is a compound that can be excited by light and transfer the excitation energy to polymer molecules or to oxygen molecules forming singlet oxygen.^{2,9} The photosensitizing process can be applied to controlled degradation of cured natural rubber products. If UV-absorbing groups are added into the polymer, it is expected that the rate of the degradation process will increase. It is well known that photosensitization by carbonyl, dicarbonyl, quinone, and diazo groups can promote the degradation of polymer by UV light.² The lifetime of polymers exposed to sunlight can be shortened by adjusting the ratio of sensitizer to polymer. This approach has the advantage of being directly applicable to commercial polymers without impairing the normal production processes. On the other hand, the low molecular weight sensitizer easily leaches out by diffusion and this disadvantage may restrict its application.

At present, a solution to the ever-increasing problems of waste disposal, pollution, and littering by

Correspondence to: J. T. Sakdapipanich (scjtp@mahidol.ac.th).

Contract grant sponsor: National Science and Technology Development Agency; contract grant number: CO-B-11-33-14-217M.

Contract grant sponsor: Thailand Research Fund; contract grant number: PHD/0165/2544.

TABLE I
Compounding Formulation for PV Latex

Ingredient	Formulation (phr)
60% NR	100
10% KOH	0.25
20% Potassium laurate	0.26
50% Sulfur	1.0
40% ZDEC	0.4
50% ZnO	0.5

waste materials is urgently being sought. The development of methods for making polymers that are photodegradable, to form harmless and biologically useful chemical compounds, is of great interest. This is the motivation to create possible ways to solve the waste problem. Hence controlled degradation of cured natural rubber by using photosensitizers as microencapsulated material is the main objective of this work.

EXPERIMENTAL

Materials

Benzophenone (BP), formaldehyde, methanol, and toluol-4-sulfonic acid were all of analytical grade and used as received without purification. Zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC), and sulfur (S) were of commercial grade. Concentrated high-ammonia rubber (HANR) latex used was kindly supplied by Thai Rubber Latex Co. Ltd.

Prevulcanization of natural rubber latex

In the preparation of sulfur prevulcanized (PV) NR latex, the conventional formulation shown in Table I was used. Then, the vulcanizing ingredients S, ZDEC, and ZnO in the form of a 50%, 10%, 50% dispersion, respectively, were added into the HANR latex at 60°C under continuous stirring for 5 h.

Preparation of microcapsule

Prepolymer

Urea was added with agitation to a 37% formaldehyde solution, buffered with potassium hydroxide at pH 8 in a 500-mL three-neck flask equipped with stirrer and reflux condenser. The mole ratio of urea and aldehyde used for the prepared capsules was 1 : 1. The urea was dissolved in formaldehyde solution and maintained at a temperature between 25 and 30°C. The reaction mixture was heated, using a water bath, at about 65–70°C to reflux with vigorous agitation for about 1 h. Then, the reaction was cooled to room temperature. This solution is called the prepolymer.

Microcapsule

BP (20 g) was dissolved in 20 mL of toluene. Rapid stirring of BP solution in 40 mL of 1% w/v sodium dodecyl sulfate (SDS) aqueous solution was carried out to make emulsion by using a homogenizer at 7000 rpm. Capsules were prepared by gradually adding 60 mL of prepolymer into the above emulsion, followed by adjusting pH to 2, by toluol-4-sulfonic acid. Then, the mixture was stirred vigorously by a homogenizer at 7000 rpm for 20 min. The mixture was kept in the dark, without stirring, for 24 h at room temperature. Then, the pH of the solution was adjusted to 7 by 10% w/v KOH solution. The resulting capsules were filtered using vacuum suction and then dried under vacuum.

Determination of BP concentration

First, the stock suspension of BP–urea–formaldehyde capsules, with an accurate weight of 1.0000 g, in chloroform was prepared in a 100-mL volumetric flask. The concentration of released BP from the capsule was determined from this suspension. The amount of released BP fraction in chloroform was determined by sampling the solution at several intervals, that is, 10 min, 1–60 days, until a constant amount of released BP was obtained. Aliquots of each solution (5 mL) were obtained and diluted with chloroform in a 10-mL volumetric flask. Then, 2 mL of this freshly prepared sample was subjected to analysis by a UV-visible spectrophotometer at $\lambda = 336$ nm.

Preparation of rubber specimens

The HANR latex was the starting material to prepare the HANR sheet. In this study, the raw rubber and cured rubber were used to study the photodegradation under accelerating condition. Both the controlled raw rubber and vulcanized rubber sheets were prepared by pouring the HANR latex or the prevulcanized HANR latex into a glass plate (150 × 150 × 0.45 mm). The thickness of the sheet was controlled by determining the dry rubber content of HANR latex or prevulcanized HANR latex before drying. All samples were dried at room temperature, except for the prevulcanized sheet, which was further subjected to post-curing at 60°C for 2 h.

The HANR latex and PV latex were mixed with BP at concentrations of 0.10, 0.25, 0.50, 1.00, 2.50, and 5.00% w/w. In the case of encapsulated or unencapsulated BP, it was added to the HANR compound at concentrations of 0.10, 0.25, 0.50, and 1.00% w/w. Before the benzophenone was added to the latex, in a 1% SDS aqueous solution, it was prepared in a ball mill to reduce agglomerates. In the case of encapsulated BP, it was dispersed in 1.0% SDS aqueous solution and then added to the latex under continuous

stirring. A solid thin film was obtained by drying the rubber/photosensitizer mixtures at room temperature. Only the prevulcanized sheet was further subjected to postcuring at 60°C for 2 h. The sample was kept in the dark before being subjected to irradiation.

UV exposure

Solid rubber sheets with approximate thickness of 0.40–0.45 mm containing BP were exposed in a Q-UV Accelerated Weathering Tester (the Q. Panel Company, Cleveland, OH), at 160 W at 60°C.

Particle size measurement

The particle size of capsules was determined by using a laser particle size analyzer (Malvern Instruments, UK). At first distilled water was added into the chamber and then flushed into the cell with continuous stirring, for use as a background measurement. Then, the capsule sample was held in the sample chamber until the observation was in the range of 10–30%.

Viscosity of degraded raw rubber

The molecular weight of degraded raw rubber was measured by the dilution solution viscometric method. The intrinsic viscosity of 0.05 g/dL of rubber in toluene solution was determined at $30 \pm 0.01^\circ\text{C}$ using a Ubbelohde viscometer. The viscosity-average molecular weight (\overline{M}_v) was calculated from the Mark-Houwink equation¹⁰:

$$[\eta] = 1.90 \times 10^{-4} \overline{M}_v^{0.745}$$

Determination of crosslink density

The crosslink density of natural rubber sheet was determined by the swelling method. The rubber sheet of known weight, approximately 0.3 g, was immersed in toluene at room temperature for 1 week. The weight of the swollen rubber was determined after blotting the wet surface of the swollen fraction with filter paper. The swelling ratio (Q) was calculated as follows:

$$Q = (W_2 - W_1) / W_1$$

where W_1 is the initial weight of rubber (g) and W_2 is the swollen rubber weight at equilibrium (g).

Tensile properties determination

A 1-kN load cell and appropriate grips were set in an Instron Tensile Tester Model 4301. The dumbbell-shape specimens were stamped out from molded sheet using a sharp die. After calibrating the machine,

the sample was placed in the grips of the testing machine, with care taken to align the specimen symmetrically to distribute the tension uniformly over the cross section. The machine crosshead speed was 500 mm/min and the distance in the extensometer was noted continuously. At least three specimens were used for a measurement. Tensile strength and elongation at break were determined.

RESULTS AND DISCUSSION

Preparation of microcapsule

Urea-formaldehyde (UF) was prepared by gradually adding the prepolymer into the emulsion mixture of toluene, BP, and 1.0% SDS aqueous solution after the pH of the solution was adjusted to 2 by toluol-4-sulfonic acid. The emulsion was stirred vigorously by a homogenizer (Societa Perazzioni Miland Italia). If the reaction was conducted in acid solution, a series of linear molecules from 200 to 500 g/mol were expected to form the product, finally becoming gel as a result of crosslinking by toluol-4-sulfonic acid catalyst.

The UF resin, obtained by interfacial polymerization, was characterized by FTIR analysis. Figure 1 shows that the absorption frequencies are very broad and overlapped, which might be attributable to the presence of byproducts in the resin, such as water and excess formaldehyde, which allow hydrogen bonding with the reactive functional groups such as $-\text{CH}_2\text{OH}$, $-\text{NH}_2$, and $-\text{NH}-$. In the NH stretching region of $\text{H}_3\text{C}-\text{NH}-\text{CO}-\text{NH}_2$, three absorption bands around 3432, 3324, and 3230 cm^{-1} may be assigned by analogy to the NH_2 group of the asymmetric and symmetric stretching mode of the NH group and the band at 3324 cm^{-1} to the secondary NH group. In the region between 1540 and 1700 cm^{-1} , there are mainly three absorption bands at 1670–1685, 1611, and 1582 cm^{-1} in methyl urea and at 1656 and 1574 cm^{-1} for monomethylolurea methyl ether. A strong band between 3340 and 3350 cm^{-1} is normally observed for dimethylolurea dimethylether and methylene diurea. In dimethylolourea a strong absorption band at 3384 cm^{-1} and a weak band at 3185 cm^{-1} should be observed, attributed to the secondary amide NH group.

It has been reported that the structure of UF is dependent on the composition ratio between urea and formaldehyde. It was found that the methylol and ether contents increase as the feed ratio increases. The maximum contents of ether methylol and ether was found in the F/U prepolymer at a ratio of 1.85.^{11–13} Figure 2 shows the particle size distribution of the prepared UF microcapsules. The average particle size of UF microcapsules was about 15 μm . It is known that the particle sizes of vulcanizing ingredients in rubber compound are about 50 μm . Because the particle sizes of the prepared BP-UF beads are smaller

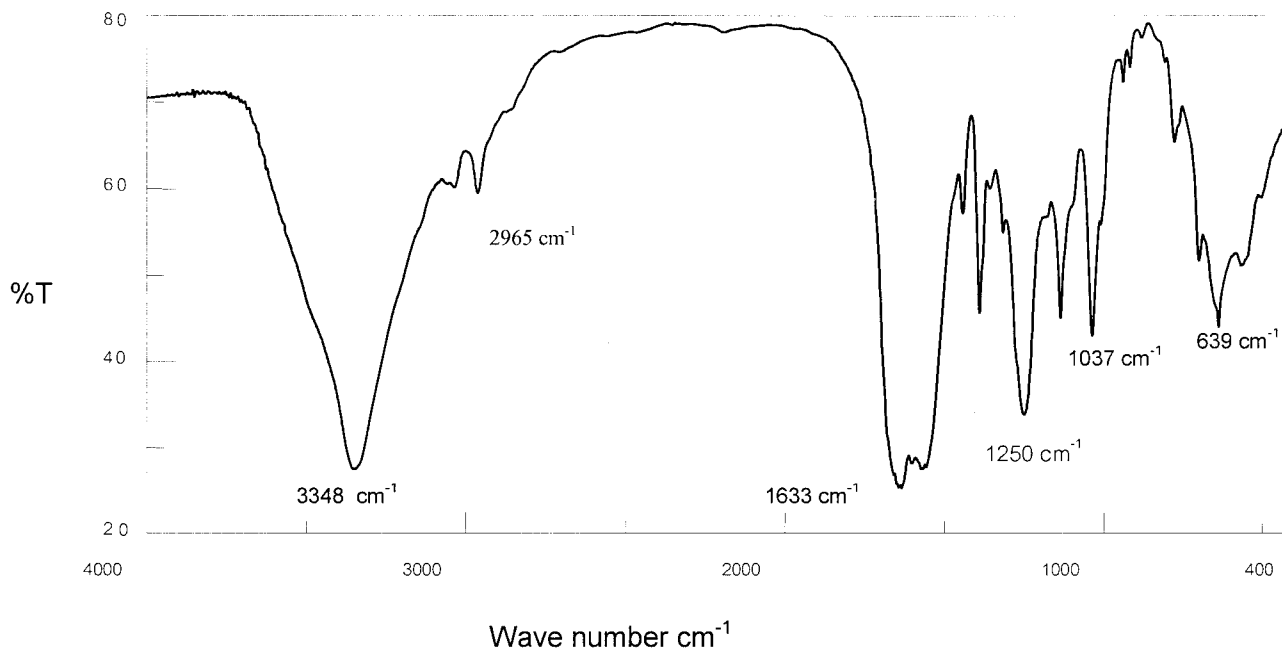


Figure 1 FTIR spectrum of urea-formaldehyde resin.

than 50 μm , the inclusion of BP-UF beads in the rubber vulcanizates should not affect the properties.

Release of BP in the UF capsule

To study the effect of BP concentration on the release rate of BP from the capsule in chloroform used a medium, 40% w/w of BP loading content in the capsule was used. Figure 3 shows the release rate of BP from UF microcapsules. It is clear that the release rate of BP from UF microcapsules was proportional to the release time. The release rate of BP from UF microcapsules was high during the first 15 days. Subsequently, the release rate of BP released from UF microcapsules was slow. Release of BP from UF microcapsules was found to be almost complete within about 2 months.

This result indicates that BP was entrapped in the polymer matrix. This could be explained as that the amount of BP released is dependent on its hydrophobicity as well as its solubility in chloroform. Thus, the desired amount of released BP can be controlled by manipulation of its concentration in the matrix.

Effect of photosensitizer on photodegradation of raw natural rubber

The photosensitizer used to initiate the photodegradation of HANR was benzophenone (BP). This compound can interact with light and generate singlet oxygen ($^1\text{O}_2$) upon changing to a lower energy state. The characteristic range of wavelength absorbed by photosensitizer was first determined. It was found that BP in chloroform solution absorbs UV light of

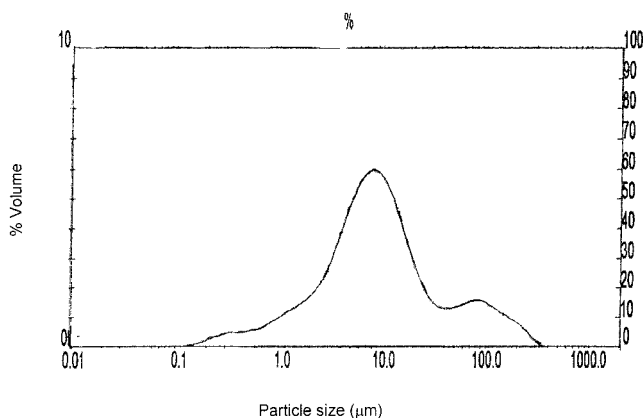


Figure 2 Particle size distribution of UF microcapsule containing BP.

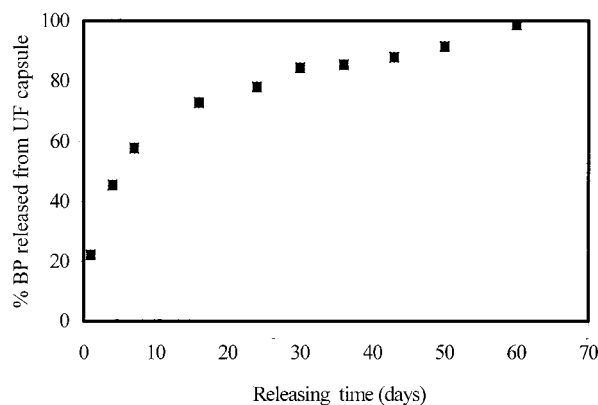


Figure 3 Relationship between release rate of BP and release time from 40% of BP UF microcapsules.

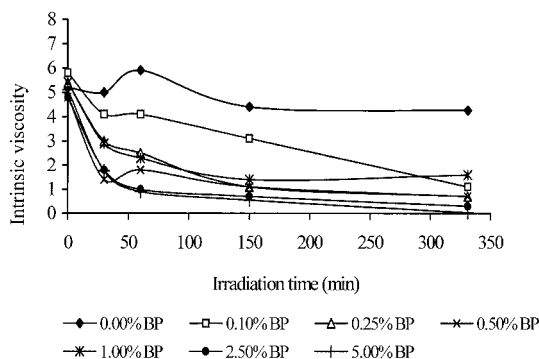


Figure 4 Changes of intrinsic viscosity as a function of irradiation time for various amounts of BP added HANR under accelerating condition.

wavelength between 305 and 360 nm, with the maximum absorptivity at $\lambda = 336$ nm.² The extent of photodegradation would be expected to depend on chromophore and UV irradiation time. The change in intrinsic viscosity of raw HANR with BP under accelerating conditions is shown in Figure 4. During the initial period of photodegradation, the intrinsic viscosity $[\eta]$, of BP-added HANR, was dramatically decreased after irradiation under accelerating conditions within 60 min. In particular, in the case of 5.00% w/w BP, the $[\eta]$ value was reduced to 0.036, which corresponds to $M_v = 9 \times 10^3$. However, after 60 min of irradiation, there was no significant decrease in the $[\eta]$ for any concentration of BP. In the case of 0.25, 0.50, and 1.00% w/w BP-added HANR, the $[\eta]$ value was

reduced about twice the original value within 60 min of irradiation time. The intrinsic viscosity and the number of repeating units of the rubber containing 1% w/w BP were decreased by about 5 and 10 times compared to those of the original, after 300 min of irradiation time. The control sample showed an insignificant change in the $[\eta]$ value.

This indicates that the rate of photodegradation of HANR depended on the irradiation time and amount of photosensitizer used. The rate of photodegradation can be expressed by the photolysis rate of a given chromophoric group.

Structural characterization of degraded raw rubber by photodegradation

FTIR analysis was used to characterize the structure of degraded raw rubber. The main absorption bands of C=C stretching and *cis* C=C deformation were observed at wavenumbers ($\bar{\nu}$) 1660 and 835 cm^{-1} , respectively, in all spectra, as shown in Figure 5. According to photodegradation, the new absorption band at $\bar{\nu}$ 1710 cm^{-1} and a broad band around $\bar{\nu}$ 3500 cm^{-1} were clearly observed. The former band is attributed to the carbonyl group of the degraded rubber molecule, whereas the latter is attributed to the hydroxyl group.¹⁴

The carbonyl index, representing the progress of oxidation, could be estimated from the ratio of transmission peak at carbonyl group $\bar{\nu}$ 1710 cm^{-1} and methyl group 1378 cm^{-1} .¹⁵ Table II shows the car-

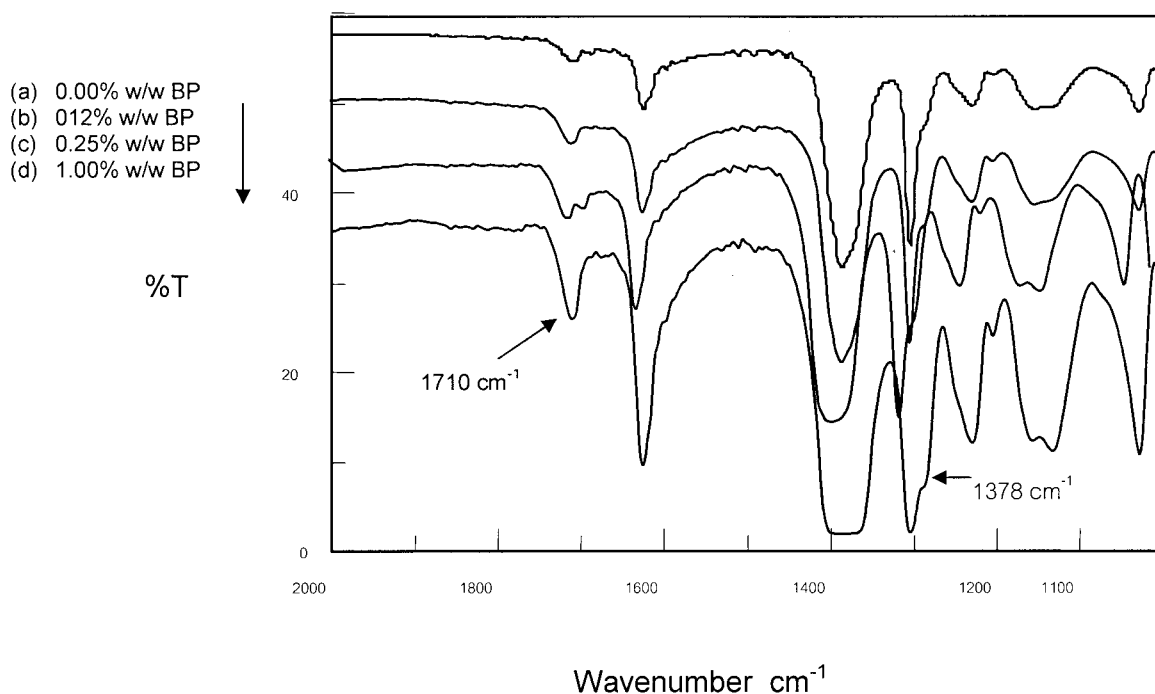


Figure 5 FTIR spectra of photodegraded HANR: (a) in the presence of 0.12% w/w; (b) in the presence of 0.25% w/w; (c) in the presence of 1.00% w/w; and (d) in the absence of BP, after exposure to UV light for 40 min (thickness 0.40 ± 0.05 mm).

TABLE II
Carbonyl Index of Photodegraded HANR in the Presence of Various Amounts of BP Under Accelerating Condition for 40 min, from FTIR Data (Trial 1)

Concentration of BP (% w/w)	Carbonyl index
0.00	0.44
0.10	0.60
0.25	0.88
1.00	0.92

bonyl index of the photodegraded HANR in the presence of various amounts of added BP, under accelerating conditions for 40 min. It is clear that the carbonyl index increased as the concentration of BP increased.

The ratio of this new signal to the methine proton of polyisoprene ($=CH$) at 5.1 ppm for the HANR sample mixed with various amounts of BP, under accelerating conditions for 40 min, is presented in Table III. In addition to the main signals of *cis*-1,4-polyisoprene, as observed in the 1H -NMR spectrum of the control sample, a new signal at 9.36 ppm was also clearly detected, as shown in Figure 6. This new signal is attributed to the aldehydic proton at the end of degraded rubber molecule. It is obvious that this ratio increases as the amount of added BP increases. This indicates the efficient photodegradation of rubber in the presence of a higher amount of added BP.

Kinetic determination on photodegradation of HANR vulcanizates

The encapsulated BP in UF was added to the NR latex compound, at concentrations of 0.10, 0.25, 0.50, and 1.00% w/w. The latex was then cast onto glass plates and left to obtain a dried thin film with thickness of 0.40 ± 0.05 mm. The other samples were prepared by adding BP directly to the NR latex compound. The prepared films were subjected to UV irradiation under accelerated conditions. The extent of deterioration of cured samples was determined by tensile measurement and swelling analysis.

TABLE III
Ratio of Aldehydic Proton ($\delta = 9.36$) Compared to Methine Proton [$\delta = 5.14$ from 1H -NMR Spectra of Degraded HANR for 40-min Sample Under Accelerating Condition (Trial 2)]

Concentration of BP (% w/w)	Intensity ratio of ($-COH/ =CH-$)
0.00	0.77
0.05	0.61
0.12	0.59
0.25	1.44
0.50	1.43
1.00	5.89

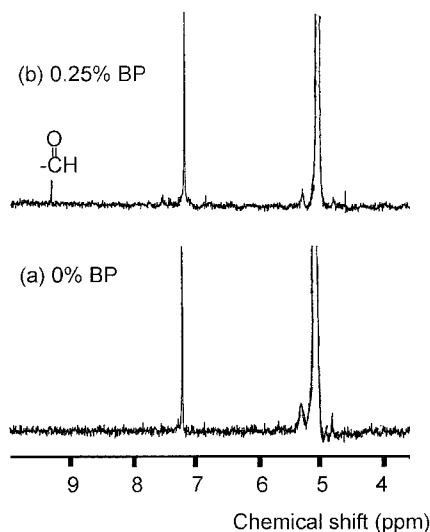


Figure 6 1H -NMR spectra of rubber in the presence of (a) 0% BP and (b) 0.25% BP, after UV irradiation under accelerating conditions for 40 min.

The film samples were exposed to UV irradiation for 0, 1, 2, 5, 7, and 12 h. Then, tensile strength and elongation at break of the samples prepared from both systems were determined. Figure 7(a) and (b) show the reduction in tensile strength of the cured HANR in the presence of unencapsulated BP and encapsulated BP, at concentrations of 0.05–0.25% w/w and 0.50–1.00% w/w, respectively, in the course of UV irradiation. The decrease in tensile properties was very fast, if the amount of added BP was higher than 0.50% w/w. It can be seen from Figure 7 that the tensile strengths of HANR vulcanizates show significant differences between samples that contained unencapsulated and encapsulated BP. As expected, the photodegradation of HANR vulcanizates containing unencapsulated BP was greater than that in the case of encapsulated BP. There was an insignificant change in the tensile properties for the control sample up to 18 h. However, it became one-half and one-fourth of the initial value, after irradiation for 24 and 36 h, respectively. The tensile strength, in the case of cured HANR filled with 1.00% w/w unencapsulated BP, decreased from 24.4 to 7.6 MPa or 32% within 5 h of irradiation time. It was observed that the rubber specimens in the presence of unencapsulated BP at 0.12 and 0.25% w/w, after UV exposure longer than 24 h, became liquid rubber, so these samples could not be measured by the tensile test. The same results were observed in the case of 0.25% w/w encapsulated BP in the HANR sample.

The elongation at break of degraded samples is shown in Figure 8. At a concentration of 0.25% w/w BP, the HANR containing unencapsulated BP showed a dramatic decrease in the elongation at break from 1080 to 250%, or one-fourth of the initial value within

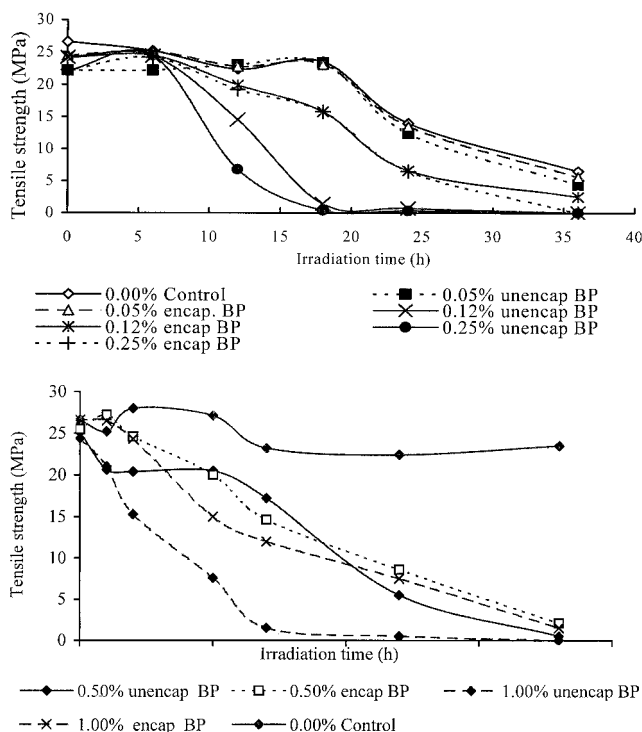


Figure 7 Changes in tensile strength of photodegraded cured HANR in the presence of unencapsulated and encapsulated BP at concentration (a) 0.00–0.25% w/w and (b) 0.50–1.00% w/w under accelerating condition.

24 h of irradiation time. If the encapsulated BP at the same concentration was used instead, it was found that the elongation at break decreased from 1200 to 900%, maintaining 75% of the initial value after the same period of irradiation. This implies good efficiency of controlled release of BP from the capsule.

It can be seen from Table IV that, at concentrations of BP higher than 0.50% w/w, the decrease in tensile strength was rapid. It took only 12 h of irradiation time to deteriorate the tensile properties of rubber vulcanizates to inapplicable values.

The swelling ratio was also determined to evaluate the extent of deterioration of photodegraded HANR vulcanizates filled with unencapsulated BP and encapsulated BP. It is clear from Figure 9 that the swelling ratio of the original cured HANR was about 3.8, indicating a highly crosslinked structure. At longer exposure times to UV, the swelling ratio increased significantly (to about 15–20), depending on the amount of added BP. By comparing the addition of unencapsulated BP and encapsulated BP, it was observed that the swelling ratio of the former sample was higher than that of the latter, especially at higher BP concentrations of 0.50 and 1.00% w/w.

It is known that sulfur, like oxygen, can activate the carbon atom by alkylperoxyl radical. However, hydroperoxides cannot be formed in the rubber molecule because the sulfidic group has the ability to destroy

hydroperoxides, initially in a stoichiometric reaction but subsequently in a catalytic process attributed to the formation of sulfur acids (see Fig. 10). This anti-oxidation process is the reason for the auto-retard oxidation observed in the latter stage of the oxidation of sulfur vulcanizates.^{16,17}

According to Cuneen et al.,¹⁶ two crosslinks are broken for every main chain scission event. It is important to note that crosslinking and scission are consequent to attack by radicals or hydroperoxides involved in the main-chain scission. Consequently, if oxidation of the primary main chain is prevented, crosslinking and scission should also occur. The proposed mechanism of photodegradation of cured rubber is shown in Figure 10.

Comparative study of photodegradation of cured HANR, in the presence of unencapsulated BP or encapsulated BP, with a control sample

The aim of this part of the investigation was to compare the efficiency of photodegradation between the cured HANR in the absence of BP and the samples containing unencapsulated BP or encapsulated BP. This estimation was based on defining the efficiency of photodegradation data, as the irradiation time (in hour unit) needed to reduce tensile strength of the cured rubber to half the initial value: it would be used to

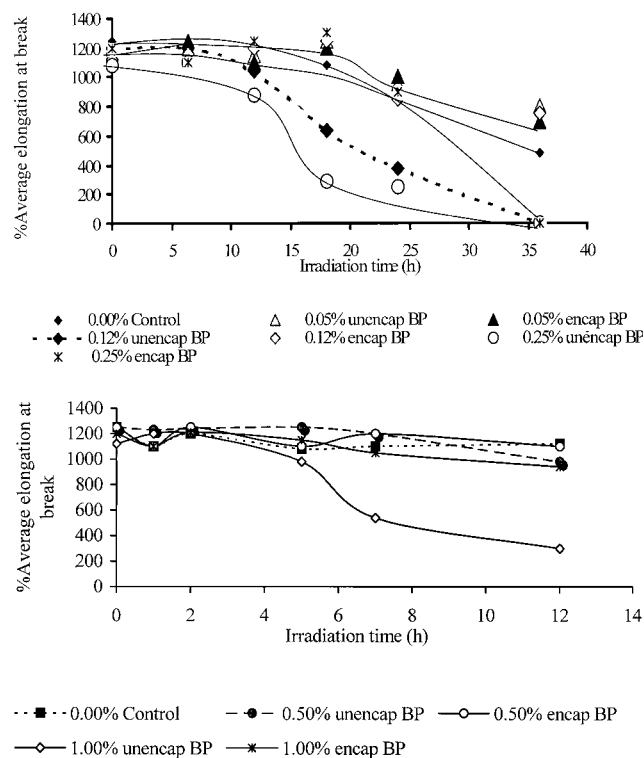


Figure 8 Changes in elongation at break of photodegraded cured HANR in the presence of unencapsulated BP and encapsulated BP at concentration (a) 0.00–0.25% w/w and (b) 0.50–1.00% w/w under accelerating condition.

TABLE IV
Efficiency of Photodegraded HANR Vulcanizates Filled with Unencapsulated BP or Encapsulated BP Under Accelerating Condition

Amount of BP (% w/w)	Efficiency of photodegradation (h) ^a		Efficiency (encap BP)/ Efficiency (unencap BP)
	Unencapsulated	Encapsulated	
0.00	34	34	1.0
0.05	29	31	1.1
0.12	20	27	1.4
0.25	18	24	1.3
0.50	14	17	1.2
1.00	8	12	1.5

^a Efficiency of photodegradation means the irradiation time (in h unit) needed to reduce tensile strength of the cured rubber to one-half of the initial value.

compare the efficiency of photodegradation for cured HANR under accelerated conditions. It is clear that the efficiency of photodegradation of HANR vulcanizate in the presence of unencapsulated BP from 0.05 to 1.00% wt was 1 to 4 times that of the control sample under the accelerated test. In the case of the addition of encapsulated BP from 0.05 to 1.00 wt %, it was about 1 to 3 times that of the control sample. At high concentration of BP, the photodegradation of cured rubber containing BP was faster than that of the control sample with no BP addition. The photodegradation of cured NR in the presence of 1.00% w/w unencapsulated or encapsulated BP was about 4 and 3 times that of the control sample, respec-

tively. At low BP concentration (0.05% w/w), the efficiency of photodegradation was 1.1–1.2 times that of the control sample. It became higher, ranging from 1.2 to 2.2 times, at BP concentrations in the range of 0.12–0.50% w/w. Hereafter, the irradiation time needed to reduce the tensile strength of cured rubber to half the initial value can be used to compare the efficiency of photodegradation. Table IV shows the efficiency of photodegradation of cured HANR under accelerated conditions. By comparing the efficiency of photodegradation values of the degraded rubber vulcanizates, it was found that direct addition of BP into the cured rubber gave faster photodegradation than in the case of encapsulated BP. However, this was true only if the concentration of BP used was greater than 0.25% w/w. Below this concentration, there was little difference in the efficiency of photodegradation values. For instance, at concentrations of 0.50 and 1.00% w/w of unencapsulated BP, the efficiency was 14 and 8 h, respectively. In the case of the encapsulated system, it was found to be 17 and 12 h, respectively. Thus, the photodegradation of NR vulcanizates in the presence of an encapsulated one by photosensitizer was slower than that in the case of an unencapsulated one by a factor of 1.2–1.5.

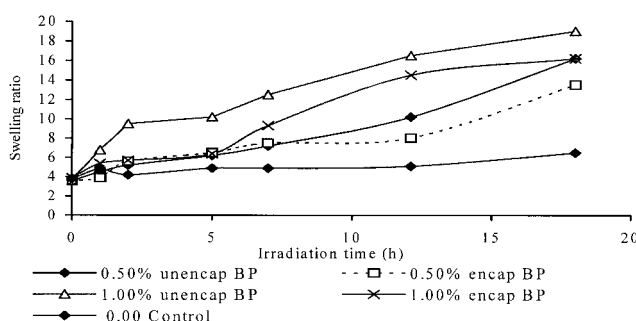
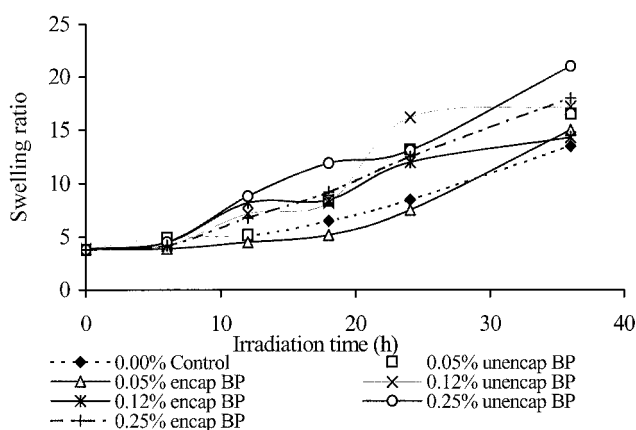


Figure 9 Changes in swelling ratio of photodegraded cured HANR in the presence of unencapsulated BP and encapsulated BP at concentration (a) 0.00–0.25% w/w and (b) 0.50–1.00% w/w under accelerating condition.

CONCLUSIONS

UF capsules can be used as a matrix for encapsulating a photosensitizer such as benzophenone (BP). The release rate of BP from the capsule depended on the loading of BP entrapped in the UF capsule and the exposure time to UV light. The capsule could retard the activity of unencapsulated BP for photodegradation of HANR vulcanizates, compared to that of the directly added encapsulated BP, by a factor of 1–2. The efficiency of photodegradation of HANR vulcanizates in the presence of unencapsulated BP or encapsulated BP was 1 to 4 times that of the HANR in the absence of BP sample under accelerated conditions. Normally the degradation of the cured NR needs considerable time, and it might become a waste problem. If the BP encapsulated UF capsule was added into the cured

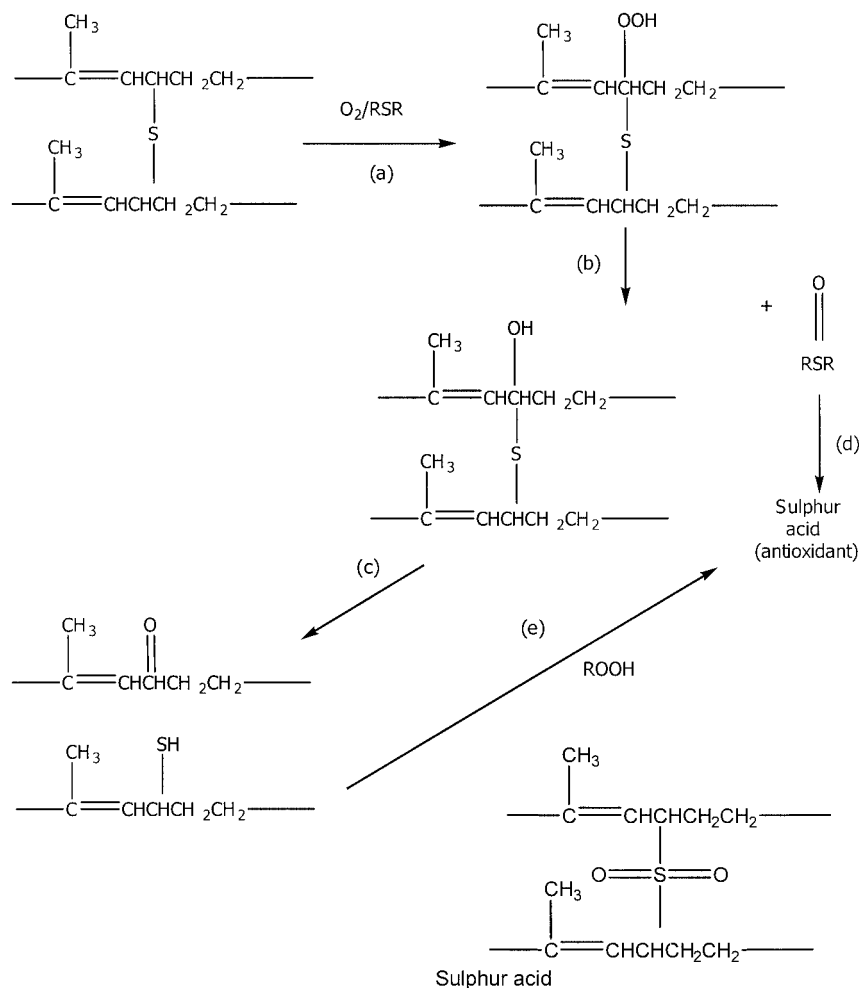


Figure 10 Proposed mechanism of degradation of cured NR.

NR product, the photodegradation could be accelerated. Therefore, it can be used to control the degradation of cured NR by UV light after consumption. In other words, the applicability of an efficient photosensitizer system will also provide an alternative method of degrading rubber.

This study was supported by a Local Graduate Scholarship of the National Science and Technology Development Agency (CO-B-11-33-14-217M) and from the Thailand Research Fund (PHD/0165/2544).

References

1. Roberts, A. D. *Natural Rubber Science and Technology*, 2nd ed. Oxford University Press: New York, 1988; pp. 621–673.
2. Rabek, R. B. *Photodegradation, Photo-oxidation, and Photostabilization of Polymers: Principles and Applications*, 1st ed.; Wiley: London, 1975; pp. 276–326.
3. Abdul Aziz, bin S. A. *Natural Rubber Current Development in Product Manufacture and Applications*; Rubber Research Institute of Malaysia: Kuala Lumpur, 1993; pp. 101–110.
4. Gerald, D. A.; Pallatherim, S. *Emerging Technologies in Plastics Recycling*, 1st ed.; American Chemical Society: Washington, DC, 1992; pp. 16–21; Singh, R. P.; Desai, S. M.; Solanky, S. S.; Thanki, P. N. *J Appl Polym Sci* 2000, 75, 1103.
5. Yamashita, S.; Kato, S.; Kawabata, N.; Okamoto, T. *J Appl Polym Sci* 1978, 22, 353.
6. Benko, D. A. (The Goodyear Tire and Rubber Company). U.S. Pat. 895,884, 1990.
7. Allen, N. S.; Edge, M. *Current Trends Photochemistry*, 2nd ed.; Ellis & Horwood: New York, 1995; pp. 1–20.
8. Challa, G. *Polymer Chemistry: An Introduction*, 3rd ed.; Ellis & Horwood: New York, 1993; pp. 41–64.
9. Rodrigues, J. F. *Polym Bull* 1996, 36, 347.
10. Stanley, R. S. *Sourcebook of Advanced Polymer Laboratory Preparations*, 1st ed.; Academic Press: London; 1998; pp. 126–127.
11. Masataka, K.; Viasuhiro. U.S. Pat. 3,981,821 (1976).
12. Sivananda, S. J. *J Appl Polym Sci* 1988, 35, 1573.
13. Luzzi, A. L. *J Pharm Sci* 1970, 59, 1367.
14. Eng, A. H.; Tanaka, Y.; Gan, S. N. *J Nat Rubber Res* 1992, 7, 152.
15. Nor, H. M.; Ebdon, J. R. *Polymer* 2000, 41, 2359.
16. Norman, G. G. S. *Polymer Degradation and Stabilization*, 1st ed.; Cambridge University Press: Cambridge, UK, 1985; pp. 68–118.
17. Willis, J.; Frohlich, H.; Mott, N. F.; Edward, B. *The Physics of Rubber Elasticity*, 2nd ed. Oxford University Press: London, 1958; pp. 123–180.