The Effect of Amount of Oxidising Agent and Reaction Time on the Properties of Hydroxyl Terminated Epoxidised Natural Rubber (HTENR) via Oxidative Degradation

Siti Maizatul Farhain Salehuddin[a], Norfhairna Baharulrazi[a,*], Nor Erma Shuhadah Abdul Razak[a], Siti Hajjar Che Man[a], Hussin Mohd Nor[a], Wan Khairuddin Wan Ali[b]

[a]Bioprocess and Polymer Engineering Department, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Aeronautical Engineering Department, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia
 norfhairna@utm.my

Hydroxyl terminated epoxidised natural rubber (HTENR) was synthesised via oxidative degradation method to produce a low molecular weight rubber. Epoxidised natural rubber (ENR) was depolymerised via chemical degradation method using cobalt (II) acetylacetonate (CAA) as the oxidising agent, followed by a treatment with sodium borohydride as a reducing agent to introduce hydroxyl (OH) functional group at both chain ends. The reaction times and the amount of oxidising agent tested were varied from one, three, five and twenty hours and 1 to 5 wt% of CAA to obtain the low molecular weight of HTENR. The molecular weight of HTENR was determined using gel permeation chromatography (GPC). The lowest molecular weight of HTENR was achieved at 3 wt% of CAA after 5 h of reaction time at 60 °C where average number (M_n) and average weight (M_w) were 34,000 g/mol and 62,000 g/mol FTIR analysis confirmed that HTENR contained OH group with the appearance of a broad peak around 3,200 - 3,600 cm^{-1} after the reaction. The presence of OH end groups was verified by NMR analysis with the appearance of two peaks at 3.38 ppm and 3.88 ppm, corresponding to methylene proton adjacent to hydroxyl group in $HOCH_2CH_2CH_2$ and methane proton adjacent to OH group in $CH_2CH_2CH(OH)CH_3$.

1. Introduction

Natural rubber (NR) is one of the most valuable renewable resources that has a very high molecular weight. NR has been used extensively in many applications and products due to its outstanding elastic property and high mechanical strength. It has gain increasing popularity and importance, and has been highly utilised in the manufacturing industry to produce tyres, gloves and many more natural rubber-based products in Malaysia. The degradation of natural rubber into low-molecular-weight rubber and functionalisation with specific functional groups, such as epoxide, would widen the applications of NR. Epoxidised Natural Rubber (ENR) can be a good candidate to produce self-healing material due to the presence of the epoxy group in the structure. ENR is obtained from the partial epoxidation of the natural poly cis-isoprene molecules, resulting in a completely new type of elastomer. ENR molecule exhibits three different functionalities that are available for possible cross-linking. These include double bonds, epoxy, and acid groups in the main chain, while retaining most of the properties of natural rubber (Ravindran et al., 1988). The epoxide groups are randomly distributed along the natural rubber chain. Epoxy group is expected to react to produce hydroxyl terminated epoxidised natural rubber (HTENR) via the reduction process. The obtained HTENR with hydroxyl terminated at both chain ends can be further reacted with diethylene triamide (DETA) and urea for the formation of supramolecular polymer network that exhibits the self-healing property. ENR exhibits special elastomer characteristics that can be tailored for various usages. By doing an exploration of ENR, current research intends to focus on the synthesis of a supramolecular self-healing HTENR that obtained from the depolymerisation of ENR via two steps reactions. Montarnal et al. (2008) had reported a research on self-

healing supramolecular rubber like material using vegetable oil, unsaturated fatty acid derivatives, combined with diethylene triamine and urea. A mixture of fatty diacid and triacid was condensed first with diethylene triamine and then reacted with urea resulting in an oligomeric supramolecular self-assembled thermoreversible rubber having self-healing property (Cordier et al., 2008). By conducting this research, an in-depth study on the properties of ENR can be done extensively to further develop and improve its usage for a wider range of applications in the future. One of the most important aspects of the materials development is to achieve a good combination of properties and process ability at a moderate cost. Due to that reason, the development of polymers that can repair damages autonomously would be useful to improve the lifetime of polymeric materials. To date, limited attention has been dedicated to developing elastomers with autonomic self-healing ability, which can recover damages without the need for an external or internal source of healing agents. This research focus on synthesis HTENR which can be used for next step to develop new material with self-healing ability.

2. Experimental

2.1 Materials

The raw material used throughout this work was ENR-50 that was obtained from Malaysian Rubber Board (MRB), Sungai Buloh, Selangor.

2.2 Synthesis of HTENR

10.0 g of ENR-50 was dissolved in 900 mL of toluene by stirring at 500 rpm overnight using a magnetic stirrer. The degradation of ENR-50 was done via the oxidative degradation method. The oxidising agent, namely cobalt (II) acetylacetonate (CAA), was used in the presence of ethanol, where 10 mL of ethanol was added to the rubber solution and followed by the addition of a specific amount of CAA. The effects of reaction parameters on the reduction of molecular weight were studied by varying the reaction times from 1, 3, 5 and 20 h while the amounts of the oxidising agent were being varied from 1 to 5 wt%. All the sample bottles were then placed into the thermostat water bath shaker at 60 ºC and 150 rpm under continuous stirring.

2.3 Introduction of Sodium Borohydride (H_2SO_4) to Produce HTENR

50 mL of ethanol were dissolved in 50 mL of distilled water to produce 50 % aqueous ethanol. 2.6 g of sodium borohydride was dissolved in 100mL of 50 vol% aqueous ethanol, with a shaking amplitude at 150 rpm. While stirring the rubber solution vigorously, sodium borohydride solution was being added slowly at 25 ºC within 20 min. The solution was being heated and maintained at 60 ºC for 2 h. The solution was then left overnight at room temperature before the washing process.

2.4 Washing Process

The process began by acidifying the solution with 10 vol% sulfuric acid (H_2SO_4) solution to eliminate unreacted sodium borohydride, followed by washing with distilled water for three times to eliminate the remaining H_2SO_4, and being dried overnight on anhydrous magnesium sulphate ($MgSO_4$) to eliminate the remaining water. The solution was then filtered and concentrated using a rotary evaporator to give a viscous solution. The liquid rubber was then recovered by dissolving the viscous solution in an excess amount of methanol in which the precipitate did not dissolve. The liquid fraction in milky white colour was collected and then dried in vacuum desiccators to a constant weight.

2.5 Sample Characterisation

2.5.1   Gel Permeation Chromatography (GPC)

The GPC used in this experiment consists of the water pump of model Waters 1500 Series HPLC Pump and a manual injector with refractive index detector model Waters 2410. Tetrahydrofuran (THF) was used as a solvent at a flow rate of 1 mL per min. About 20 mg of sample was dissolved in 2 mL of tetrahydrofuran using 4mL of vials. The solutions were filtered using 0.5 μm pore size filter unit (Millipore, Millex-PRC). 20 μL of the solutions were injected into the chromatograph using 25 μL syringes.

2.5.2 Fourier Transform Infrared (FTIR)

FTIR spectrum was recorded using Perkin Elmer spectrum 2000 explorer at room temperature. Infrared spectra were recorded in the transmission mode as a result of 20 scans. Different methods were being used for each liquid or solid samples. In terms of liquid samples, one drop of 5 mg/ml concentration was placed on the potassium bromide (KBr) disk. For the solid sample, about 2 mg of sample was mixed with 5 mg of KBr powder and applied for the test. An exact amount of 0.005 g of the sample was dissolved in 1.0 mL

chloroform. About two to three drops of solution were placed on the KBr disk. The solvent was evaporated from the sample prior to test using 100-watt lamp and was placed on FTIR holder to record the spectrum.

2.5.3 Nuclear Magnetic Resonance (NMR)
The instrument used was a BRUKER 400 ULTRASHIELD FT-NMR. The spectrometer was working at 100 MHz for carbon-13 and 400 MHz for proton. For sample preparation, the sample should be at least 95 % pure and the quantity is in the range of 1 - 10 mg, where the sample must be in liquid form to be analysed in high resolution NMRThe pristine sample was dissolved in NMR solvents prior to being tested. About 1 - 5 mg of sample was used for proton-1 and 10 - 20 mg of the sample for carbon 13.5 mm Pabbo-BB probe was used for all measurements.

3. Result and Discussion

3.1 Gel Permeation Chromatography (GPC)

3.1.1 Effect of Reaction Time on M_n and M_w of HTENR
The use of GPC to study the reduction in molecular weight of polymers during the reaction has been reported previously by many researchers (Sathiskumar and Madras, 2012). In the present work, the oxidative degradation of ENR-50 has been monitored at 60 °C at constant amount of CAA (1 wt%) after 1, 3, 5 and 20 h of reaction. Figure 1a shows the effect of reaction time on M_n and M_w of ENR-50. The M_n of the ENR-50 before oxidative degradation (133,000 g/mol) with a polydispersity of 5.5 was quickly cut off almost into half for the first 1 h of reaction and slowly decreased afterwards. By prolonging the reaction time to 3, 5 and 20 h had resulted in a slow decreasing of M_n to 66,000, 60,000 and 34,000 g/mol. A similar trend was observed for the reduction of M_w at 1, 3, 5 and 20 h which were 183,000, 154,000, 123,000 and 62,000 g/mol. These results showed that M_n and M_w decreased with increasing reaction time from 1 to 20 h. In general, the longer reaction time had led to more chain scissions. The lowest M_n and M_w which were achieved after 20 h reactions were 34,000 and 62,000 g/mol.
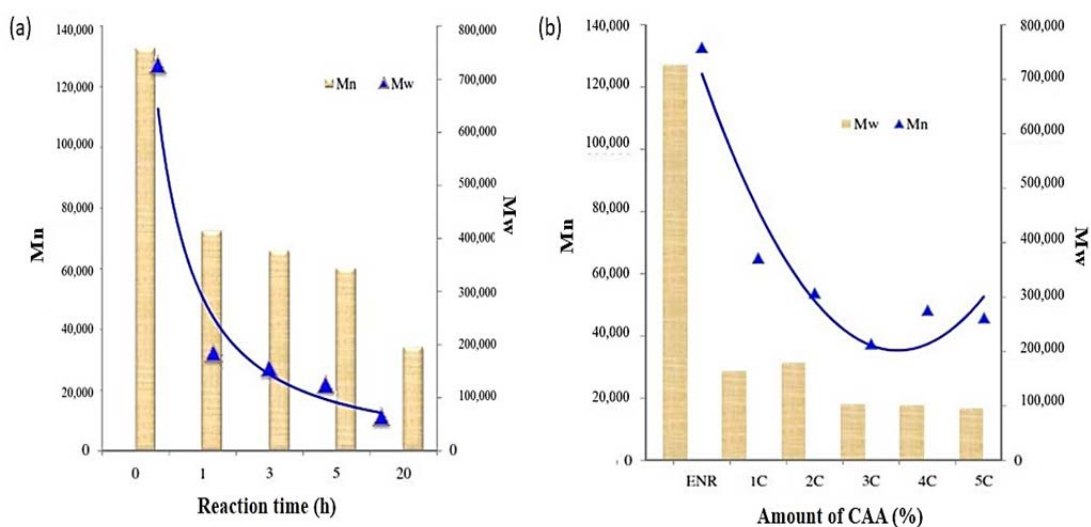

Figure 1: (a) Effect of reaction time on M_n and M_w of HTENR (b) Effect of CAA on M_n and M_w of HTENR

3.1.2 Effect of CAA Amount on the M_n and M_w of HTENR
In this work, CAA was used as a chain scission agent during the degradation process. Figure 1b shows the effect of CAA on M_n and M_w of HTENR. It was clearly seen that by increasing the amount of CAA from 1 wt% to 2 wt% and 3 wt% at constant reaction time, which was 5 h, had caused the reduction of M_n and M_w from 65,000 to 53,000 and 37,000 g/mol. Significant reduction of M_n was achieved upon the introduction of 3 wt% of CAA with M_n 37,000 g/mol. The increases of M_n after the use of 4 wt% of oxidising agent suggested that a faster recombination reaction occurs at a higher amount of CAA rather than the chain scission reaction. More active sites were produced, thus increases the possibility for recombination through aldol condensation. However, the recombination reaction occurs at a slow rate in the presence of ethanol in contrast to methanol, owing to more stable terminal groups (Baharulrazi et al., 2017). A higher amount of oxidising agents might produce more active sites for further reaction process. Excessive oxidising agent would cause high formation of the unstable terminal group, thus leads to recombination process (Baharulrazi, 2015). The recombination

reaction will contribute to increasing the molecular weight of the degraded rubber, hence reduces the chain scission reaction and the number of reactive sites to react with NaBH$_4$ to produce hydroxyl (OH) groups. As a result, the OH concentration reduces and the average molecular weights of degraded rubber increases. Higher reduction in molecular weight was observed by varying CAA amount rather than varying the reaction time. These results were significant with the properties of CAA to enhance chain scission during oxidative degradation reaction.

3.2 FTIR Analysis

3.2.1 Effect of Reaction Time on Oxidative Degradation of ENR-50

The effect of reaction time on oxidative degradation of ENR-50 has been evaluated at 1, 3, 5, 8 and 20 h in the presence of the oxidising agent. The original colour of ENR-50 block which was light yellow had turned into yellowish sticky solid rubber after the degradation process. In order to confirm the chemical structure of the degraded sample, FTIR analysis was performed. Figure 2 shows the FTIR spectra of HTENR after oxidative degradation of ENR-50 at 1, 3, 5 and 20 h for 5 % of CAA.
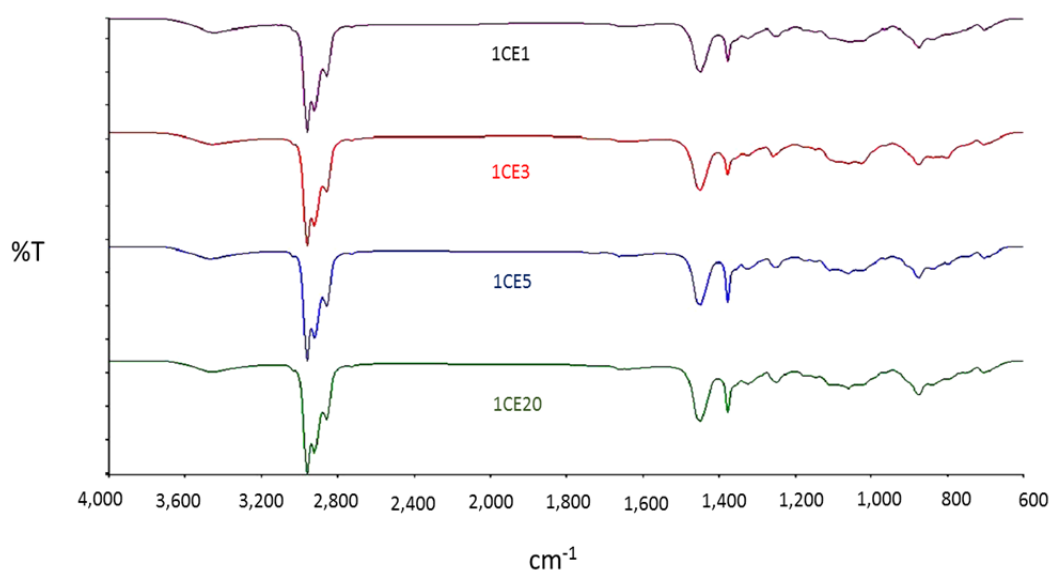

Figure 2: FTIR spectra of oxidative degradation of ENR-50 at constant amount at 1 wt% CAA at different reaction time (1 h, 3 h, 5 h and 20 h)

It can be clearly observed that all spectra looked very similar and no significant changes had occurred. The presence of a peak at 1,251 cm^{-1} and 876 cm^{-1} were corresponding to an epoxy functional group which does not appear in FTIR spectra of NR. These two peaks remained along the degradation reaction. The peak at 1,731 cm^{-1} appeared after 1 h reaction time, which indicated the presence of carbonyl groups (C=O). The broad peak at 3,494 cm^{-1} was assigned to the bonded O-H group after the degradation reaction. Other peaks that appeared similarly as the ENR-50 spectrum were at 2,963 cm^{-1}, 2,928 cm^{-1}, 2,862 cm^{-1}, 1,648 cm^{-1}, 1,451 cm^{-1}, 1,063 cm^{-1}, and 837 cm^{-1}. According to the graph, the characteristic peaks of ENR-50 decreased in intensity relatively to the peak at 1,378 cm^{-1}, proving that ENR-50 had undergone profound structural changes during the degradation process. In other words, the attack of CAA on ENR-50 led to chain scissions resulting in low molecular species.

3.2.2 Effect of Amount of CAA on Oxidative Degradation of ENR-50

Figure 3 shows the FTIR spectra of the oxidative degradation of ENR-50 at various amount of CAA at a constant reaction time, which was at 5 h. The same trends were being observed for all functional groups (i.e. O-H, C-H (CH$_3$), C-H (CH$_2$), C-H (CH$_2$ and CH$_3$), C=C, C-O and =C-H) which gave the maximum intensities at 3 % of CAA.

An increase in the amount of CAA from 1 - 2 % had caused a significant reduction in relative intensities for nine out of ten characteristic functional groups. The trend then increased at 3 % of CAA and slowly decreased until 5 % of CAA, at which the relative intensities are similar to those at 1 % of CAA. No significant changes on the observed peak was found even by increasing the amount of CAA up to 5 %.
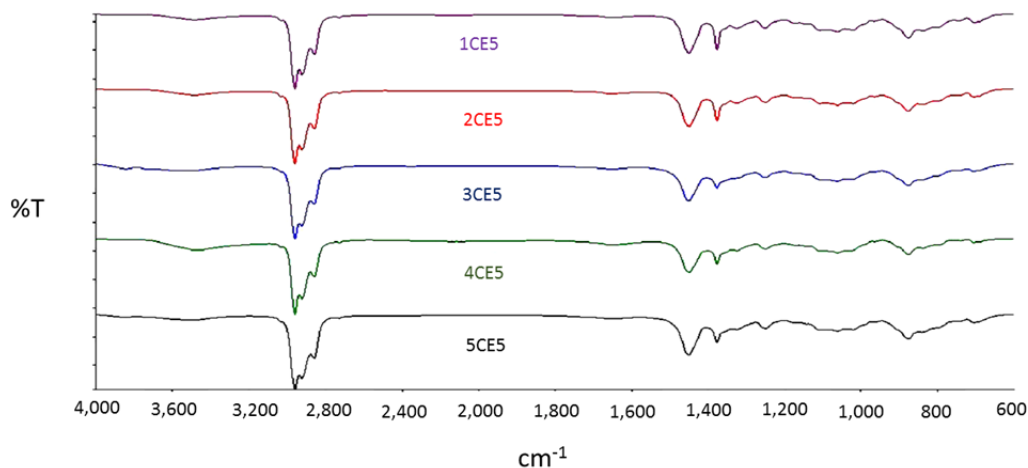
Figure 3: FTIR spectra of HTENR with different amounts of CAA (1 %, 2 %, 3 %, 4 % and 5 %) at a constant reaction time

3.3 NMR Analysis

3.3.1 $_{13}$C NMR Spectrum of HTENR

Figure 4 shows a $_{13}$C NMR spectrum of HTENR. By referring to the HTENR spectrum, the main peaks on behalf of isoprene unit still maintain on the respective region, although it shifted slightly up-field comparable to the main ENR-50 spectrum. This might be due to the variation of molecular weight between HTENR that possess lower molecular weight, in contrast to the virgin ENR-50 with high molecular weight (Nor and Ebdon, 1955). The main peaks which represent isoprene unit were being observed at 134.76 ppm ($-C(CH_3) = CH-$), 125.15 ppm ($-C(CH_3) = CH-$), 32.00 ppm ($-CH_2C(CH_3)=$), 26.29 ppm ($=CHCH_2$) and 23.32 ppm ($-C(CH_3)=CH$). The peaks at 64.44 ppm and 60.78 ppm corresponded to $-C(CH_3)OCHCH_2$ and $C(CH_3)OCHCH_2$ of the epoxy unit.
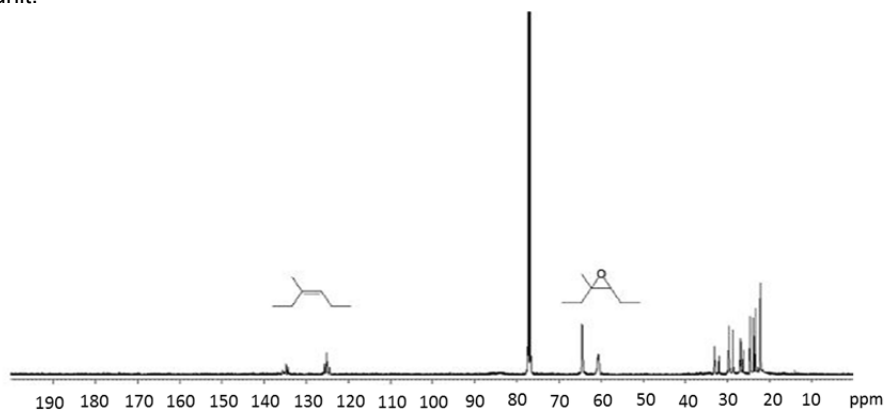

Figure 4: $_{13}$C NMR spectrum of HTEN

3.3.2 $_1$H NMR Spectrum of HTENR

Figure 5 shows a 1H NMR spectrum of HTENR. Instead of the main signals of ENR-50, there are several other signals which were detected. Thisconfirmed that the chemical reaction had changed the chemical structure of the original ENR-50. In the HTENR spectrum, the main characteristic peaks of ENR-50 were preserved with the appearance of additional peaksconfirming that the original structure of ENR-50 had undergone a transformation during the degradation process (Nor and Ebdon, 1955). It was concluded that the HTENR contains hydroxyl terminated end group at both chain ends with the appearance of a peak at 3.36 ppm and 3.86 ppm that corresponded to CH and CH2 nearby OH end groups in CH2CH2CH(CH3)OH and CH2CH2CH2(OH).
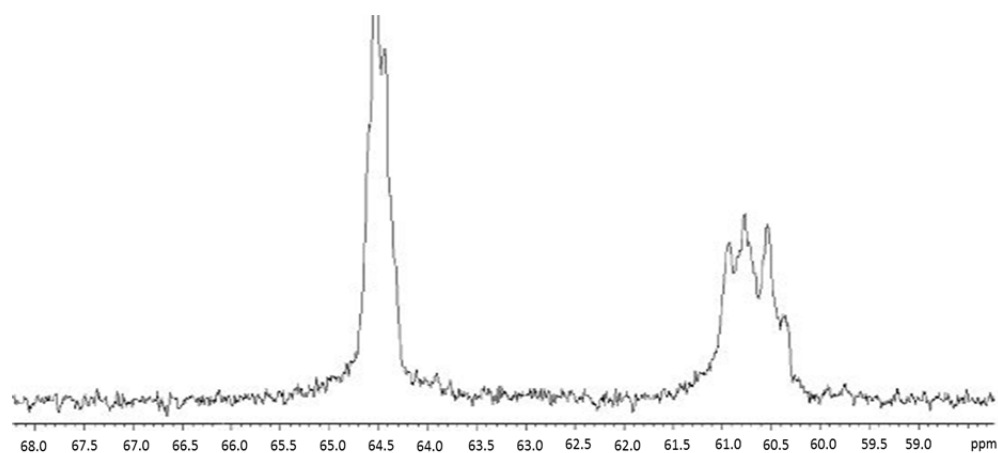
Figure 5: ₁H NMR spectrum of HTENR

4. Conclusion

Hydroxyl terminated epoxidised natural rubber (HTENR) had been successfully synthesised via the oxidative degradation method using cobalt acetylacetonate (CAA) as an oxidising agent for chain scission reaction. The reaction was carried at the temperature of 60 °C, in the presence of ethanol and followed by a treatment with sodium borohydride as a reducing agent to introduce the hydroxyl functional groups. The presence of hydroxyl (OH) functional group was verified using FTIR analysis with the appearance of a peak at 3,447 cm^{-1} that corresponds to OH groups. The lowest M_n and M_w of HTENR that were obtained from the oxidative degradation method were found to be 37,000 g/mol and 102,000 g/mol. The chemical structures of the obtained HTENR were confirmed by FTIR and NMR analyses. The appearances of OH end groups were verified by FTIR and NMR analyses to validate the position of each OH functional groups. ₁H NMR indicated that the end groups structures of HTENR were $HOCH_2CH_2CH_2$- at one chain end and $CH_2CH_2CH(OH)CH_3$ at the other chain end. It can be concluded that the HTENR contained OH groups as terminal chain ends. The development of polymers that can repair damage autonomously would be useful to improve the lifetime of polymeric materials. To date, limited attention has been dedicated to developing elastomers with autonomic self-healing ability, which can recover damages without the need for an external or internal source of healing agents.

Acknowledgments

References

Baharulrazi N., 2015, Thermal and Oxidative Degradation Mechanism of Hydroxyl Terminated Natural Rubber for Solid Rocket Propellant Binders, Ph.D. Thesis, Universiti Teknologi Malaysia, Johor, Malaysia

Baharulrazi N., Che Man S.H., Mohamad Z., Mohd Nor H., Wan Ali W.K., 2017, Effect of Various Alcohols and Reaction Time on the Properties of Hydroxyl Terminated Natural Rubber Synthesized via Oxidative Degradation, Chemical Engineering Transaction, 56, 583-588.

Cordier P., Tournilhac F., Ziakovic C., Leibler L., 2008, Self-healing and Thermoreversible Rubber from Supramolecular Assembly, Nature, 451, 977-980.

Montarnal D., 2009, Versatile One-pot Synthesis of Supramolecular Plastic and Self-healing Rubbers, Journal of the American Chemical Society USA, 131, 7966-7967.

Nor H.M., Ebdon J.R., 2000, Ozonolysis of Natural Rubber in Chloroform Solution Part 1: A Study by GPC and FTIR Spectroscopy, Polymer, 41, 2359-2365.

Ravindran T., Gopinathan Nayar M.R., Joseph D., 1988, Production of Hydroxyl Terminated Liquid Natural Rubber – Mechanism of Photochemical Depolymerization and Hydroxylation, Journal of Applied Polymer Science, 35, 1227-1239.

Sathiskumar P.S., Madras G., 2012, Ultrasonic Degradation of Butadiene, Styrene and their Copolymers, Ultrasonics Sonochemistry, 19, 503–508.