Malaysian Journal of Analytical Sciences, Vol 22 No 6 (2018): 1023 - 1030
DOI: https://doi.org/10.17576/mjas-2018-2206-11

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society

ISSN
1394 - 2506

DIIMIDE REDUCTION OF LIQUID NATURAL RUBBER IN HYDRAZINE HYDRATE/HYDROGEN PEROXIDE SYSTEM: A SIDE REACTION STUDY

(Penurunan Diimida Getah Asli Cecair dalam Sistem Hidrazin Hidrat/Hidrogen Peroksida: Kajian Tindak Balas Sampingan)

Muhammad Jefri Mohd Yusof[1], Nur Aidasyakirah Mohd Tahir[1], Fazira Firdaus[1], Siti Fairus M. Yusoff[1,2]*

[1]School of Chemical Sciences and Food Technology, Faculty of Science and Technology
[2]Polymer Research Centre, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: sitifairus@ukm.edu.my*

Received: 27 July 2017; Accepted: 28 April 2018

Abstract

Hydrogenation of liquid natural rubber (LNR) has been successfully accomplished via diimide reduction using hydrazine hydrate/hydrogen peroxide (HH/H_2O_2) system. Each parameter in the system was optimized to obtain maximum hydrogenation degree such as the mass of boric acid, mole ratio of HH: H_2O_2, reaction time and reaction temperature. As a result, the highest degree of hydrogenation was achieved at 91.2% using a molar ratio HH: H_2O_2 of 2:3, in the presence of boric acid as a promoter at 60 °C for 8 hours. In this research, we report on possible side reactions that led to lowering the hydrogenated rubber product. Reactivity of diimide species as well as decomposition of hydrogen peroxide were postulated based on literature reviews to be one of the factors hindering hydrogenation of LNR. The presence of side reactions such as degradation, cyclization, and crosslinking had been confirmed by gel permeation chromatography (GPC), ^{1}H nuclear magnetic resonance (^{1}H NMR), and swelling test, respectively.

Keywords: hydrogenation, liquid natural rubber, side reactions, hydrazine hydrate, hydrogen peroxide

Abstrak

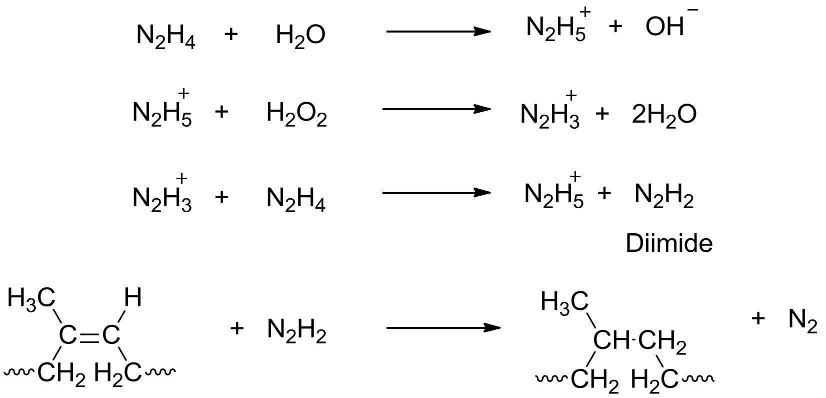
Penghidrogenan getah asli cecair (LNR) telah berjaya dijalankan menggunakan sistem hidrazin hidrat/hidrogen peroksida (HH/H_2O_2). Setiap parameter dalam sistem tersebut dioptimumkan bagi mendapatkan darjah penghidrogenan yang maksimum seperti jisim asid borik, nisbah mol HH: H_2O_2, masa dan suhu tindak balas. Hasilnya, peratus penghidrogenan sebanyak 91.2% diperolehi apabila menggunakan nisbah molar HH: H_2O_2 sebanyak 2:3, dalam kehadiran asid borik sebagai penggalak pada suhu 60 °C selama 8 jam. Dalam kajian ini, kami melaporkan tindak balas sampingan yang berkemungkinan berlaku yang menyebabkan pengurangan hasil getah terhidrogen. Berdasarkan kajian-kajian lepas, kereaktifan spesis diimida dan penguraian hidrogen peroksida dipercayai merupakan antara faktor yang merencatkan penghidrogenan LNR. Kehadiran tindak balas balas sampingan seperti degradasi, pengkitaran, dan taut silang telah dikenal pasti masing-masing melalui kromatografi penelapan gel (GPC), resonans magnetik nuklear proton, dan ujian bengkakan.

Kata kunci: penghidrogenan, getah asli cecair, tindak balas sampingan, hidrazin hidrat, hidrogen peroksida

Introduction

Hydrogenation is a method for chemical modification that reduces the degree of C=C unsaturation. Previously, many researchers focused on decomposition of *p*-TSH in toluene as diimide source for non-catalytic hydrogenation [2]. However, hydrazine hydrate/hydrogen peroxide (HH/H_2O_2) system was introduced by Wideman in 1984 as one

of the non-catalytic methods to hydrogenate unsaturated polymers [1]. This HH/H_2O_2 system was developed as an alternative for diimide supply due to its conventional preparation in aqueous medium and economical value with simple apparatus set up [3]. Simma et al. applied similar system on their hydrogenation of styrene-butadiene latex resulting in production of thermoplastic elastomer that was stable at high temperature and pressure [4].
Hydrogenation using diimide reduction involves reaction between HH with H_2O_2 to produce diimide species before it can be used to reduce the unsaturated units [5]. Scheme 1 shows the reaction mechanism for the formation of diimide species followed by its action on unsaturated unit reduction. Hydrazine in aqueous medium will dissociate into hydrazinium and hydroxyl ion. The hydrazinium ion then reacts with hydrogen peroxide to produce hydrazinylium ion, and water molecule. Subsequently, hydrazine and hydrazinylium will react to produce diiimide that are needed to hydrogenate the unsaturated units of LNR.



Scheme 1. Formation of diimide species and its action on unsaturated units [6]

Due to *in situ* nature of this reaction, several side reactions are prone to happen and affect the hydrogenation process as reported by past researches [3, 7]. Typical side reactions for non-catalytic hydrogenation would be chain-scissoring, cyclization, crosslinking, gel formation and *cis-trans* isomerism [8].

Wang et al. in 2013 studied on hydrogenation of styrene-butadiene rubber (SBR) using this system. In their work, they discovered that the hydrogenation percentage was decreased when larger particle size of SBR has been used. They suspected that larger particle size provided further penetration surface for the diimide species to inefficiently hydrogenate the double bond units [9]. Meanwhile, Simma et al. demonstrated that HH/H_2O_2 system would promote crosslinking that affected the yields of their hydrogenated acrylonitrile-butadiene rubber (NBR) as proven by gel fractioning of the products [4]. Han et al. also found out that their hydrogenated SBR were high in gel content (89.8% - 98.6%) prior to this reaction [10].

In this paper, we report on a number of side reactions that occurred throughout our hydrogenation of LNR using HH/H_2O_2 system. This information would be useful to explain variation of yield percentages of hydrogenated products as well as providing synthetic route to produce chemically and physically modified LNR. Based on our results, the products have been identified to contain gel, possess shorter chain, and bear cyclization group. These remarks are useful for applications development. Materials with gel content are used as lubricant (low gel content) or adhesive (high gel content) [11] as polymers with shorter polymeric chain can act as compatibilizer in polymer blends [12]. Meanwhile, cyclic polymers are widely synthesized in bio-related properties and applications [13].

Materials and Methods

Materials

Natural rubber from Rubber Research Institute of Malaysia (RRIM) has been used as starting material. Hydrazine hydrate 80% was purchased from R&M Chemicals. A 30% aqueous solution of hydrogen peroxide (90% purity) was obtained from Sigma Aldrich. Sodium dodecyl sulfate (98%) and boric acid (≥99.5%) were purchased from Systerm.

Diimide reduction of LNR

The emulsion of LNR (5 g), sodium dodecyl sulphate (0.00035 mol, 0.10 g) as a surfactant, few drops of silicone oil, and distilled water (50 mL) were added in the three-neck round-bottom flask. After stirring for 30 minutes, hydrazine hydrate was added and continued stirring for another 30 minutes at 60 °C while stirring. The solution of hydrogen peroxide and boric acid was prepared by dissolving 1.5 g of boric acid (0.024 mol) in 40 ml of hydrogen peroxide. Then, the mixture was added drop wise for 8 hours. The product obtained was coagulated in ethanol and dried in vacuum oven for at least 12 hours.

^{1}H-NMR characterization

NMR spectroscopy was used to examine the microstructure of the product. In addition, integration of signals from proton NMR (^{1}H-NMR) was used to estimate the percentage of conversion from LNR to HLNR. Peak areas of aliphatic region (a) and olefinic region (b) were used to calculate the percentage of hydrogenation using the formula in equation 2:

$$Percentage\ of\ hydrogenation, \% = \frac{a-5b}{a+3b} \quad (1)$$

Samples were dissolved in deuterated chloroform ($CDCl_3$) for measurements with NMR spectrometer (JNM-ECP 400 MHz).

Swelling Test

Swelling test was performed to determine the degree of crosslinking of the samples. It can be obtained by the change in weight using the following method. The samples with weight of 0.5-1.0 g (M_I) were weighed and immersed in 20 ml toluene for 2 hours at room temperature. Samples were removed and weighed (M_{II}). The percentage of weight change was calculated by the following formula in equation 2.

$$Change\ in\ weight, \% = \left(\frac{M_{II}}{M_I} - 1\right) \times\ 100 \quad (2)$$

GPC analysis

The Waters Model 1515/2414 gel permeation chromatograph has been used to study the average molecular weights (Mw) and polydispersity index (PDI) of LNR and HLNR. About 5 mg of the samples were dissolved in 5 mL tetrahydrofuran (THF) before scanning. The analysis was carried out using three Styragel HR columns. Measurements were made at column temperature of 40 °C using THF as eluent at a flow rate of 1 mL min^{-1}, and the samples were monitored by Breeze™ system.

Results and Discussion

The conversion percentages of hydrogenated products from this reaction ranged from 15.9% to 91.2%. Table 1 shows the degree of hydrogenation with respective parameters optimization. The differences in hydrogenation degree when the reaction parameters were manipulated could be explained by the occurrence of these following side reactions.

Table 1. Degree of hydrogenation with respective parameters optimization

Mole of Acid Boric (mol)	**Molar Ratio of HH:H_2O2**	**Reaction Time (hours)**	**Reaction Temperature (^{o}C)**	**Hydrogenation Degree (%)**
0	1:1	6	40	15.9
0.008	1:1	6	40	34.8
0.016	1:1	6	40	35.2
0.024	1:1	6	40	38.5

Table 1 (cont'd). Degree of hydrogenation with respective parameters optimization

Mole of Acid Boric (mol)	Molar Ratio of HH:H_2O2	Reaction Time (hours)	Reaction Temperature (^{o}C)	Hydrogenation Degree (%)
0.08	1:1	6	40	34.9
0.024	1:2	6	40	56.2
0.024	1:3	6	40	71.2
0.024	1:4	6	40	73.0
0.024	1:5	6	40	56.3
0.024	2:1	6	40	61.5
0.024	3:1	6	40	51.5
0.024	2:3	6	40	78.0
0.024	2:3	2	40	45.6
0.024	2:3	4	40	65.1
0.024	2:3	6	40	68.0
0.024	2:3	8	40	82.9
0.024	2:3	10	40	67.0
0.024	2:3	8	27	43.4
0.024	2:3	8	50	53.6
0.024	2:3	8	60	91.2
0.024	2:3	8	70	56.5

Reactivity of diimide species

At mole ratio of 3:1 (HH: H_2O_2), the hydrogenation degree was found to be at 51.5%. The amount was reduced from 61.5% at 2:1 of HH: H_2O_2. Highly excessive HH signified with prolonged reaction time increased amounts of diimide molecules that could lead to self-reaction of diimide. Equation 3 shows the diimide self-reaction [9]. Besides, excess diimide species were reported to penetrate aqueous phase instead of rubbery phase of the reaction [14]. This would reduce the addition of hydrogen into LNR unsaturated units [9].

$$NH{=}NH + NH{=}NH \longrightarrow N_2H_4 + N_2 \qquad (3)$$

De Sarkar et al. proposed the reaction scheme of diimide decomposition when the reaction time was extended (equation 4 and 5) [7]. Longer reaction time in this study (10 h) showed decrement in percentage of hydrogen due to unavailability of diimide species that were needed to hydrogenate the unsaturated units [7].

$$NH{=}NH \longrightarrow N_2 + H_2 \qquad (4)$$

$$2NH{=}NH \longrightarrow N_2H_4 + N_2 \qquad (5)$$

Decomposition of Hydrogen Peroxide

The percentage of hydrogenation dropped from 73.0% to 56.0% when the mole ratio of H_2O_2 to HH was increased from 4:1 to 5:1. De Sarkar et al. in 1997 suggested side reactions of H_2O_2 that prevented the formation of diimide species (equation 6-8) [15]. Consequently, the amounts of diimide were insufficient to yield more hydrogenated products.

$$2H_2O_2 + N_2H_4 \longrightarrow N_2 + 4H_2O \qquad (6)$$

$$H_2O_2 + N_2H_2 \longrightarrow N_2 + 2H_2O \qquad (7)$$

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \tag{8}$$

At high H_2O_2 concentration, hydroxyl radicals were formed that could attack the polymeric chains of LNR. This would cause chain-scissoring and crosslinking reaction [16]. The mole ratio of HH: H_2O_2 should be at right amount to produce sufficient diimide species for maximum hydrogenation. It was reported that Kongsinlark et al. used ratio of 1:3 to hydrogenate their latex at maximum degree (89%) [17].

Cyclization

The decomposition of H_2O_2 gives acidic medium which increases the tendency of reaction to undergo Markovnikov addition [18]. The product of the hydrogenation reaction at 50 ^{o}C for 6 hours with mole ratio HH: H_2O_2 = 1:2, boric acid (2x10^{-4} mmol) underwent cyclization reaction as can be seen from the ^{1}H NMR spectrum (Figure 1).

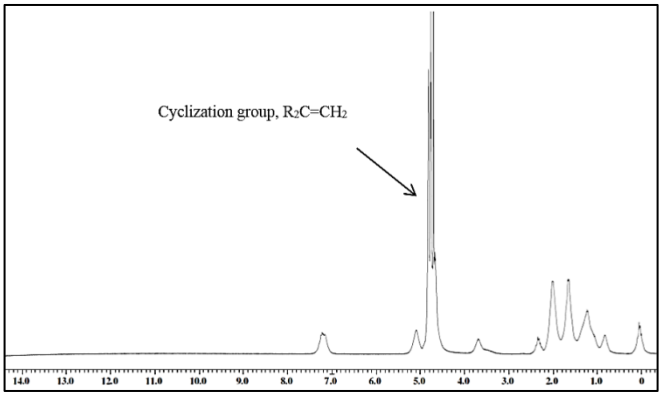


Figure 1. ^{1}H-NMR for detection of cyclization group in hydrogenated product

In cyclization reaction, the addition of acidic reagent causes the formation of carbonium ion which leads to formation of polycyclic ring structure of polymeric chain (mono-, bi-, and tricyclic) [19]. These cyclic structures would prevent penetration of diimide species to hydrogenate unsaturated units of LNR. Figure 2 shows that the cyclization reaction that starts when the carbonium ion attacks on an adjacent double bond, forming a ring structure.

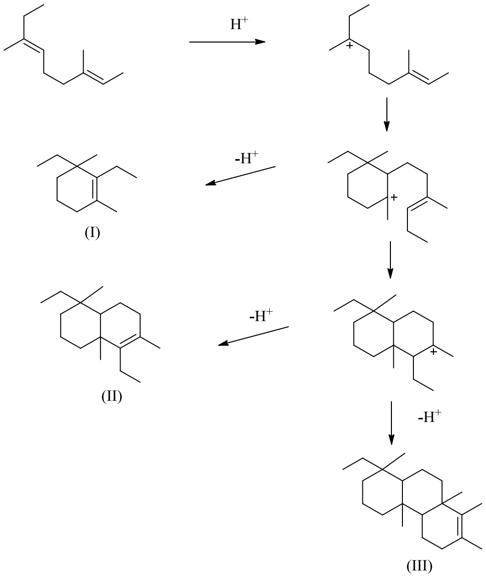


Figure 2. Mechanisms of cyclization reaction [6]

Crosslinking

The presence of H_2O_2 in the system can also contributes to crosslinking reaction. H_2O_2 prone to be dissociated into hydroxyl radicals that attacks the allylic proton of the *cis*-1,4-poliisoprene unit, forming macroradical units [20]. The macroradical can interact with each other to produce a cross-linked product. Figure 3 shows the mechanism for crosslinking reaction. Next, swelling test was performed to determine the degree of crosslinking of the samples.

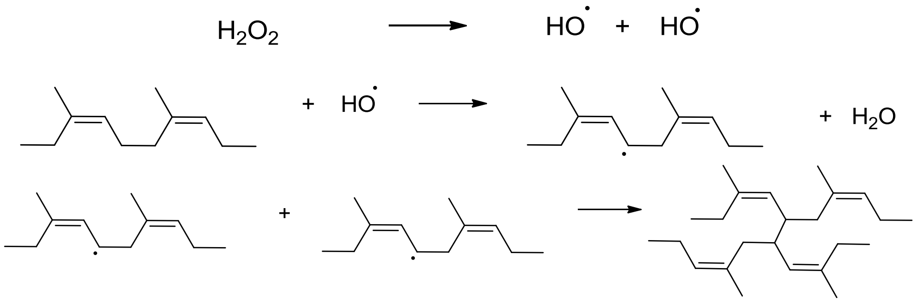


Figure 3. Mechanisms of crosslinking reaction [6]

Swelling test

Swelling test is carried out to determine the degree of crosslink in the samples after hydrogenation. The aim of this method is to identify the solvent (water) uptake into the polymer matrix which is expected to decrease with an increase of crosslinking [21]. Table 2 shows the outcomes of the swelling test on selected samples.

The weight increases with the decrease in degree of crosslinking [22]. From this study, lower value of crosslinking ratio indicated high degree of crosslinking (lower percentage of hydrogenation). Similarly, samples with highest hydrogenation percentage (91%) showed higher crosslinking ratio as a result of efficient hydrogenation due to less formation of hydroxyl radicals that triggered crosslinking reaction.

Table 2. Swelling test data

Samples	**Initial Weight W_1 (g)**	**Final Weight W_2 (g)**	**% Weight Increment**	**Crosslinking Ratio**
34% HLNR	1.06	11.52	1020.00	9.86
42% HLNR	0.30	3.55	1084.13	10.87
50% HLNR	0.17	2.56	1393.57	13.97
68% HLNR	0.25	3.70	1378.80	14.03
91% HLNR	0.20	3.06	1428.57	14.27

Degradation

Changes in molecular weight and its distribution during hydrogenation reaction can be determined by using GPC. Table 3 shows the comparison of polydispersity index, Đ for each sample. Hydrogenated products had lower molecular weight than LNR. It can be said that degradation process occurred during hydrogenation reaction in which causing the breakage of polymer chain and increasing the dispersity of polymer chain. These changes might happen as the results of thermal or acid degradation in the system related to effects of HH: H_2O_2 ratio [10].

Table 3. GPC analysis data

Samples	% Hydrogenation	M_w	M_n	Đ
LNR	-	96 400	10 800	8.93
HLNRi	50.1	9 500	7 400	1.28
HLNRii	71.3	9 500	7 200	1.32
HLNRiii	91.2	6 700	5 500	1.21

Conclusion

LNR has been successfully hydrogenated using HH: H_2O_2 system at various percentages of hydrogenation with respond to parameter optimization. The radicals formed in this system through reactivity of diimide species and decomposition of hydrogen peroxide have contributed to the manifestation of several side reactions such as cyclization, crosslinking, and degradation. Those identifications were based on spectrum analysis of NMR and GPC as well as swelling test.

Acknowledgement

The authors would like to acknowledge Universiti Kebangsaan Malaysia (UKM) for the research grants (GUP-2015-020 and FRGS/1/2016/STG01/UKM/02/4) and Centre for Research and Instrumentation (CRIM) at UKM for their facilities.

References

1. Zhou, S., Bai, H. and Wang, J. (2004). Hydrogenation of acrylonitrile–butadiene rubber latexes. *Journal of Applied Polymer Science*, 91(4): 2072-2078.
2. Jamaluddin N., Mohd Yusof M. J., Abdullah I. and M. Yusoff S.F. (2016). Synthesis, characterization, and properties of hydrogenated liquid natural rubber. *Rubber Chemical Technology,* 89(2): 227-239.
3. Lin X., Pan Q. and Rempel G. L. (2004). Cupric ion catalyzed diimide production from the reaction between hydrazine and hydrogen peroxide. *Applied Catalysis A: General,* 263 (1): 27 – 32.
4. Simma K., Rempel G. L. and Prasassarakich P. (2009). Improving thermal and ozone stability of skim natural rubber by diimide reduction. *Polymer Degradation and Stability,* 94(11): 1914-1923.
5. Yusof M. J. M., Jamaluddin N., Abdullah I. and Yusoff, S. F. M. (2015). Hydrogenation of liquid natural rubber via diimide reduction in hydrazine hydrate/hydrogen peroxide system. *AIP Conference Proceeding*, 1678: 050001
6. Samran J., Phinyocheep P., Daniel P. and Kittipoom S. (2005). Hydrogenation of unsaturated rubbers using diimide as a reducing agent. *Journal of Applied Polymer Science*, 95(1): 16-27.
7. De Sarkar M., De P. P. and Bhowmick A. K. (2000). Diimide reduction of carboxylated styrene–butadiene rubber in latex stage. *Polymer*, 41(3): 907-915.
8. Kongparakul S., Prasassarakich P. and Rempel G. L. (2008). Effect of grafted methyl methacrylate on the catalytic hydrogenation of natural rubber. *European Polymer Journal*, 44(6): 1915-1920.
9. Wang, X., Zhang, L., Han, Y., Shi, X., Wang, W. and Yue, D. (2013). New method for hydrogenating NBR latex. *Journal of Applied Polymer Science,* 127(6), 4764-4768.
10. Han Y., Su L. and Mao L. (2014). Self-cross-Linking hydrogenated nitrile-butadiene rubber latex/polyvinyl chloride emulsion composite film and its properties. *Polymer-Plastics Technology and Engineering,* 53(3): 306-311.
11. Huang G., Yu Q. and Cai M. (2016). Highlighting the effect of interfacial interaction on tribological properties of supramolecular gel lubricants. *Advanced Materials Interfaces*, 3(3): 1500489.
12. Sojoudiasli H., Heuzey M. C. and Carreau P. J. (2014). Rheological, morphological and mechanical properties of flax fiber polypropylene composites: influence of compatibilizers. *Cellulose*, 21(5): 3797-3812.
13. Tu X., Liu M. and Wei H. (2016). Recent progress on cyclic polymers: Synthesis, bioproperties, and biomedical applications. *Journal of Polymer Science Part A: Polymer Chemistry*, 54(11): 1447-1458.
14. Pisuttisap, A., Hinchiranan, N., Rempel, G. L. and Prasassarakich, P. (2013). ABS modified with hydrogenated polystyrene-grafted-natural rubber. *Journal of Applied Polymer Science*, 129 : 94-104.

15. De Sarkar M., De P. P. and Bhowmick A. K. (1997) Thermoplastic elastomeric hydrogenated styrene-butadiene elastomer: Optimization of reaction conditions, thermodynamics, and kinetics. *Journal of Applied Polymer Science*, 66(6) : 1151-1162.
16. Lin X., Pan Q. and Rempel G. L. (2005). Gel formation in diimide-hydrogenated polymers. *Journal of Applied Polymer Science*, 96(4): 1122-1125.
17. Kongsinlark A., Rempel G. L. and Prasassarakich P. (2013). Synthesis of nanosized ethylene-propylene rubber latex via polyisoprene hydrogenation. *Journal of Applied Polymer Science*, 127(5): 3622-3632.
18. Lenko D., Schlögl S. and Temel A. (2013) Dual crosslinking of carboxylated nitrile butadiene rubber latex employing the thiol-ene photoreaction. *Journal of Applied Polymer Science*, 129(5) : 2735-2743.
19. Dinçalp H. and Içli S. (2006). Photoinduced electron transfer-catalyzed processes of sulfoamino perylene diimide under concentrated sun light. *Solar Energy*, 80(3): 332-346.
20. Jiang D. D., Levchik G. F. and Levchik S. V. (2000). Thermal degradation of cross-linked polyisoprene and polychloroprene. *Polymer Degradation and Stability*, 68(1): 75-82.
21. Hirschl C., Biebl–Rydlo M. and DeBiasio M. (2013). Determining the degree of crosslinking of ethylene vinyl acetate photovoltaic module encapsulants—a comparative study. *Solar Energy Materials and Solar Cells,* 116 : 203-218.
22. Khan .F, Kwek D., Kronfli E. and Ahmad S.R. (2007). Crosslinking of ethylene–propylene (–diene) terpolymer elastomer initiated by an excimer laser. *Polymer Degradation and Stability*, 92(8): 1640-1644.