



Storage Properties of DPNR under Various Conditions

Suhawati Ibrahim^{1,*}, Fatimah Rubaizah Mohd Rasdi¹, Nurul Hayati Yusof¹, Dazylah Darji¹, Nurul Suhaira Abdullah¹

¹ Technology and Engineering Division Malaysian Rubber Board, 47000 Sungai Buloh, Selangor, Malaysia

ABSTRACT

Maintaining the properties of deproteinised natural rubber (DPNR) after the production is critical and essential since it tends to deteriorate after the removal of proteins. During the preparation, transportation and storage, rubber may be exposed to contamination and an unfavourable environment that may affect the properties over time. Therefore, this work was conducted to determine the factors that affect the properties of DPNR during storage. In this work, DPNR samples were prepared with and without the presence of zinc oxide (ZnO) and hydrogen peroxide (H₂O₂) as contaminants. These samples were then stored under different environments such as opened room temperature (RT), closed RT, chilled and heated. Their physical properties were examined during 76 weeks of storage. NR control sample showed the most stable properties along the storage period studied. Removal of proteins in DPNR samples in overall has reduced its whole properties especially when it was contaminated with H₂O₂. These properties became worsen when the sample was stored in a hot environment (40 °C). Its properties such as Mooney viscosity and plasticity retention index (PRI) decreased significantly with time and reached below 70 MU and 40 units, respectively. This result was supported by the reduction of their molecular weight, which indicates the degradation of these samples during storage. The results showed that the quality of DPNR could be compromised by the presence of contaminants such as H₂O₂ during production and would be worsen by improper storage conditions.

Keywords:

Deproteinised rubber; Storage stability;
Rubber degradation

1. Introduction

Deproteinised natural rubber (DPNR) is a purified form of rubber that contains less non-rubber components particularly proteins. The removal of proteins from natural rubber provides a safer option for individuals with latex sensitivity or allergies [1] without sacrificing the desirable properties of NR. However, the loss of proteins, as a natural antioxidant in NR latex could affect its properties when it is susceptible to degradation when exposed to certain factors during preparation and storage [2].

Storage stability of DPNR refers to its ability to maintain their chemical and physical properties upon storage. There are a few factors that could contribute to their properties such as contamination

* Corresponding author.

E-mail address: suhawati@lgm.gov.my

<https://doi.org/10.37934/araset.63.1.153163>

and storage environment. Contamination with reactive agents, light and heat would induce the deterioration of DPNR faster/severe since it is almost free from natural antioxidant. However, there was no work reported on the effect of contaminants and environment upon storage was carried out previously. Therefore, a study should be carried out to collect the data and to be used as a guideline for DPNR production to maintain its quality and performance.

The aim of this work is to study the optimum storage conditions to minimize rubber degradation over time. Here, we studied the changes of properties in NR as a control and DPNR over time at various storage conditions such as opened, closed, heated and chilled environments. The effect of contamination by reactive agents such as zinc oxide (ZnO) and hydrogen peroxide (H₂O₂) on rubber properties was also observed.

2. Methodology

2.1 Materials

Field natural rubber latex (FNRL) was collected from Stesyen Penyelidikan Kota Tinggi, Johor, Malaysia. Industrial grade of hydrogen peroxide (H₂O₂), zinc oxide (ZnO), hydroxylamine sulphate (HNS) was bought from Distech Sdn Bhd. Non-ionic surfactant teric 16A69 and protease enzyme were obtained from FGV Rubber Industries Sdn Bhd. Analytical grade of toluene was supplied by Fluka (M) and tetrahydrofuran (THF) HPLC grade (≥99.9%) was supplied by Merck (M). All chemicals were used without further purification.

2.2 Deproteinization of Field Natural Rubber Latex

The deproteinised process used in this study was a MRB's inhouse method. The FNRL was added with surfactant, hydroxylamine sulphate and enzyme solution. The mixture was left at room temperature for 72 hours. After the reaction completed, the latex was then divided into three parts for contamination simulation. One part was used as DPNR control, one part was added with ZnO and one part was added with H₂O₂. All the latexes were coagulated with steam and creeped to remove excess water and dried in a hot air oven.

2.3 Concentration of FNRL

FNRL was concentrated by centrifugation method (alfa laval centrifuge) to produce concentrated NR as a control. The NR latex was then coagulated with steam and creeped to remove excess water and dried in a hot air oven.

2.4 Storage Conditions

In this study, two samples were used as controls, namely NR and DPNR. The other samples were DPNR that contaminated with ZnO and H₂O₂, which were named DPNR/ZnO and DPNR/H₂O₂, respectively. All samples were stored in different storage conditions such as in room temperature at open and closed environments. The effect of temperature on the samples were also studied by storing them in a cold room at temperature of 10 °C and in an oven at temperature of 40 °C. All storage conditions are marked as opened RT, closed RT, chilled and heated, respectively.

2.5 Mooney Viscosity Tests

The Mooney viscosity (VR) test was conducted according to method reported in SMR Bulletin No. 7 [3]. The test requires homogenised sample at approximately 25g in weight that later was divided into two equal portions of samples. Preheated rotor was then placed through the centre of one portion to place the sample in the lower die cavity while the second portion was placed on top of the rotor, as shown in Figure 1. Then the viscometer platen was closed immediately for 1 min. The viscosity reading from dial gauge for the initial (after 1 min) and at the end of four minutes was recorded. The test was repeated to obtain duplicate values.

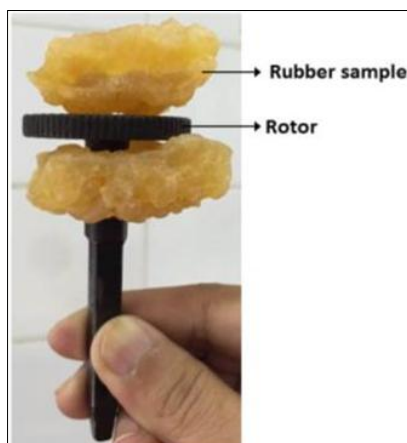


Fig. 1. The rubber position on the Mooney viscometer rotor

2.6 Determination of Plasticity Resistance Index (PRI)

The homogenised rubber at the weight of $20\text{g} \pm 5\text{g}$ was further passed through the roll mills to obtain final sheet thickness between 1.6mm to 1.8mm. The sheeted rubber piece was doubled after the first and final passes. Six test pellets were cut from the doubled sheet rubber, as illustrated in Figure 2. The test pellets should be a disc of rubber of thickness between 3.2mm to 3.6mm and approximately 13mm in diameter. The test pellets are divided into two sets of three: one set each for plasticity determination before (P_0) and after oven ageing (P_{30}).

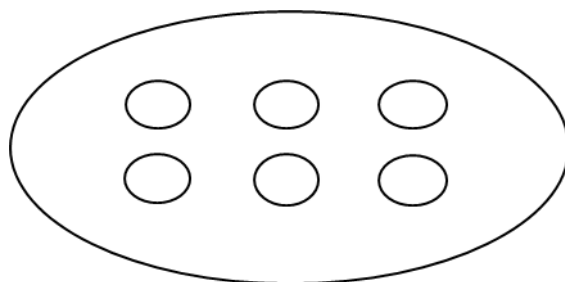


Fig. 2. Six test pellets were cut from the doubled sheet rubber

The cut test pellets were arranged onto oven tray or thick plate. Once the targeted oven temperature was reached ($\approx 140\text{ }^\circ\text{C}$), the tray was inserted and timed. After 30 ± 0.25 min, the tray was removed from the oven and allowed cooling to room temperature. The plasticity of the aged pellets was measured by compressing the disc-shaped test pellet sandwiched between two pieces of

cigarette paper (40 x 35 mm) using two parallel platens to a fixed thickness of 1.00 + ±0.01mm. The thickness was taken as the measure of rapid plasticity. The PRI was calculated to Eq. (1) below.

$$PRI = \frac{P_{30}}{P_0} \times 100 \quad (1)$$

2.7 Molecular Weight Distribution by Gel Permeation Chromatography (GPC)

Sample was weighed about 0.05 g and dissolved with 5ml THF in the dark place for 2 days. Then, the sample was filtered using PTFE membrane filter with pore size of 0.45 µm before measuring the molecular weight using (TOSOH HLC-8320GPC) equipped with two columns (TSK gel SuperMultipore HZ-M) and RI detector. The measurement was carried out with a flowrate of 0.5 ml/min °C. The molecular weight was then calculated against the polystyrene calibration curve.

2.8 Determination of Gel Content

Gel content is the percentage by mass of polymer insoluble in a specified or good solvent after extraction under specified conditions. Determination of gel content in a polymer involves the dissolution of the polymer in a suitable solvent. The gel content of sample was determined by dissolving about 2 g of sample (*mo*) in 100 ml toluene and was kept for 48 hours in a dark place. The gel fraction was then filtered and dried (*m*) in an oven at 60 °C for 24 hours. The percentage weight ratio of insoluble (dried gel) fraction and the original sample was estimated as the gel content as shown in Eq. (2):

$$Gel\ content(\%) = \left[\frac{weight\ of\ dried\ gel\ (m)}{weight\ of\ sample\ (mo)} \right] \times 100 \quad (2)$$

3. Results

3.1 Mooney Viscosity

Mooney viscosity is performed to determine the overall processability of the rubber. A higher viscosity value indicates a harder rubber which has difficulty in rubber processing. It also implies that the rubber has high MW and gel content, but poor plasticity [4]. The acceptable value of Mooney viscosity for NR and its products is in the range of 60–90 MU. Figure 3 shows Mooney viscosity for all samples studied at various storage conditions. The initial viscosity of NR was 91 MU. During the storage, sample that was kept at opened RT showed an increase in Mooney viscosity up to 76 weeks of storage and final Mooney viscosity value was 102 MU. Meanwhile, Mooney viscosity for closed RT sample showed stable trend until 28 weeks before it increased to 101 MU after being stored for 76 weeks. The viscosity of sample that being stored in chilled room also increased up to 76 weeks with Mooney viscosity of 101 MU. Similar trend was observed for heated sample when the viscosity increased to 98 MU at week 20, then became stable at 98-101 MU until 68 weeks. It was then decreased slightly to 95 MU at 76 weeks of storage, indicating the sample started to degrade after was stored at high temperature for a long period. As an overall, the viscosity of NR was relatively increased upon storage period regardless of conditions applied. The increase in viscosity was related to the formation of crosslinks during storage which so-called storage hardening phenomena [5].

Mooney viscosity of DPNR control was determined to be 75.5 MU at the initial stage, which was relatively lower compared to the NR. Upon storage, Mooney viscosity of samples that were kept at

opened and closed RT slightly increased with time and reached 82.5 and 81.5 MU, respectively at week 76. On the other hand, the sample that being kept at chilled condition showed no significant changes throughout the storage, with the Mooney viscosity was about 77.2 MU along the storage period. For the sample that was heated in the oven, the Mooney viscosity increased to 80.4 MU at week 20 before decreased to 67.2 MU after 76 weeks of storage duration.

As for DPNR/ZnO sample that being kept at opened RT, the Mooney viscosity gradually increased from 75.3 MU to 83.8 MU after 44 weeks, and then seemly stable for the rest of the studied. For the closed RT sample, Mooney viscosity increased to 84.3 MU after 76 weeks. Meanwhile, sample in chilled room showed stable against storage with average viscosity about 76.8 MU. Mooney viscosity of heated sample increased to 83.2 MU at week 20 before started to decrease to 70.1 MU at week 76. The increase in Mooney viscosity for DPNR is much lower compared to the NR is due to the lack of protein to form branches [2].

Mooney viscosity of DPNR/H₂O₂ samples increased from 75.4 MU to 81.6 and 84.0 MU when were stored at opened RT and closed RT, respectively. While the sample in chilled room remained constant along the storage studied. However, the opposite trend was observed for the heated sample where the Mooney viscosity decreased to 67.2 MU at the end of study.

In the case of DPNR samples, the lower viscosity may be explained by the protein removal that leads to the loss of branching networks at the chain ends of rubber molecules, hence reduced its flow resistance or viscosity [6,7]. Apparently, the viscosity remained constant upon storage at chilled condition whilst decreased in heated condition for DPNRs. Generally, DPNRs that contaminated with ZnO and H₂O₂ exhibited no significant difference from DPNR control suggesting the reactive agents did not affect the overall viscosity.

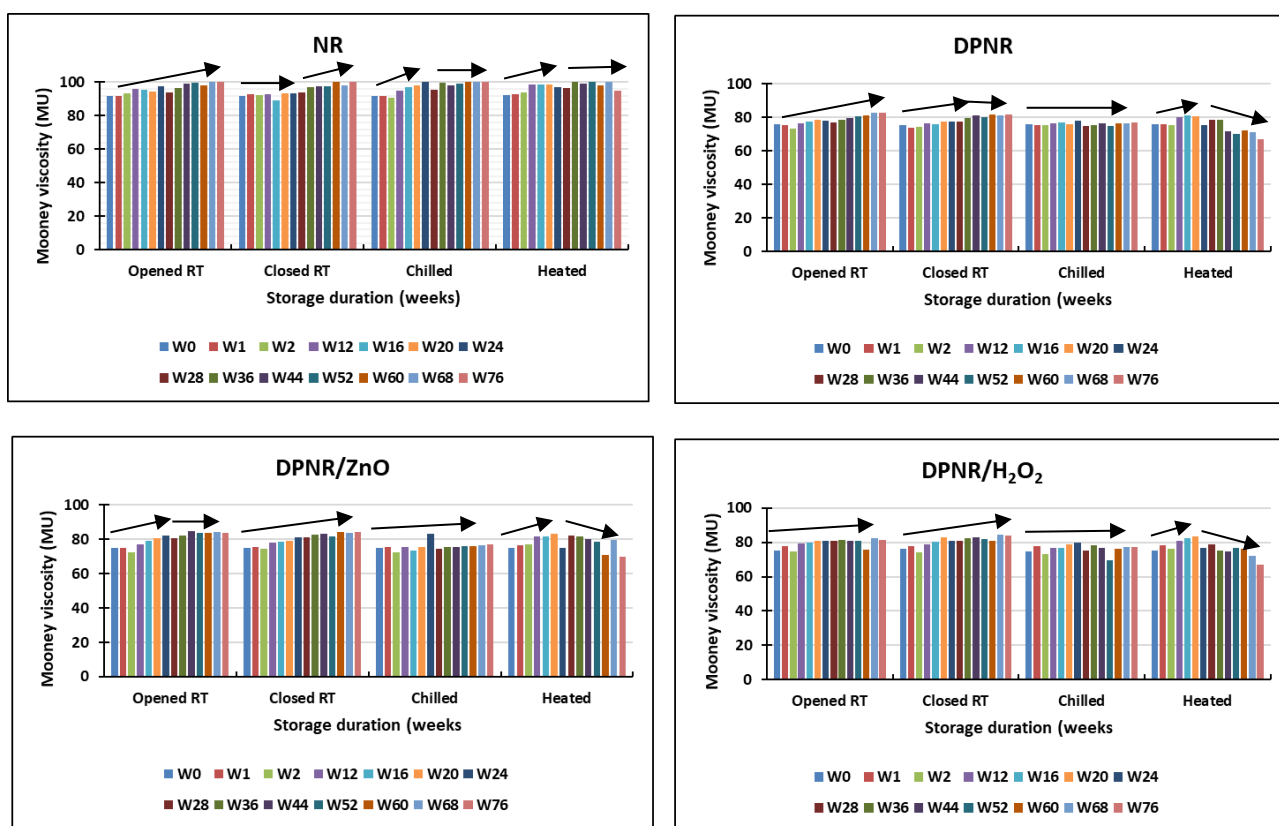


Fig. 3. Mooney viscosity of NR and DPNRs samples against time at various storage conditions

3.2 Plasticity Retention Index (PRI)

PRI is one of the important indicators to determine the resistance of a raw rubber against thermal oxidation and degradation during processing or aging [8]. A high resistance to thermal oxidation will result in high value of the PRI.

Figure 4 shows the PRI values for NR, DPNR, DPNR/ZnO and DPNR/H₂O₂ at various storage conditions. PRI value was found to decrease gradually for NR sample from initial value of 75 units to 61, 66 and 65 units at opened RT, closed RT and heated conditions, respectively. However, chilled sample showed a stable trend along the storage period studied. This indicated that their tolerance towards degradation decreased with time for the samples were stored at RT and heated conditions, however consistent when was stored in a chilled condition. This finding supports the data obtained from the Mooney viscosity, in which the values were stable throughout the storage period in a similar chilled condition.

The initial PRI value of DPNR control was 67 units, which was lower compared to the NR due to removal of proteins that act as the natural stabilizer against degradation [9]. The PRI value for opened RT sample increased to 77 units at week 20 before decreased to 69 units at week 76. Similar trend was observed for chilled sample which increased to 76 units at week 52 before decreased to 65 units after 76 weeks. Meanwhile, the closed RT sample seemed stable along the storage period up to 76 weeks with the PRI value of 64 units. On the other hand, PRI value for heated sample reduced by 38 units after 76 weeks of storage. Overall, the results showed that the PRI value of DPNR could significantly affected by heat during the storage and transportation. DPNR was more sensitive to oxidative degradation due to the absence of proteins, as one of the natural antioxidants that hinder the activity of alkyl peroxy radicals under heat condition [10].

The PRI value of the DPNR/ZnO sample after the drying process was 56 units, which have shown a significant decrease compared to the DPNR control sample. This indicates that contamination of ZnO in the DPNR process is crucial and has to be avoided. The values for opened and closed RT samples were then continuously decreased to 41 and 44 units, respectively, at the end of storage study. Chilled sample seemly more stable in their PRI value up to 76 weeks. However, PRI value increased to 74 units at week 24 before started to decrease to 52 units at week 76 for the heated sample.

The effect of H₂O₂ on DPNR was the worst when compared to the other samples in all conditions when the PRI value was the lowest amongst all that were about 40 units. A similar trend was observed for DPNR/H₂O₂ opened and closed RT samples when the PRI values decreased to 29 and 33 units, respectively, after 76 weeks of storage. The worst value obtained for opened RT sample is expected, as H₂O₂ is a photo oxidizing reagent that could induce the degradation of rubber in the presence of light [11]. Chilled sample showed better PRI value with time when it showed only a slight increased from 40 to 49 units with storage. For the heated sample, the PRI value was uncertain with no specific trend along the storage study, but the value was slight reduced to 42 units after 76 weeks of storage.

Overall, the PRI value was affected by the reactive agents which was contradict with the Mooney viscosity. This may be attributed by the heating factor during PRI measurement that led to rapid degradation in the presence of oxygen [12].

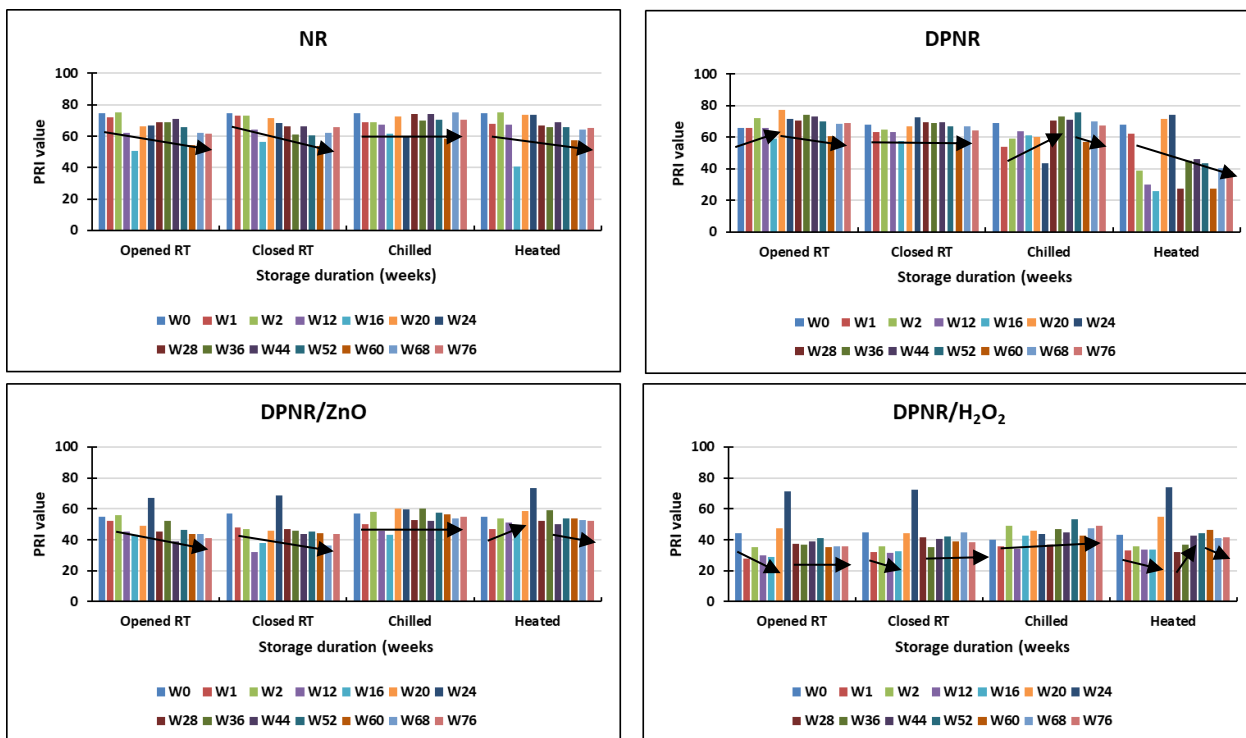


Fig. 4. Plasticity index of NR and DPNRs samples against time at various storage conditions

3.3 Gel Content Determination

Figure 5 shows the gel content of NR and DPNRs samples that were stored at different storage conditions. For NR, the gel after the drying process was 28.8%. Opened RT sample showed an increasing trend and reached 77.6% at week 60 before start to decrease to 50.0% at the end of storage study. The increasing of gel content is expected due to crosslinking reactions of rubber chains with proteins and other abnormal groups such as aldehyde and epoxide groups, which are exist in the rubber molecule. The presence of aldehyde group forms gel via aldol condensation reaction, while ring opening reaction of epoxide group with amino acid or protein was presumed to cause crosslink of rubber chains [13]. Meanwhile the decrease is expected due to degradation of rubber chains that concurrently occurred through oxidation and 'ene' reactions [14-16]. At one point when the chain breaking was greater than chain connection, hence the gel started to reduce as observed in this study.

Similar trend was observed for closed RT of NR sample when the gel increased to 64.5% at week 28 before showed a decreasing trend to 42.0% at week 76. For the chilled sample, the gel content increased to 73.4% at week 60 before decreased to 53.1% at week 76. The increasing trend at the earlier study was also observed for heated sample but it reached maximum value of 75.5% at week 20 before start to decrease and reach 49.0% at week 76. The decrease is much earlier compared to other conditions could be due to the occurrence oxidation in rubber was higher in the presence of heat. In the presence of heat, oxidative of NR could occur when oxygen and water absorbed with the proteins could be converted to hydroxyl radical and oxygen radical, respectively. These reactive species may attack natural rubber and break its chains to generate hydroxy and formyl groups [17].

The gel content of DPNR sample significantly decreased compared to the NR. This due to reduction of entanglement between protein and rubber molecules [18,19]. This result supports the finding that Mooney viscosity was also decreased for DPNR sample. The gel content of DPNR after the drying process was 4.2%. For opened RT sample, the gel content increased to 7.9% at week 68

before slightly decreased to 4.9% at week 76. Highest increased of gel content for opened RT sample could be from the abnormal groups in NR such as formyl group and epoxy group that give rise to unexpected reactions, which then resulting in crosslinking between NR chains in the presence of light [20-22]. For closed RT and chilled samples, the gel content almost stable for the whole duration studied. But for heated sample, the gel content showed up and down trends during the study duration and gave gel of 1.3% at week 76.

The presence of ZnO in the DPNR sample reduced the gel content below 5% throughout the study period. The gel content of fresh sample was 3.7%. The increasing and decreasing trends were very small for all conditions studied. However, the heated sample gave the lowest amount of gel throughout the study period. The presence of trace amounts of ZnO in the sample could act as a catalyst and hence accelerates the gel breakdown [23].

Among the samples studied, the lowest gel content was obtained from DPNR/H₂O₂ sample. The gel content after the drying process was 3.1% and almost negligible for the rest of the study. The decrease in gel is expected to be due to the characteristic of H₂O₂ itself as an agent for the decomposition of organic matter including NR [18]. In the absence of protein, the NR chain was susceptible to degradation by H₂O₂, hence reduced its gel by breaking the entanglement parts in the NR chains [24].

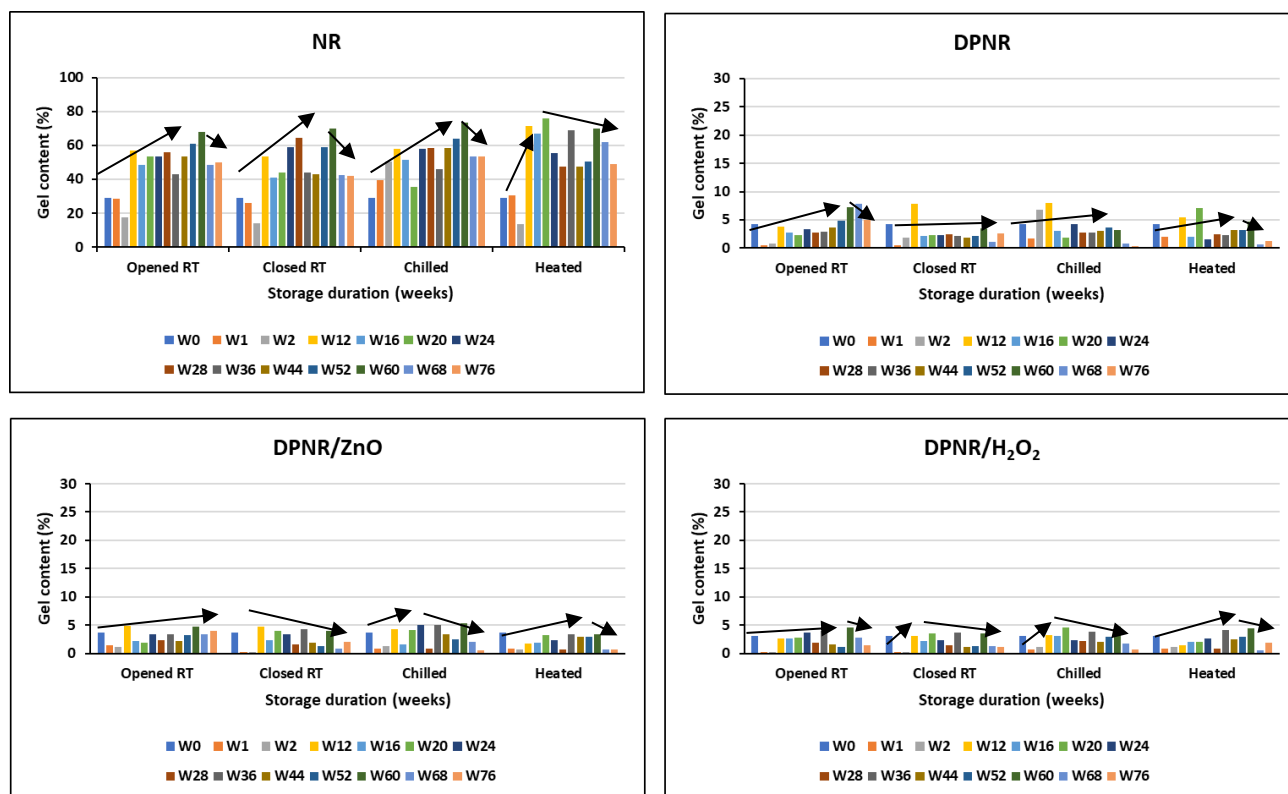


Fig. 5. Gel content of NR and DPNRs samples against time at various storage conditions

3.4 Molecular Weight Determination

The molecular weight of NR refers to the sum of the atomic weights of its polyisoprene chain. Molecular weight is a crucial factor in determining the properties and behaviour of NR, such as their mechanical strength, viscosity, and processing characteristics. In this work, the molecular weight of the sample was determined using GPC, in which the soluble fraction of NR in THF was injected into

the column. Therefore, samples with high gel content may not represent reliable result for the true molecular weight of sample because the gel fraction was filtered out during preparation.

Figure 6 shows the molecular weight of NR and DPNRs studied in this work. The M_n of NR was 4.06×10^5 g/mol after the drying process. The molecular weight of samples that being stored at opened, closed RT and heated conditions decreased for the first few months of the study, before increased and decreased again. The final M_n of opened RT, closed RT and heated samples was 3.43×10^5 , 3.17×10^5 and 3.24×10^5 g/mol, respectively. The instability of the results was expected because it was closely related to the trend of gel content during the storage period as discussed above. However, the M_n of chilled sample showed better stability until week 60 and before it started to decrease and reached 3.10×10^5 g/mol at week 76. Overall, M_n of NR regardless of the storage conditions reduced by approximately 1×10^5 g/mol after 76 weeks of study.

The M_n of DPNR control sample was lower than the NR, where the M_n after the drying process was 1.99×10^5 g/mol. The M_n for all storage conditions increased after a week of storage. For opened RT and chilled samples, the M_n increased to 3.74×10^5 and 3.86×10^5 g/mol, respectively, at week 44. The M_n then decreased to 2.65×10^5 and 2.11×10^5 g/mol, respectively, after 76 weeks of storage. The M_n of closed RT sample reached its maximum value of 4.07×10^5 g/mol at week 20 and reduced to 2.44×10^5 g/mol after 76 weeks.

The M_n of DPNR/ZnO sample after the drying process was 0.92×10^5 g/mol, which was lower than that of the DPNR control sample. All samples, regardless of storage conditions showed the same trends when their M_n increased up to week 44 before decreased with the remaining storage time. The M_n for opened RT, closed RT, chilled and heated samples increased to 3.92×10^5 , 4.88×10^5 , 4.50×10^5 and 4.16×10^5 g/mol, respectively, at week 44. Their M_n then decreased to 2.85×10^5 , 2.68×10^5 , 3.45×10^5 and 2.60×10^5 g/mol respectively, when was measured at week 76. Lower M_n of DPNR/ZnO compared to the DPNR control may be due to the catalytic characteristic of ZnO itself, which could induce for degradation of NR chains [21]. Similar trend was observed for DPNR/H₂O₂ samples when the M_n increased until week 44 before decreased toward to the end of study.

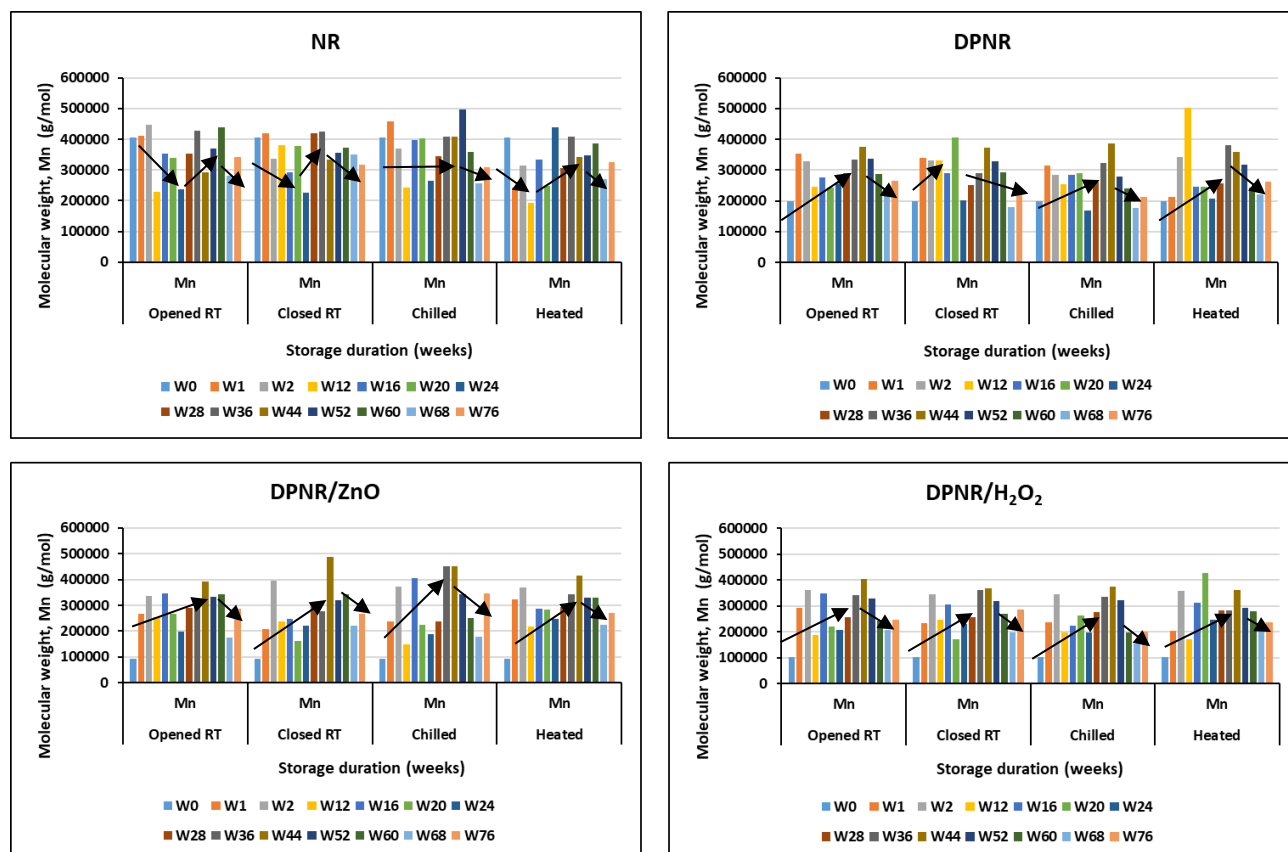


Fig. 6. Molecular weight of NR and DPNRs against time at various storage conditions

4. Conclusions

The properties of NR and DPNRs have been found to change with time, but the severity of the change depends on several factors such as light, temperature and contaminants. In this study, the properties of NR over time were more constant compared to DPNR in all observed conditions. Removal of protein from NR has reduced its ability to maintain its properties during storage. However, these changes can be minimized by storing the rubber in closed and cool rooms. The presence of light and heat would accelerate the degradation of rubber, thereby affecting its properties. The presence of ZnO and H₂O₂ significantly affects the properties of DPNR especially in the opened and heated conditions. It is hoped that the findings obtained in this work could be referred as a guideline for DPNR production and storage to maintain the quality.

Acknowledgement

Authors would like to acknowledge the technical and financial support provided by the Malaysian Rubber Board under the SEAC grant no. S21UPIB 0751.

References

- [1] Berthelot, Karine, Sophie Lecomte, Yannick Estevez, and Frédéric Peruch. "Hevea brasiliensis REF (Hev b 1) and SRPP (Hev b 3): An overview on rubber particle proteins." *Biochimie* 106 (2014): 1-9. <https://doi.org/10.1016/j.biochi.2014.07.002>
- [2] Nawamawat, Kanjane, Jitladda T. Sakdapipanich, and Chee C. Ho. "Effect of deproteinized methods on the proteins and properties of natural rubber latex during storage." In *Macromolecular Symposia*, vol. 288, no. 1, pp. 95-103. Weinheim: WILEY-VCH Verlag, 2010. <https://doi.org/10.1002/masy.201050212>
- [3] Ng, Yu Tong. "RRIM test methods for standard Malaysian rubbers." (1992).

- [4] Okieimen, F. E., and A. K. Akinlabi. "Processing characteristics and physicochemical properties of natural rubber and liquid natural rubber blends." *Journal of applied polymer science* 85, no. 5 (2002): 1070-1076. <https://doi.org/10.1002/app.10666>
- [5] Yunyongwattanakorn, Jintana, and Jitladda T. Sakdapipanich. "Physical property changes in commercial natural rubbers during long term storage." *Rubber chemistry and technology* 79, no. 1 (2006): 72-81. <https://doi.org/10.5254/1.3547930>
- [6] Nun-anan, Phattarawadee, Suwaluk Wisunthorn, Skulrat Pichaiyut, Chatchamon Daengkanit Nathaworn, and Charoen Nakason. "Influence of nonrubber components on properties of unvulcanized natural rubber." *Polymers for Advanced Technologies* 31, no. 1 (2020): 44-59. <https://doi.org/10.1002/pat.4746>
- [7] Sansatsadeekul, Jitlada, Jitladda Sakdapipanich, and Porntip Rojruthai. "Characterization of associated proteins and phospholipids in natural rubber latex." *Journal of bioscience and bioengineering* 111, no. 6 (2011): 628-634. <https://doi.org/10.1016/j.jbiosc.2011.01.013>
- [8] Bonfils, Frédéric, Jean-Claude Laigneau, Souleymane Sylla, and J. Sainte Beuve. "DSC valuation of PRI of raw natural rubber." *Journal of applied polymer science* 79, no. 13 (2001): 2354-2359. [https://doi.org/10.1002/1097-4628\(20010328\)79:13<2354::AID-APP1044>3.0.CO;2-S](https://doi.org/10.1002/1097-4628(20010328)79:13<2354::AID-APP1044>3.0.CO;2-S)
- [9] Payungwong, Narueporn, Surakit Tuampoemsab, Porntip Rojruthai, and Jitladda Sakdapipanich. "The role of model fatty acid and protein on thermal aging and ozone resistance of peroxide vulcanized natural rubber." *Journal of Rubber Research* 24, no. 4 (2021): 543-553. <https://doi.org/10.1007/s42464-021-00100-z>
- [10] Tuampoemsab, S., and J. Sakdapipanich. "Role of naturally occurring lipids and proteins on thermal aging behaviour of purified natural rubber." *KGK Kautschuk Gummi Kunststoffe* 60, no. 12 (2007): 678-684.
- [11] Liao, Chih-Hsiang, and Mirat D. Gurol. "Chemical oxidation by photolytic decomposition of hydrogen peroxide." *Environmental science & technology* 29, no. 12 (1995): 3007-3014. <https://doi.org/10.1021/es00012a018>
- [12] Van Amerongen, G. J. "Oxidative and nonoxidative thermal degradation of rubber." *Rubber Chemistry and Technology* 29, no. 3 (1956): 857-879. <https://doi.org/10.5254/1.3542600>
- [13] Tanaka, Yasuyuki, and Lucksanaporn Tarachiwin. "Recent advances in structural characterization of natural rubber." *Rubber chemistry and technology* 82, no. 3 (2009): 283-314. <https://doi.org/10.5254/1.3548250>
- [14] Nor, Hussin Mohd, and John R. Ebdon. "Telechelic liquid natural rubber: A review." *Progress in polymer science* 23, no. 2 (1998): 143-177. [https://doi.org/10.1016/S0079-6700\(97\)00028-2](https://doi.org/10.1016/S0079-6700(97)00028-2)
- [15] Kuczkowski, Joseph A. "Stabilization of raw dienic synthetic rubber polymers." *Rubber chemistry and technology* 84, no. 3 (2011): 273-295. <https://doi.org/10.5254/1.3592280>
- [16] Ng, Howard C., and James E. Guillet. "Photochemistry Of Cis-Polyisoprene And Its Singlet Oxygen Adduct." *Photochemistry and Photobiology* 28, no. 4-5 (1978): 571-576. <https://doi.org/10.1111/j.1751-1097.1978.tb06971.x>
- [17] Yamamoto, Yoshimasa, Siti Nadiah Binti Norulhuda, Phan Trung Nghia, and Seiichi Kawahara. "Thermal degradation of deproteinized natural rubber." *Polymer Degradation and Stability* 156 (2018): 144-150. <https://doi.org/10.1016/j.polymdegradstab.2018.08.003>
- [18] Rolere, Sébastien, Céline Bottier, Laurent Vaysse, Jérôme Sainte-Beuve, and Frédéric Bonfils. "Characterisation of macrogel composition from industrial natural rubber samples: Influence of proteins on the macrogel crosslink density." (2016). <https://doi.org/10.3144/expresspolymlett.2016.38>
- [19] Amnuayporn Sri, S., A. Nimpaboon, and J. Sakdapipanich. "Role of phospholipids and proteins on gel formation and physical properties of NR during accelerated storage." *Kgk Kautschuk Gummi Kunststoffe* 62, no. 3 (2009): 88.
- [20] Ibrahim, Suhawati, Nadras Othman, and Hanafi Ismail. "Degradation of natural rubber latex." *Natural rubber: properties, behavior and applications* (2016): 105-136.
- [21] Allen, P. W., and G. M. Bristow. "The gel phase in natural rubber." *Journal of Applied Polymer Science* 7, no. 2 (1963): 603-615. <https://doi.org/10.1002/app.1963.070070217>
- [22] Chaikumpollert, Oraphin, Kewwarin Sae-Heng, Osamu Wakisaka, Akio Mase, Yoshimasa Yamamoto, and Seiichi Kawahara. "Low temperature degradation and characterization of natural rubber." *Polymer Degradation and Stability* 96, no. 11 (2011): 1989-1995. <https://doi.org/10.1016/j.polymdegradstab.2011.08.010>
- [23] Singh, Dheerendra, Prafull Patidar, Anuradda Ganesh, and Sanjay Mahajani. "Esterification of oleic acid with glycerol in the presence of supported zinc oxide as catalyst." *Industrial & Engineering Chemistry Research* 52, no. 42 (2013): 14776-14786. <https://doi.org/10.1021/ie401636v>
- [24] Ibrahim, Suhawati, Rusli Daik, and Ibrahim Abdullah. "Functionalization of liquid natural rubber via oxidative degradation of natural rubber." *Polymers* 6, no. 12 (2014): 2928-2941. <https://doi.org/10.3390/polym6122928>