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Tensile Properties of Pre-vulcanised Natural Rubber Latex Films via Hybrid Radiation and Peroxide Vulcanisations

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Radiation pre-vulcanised natural rubber latex (RVNRL) prepared by using gamma irradiation technique has many advantages over the conventionally prepared sulphur pre-vulcanised natural rubber latex (SPVL). Despite the fact that many potential latex dipped products can be made from RVNRL, little effort was made to fully commercialise the products because of the inferior strength of RVNRL products compared to SPVL products. An attempt was made to improve the tensile strength of RVNRL by combining both radiation and peroxide vulcanisation in order to ensure that the products will not tear or fail, and has sufficient stretch. Hexanediol diacrylate (HDDA) plays the main role as sensitizer during radiation vulcanisation and tert-butyl hydroperoxide (t-BHPO) as the co-sensitizer in peroxide vulcanisation. Pre-vulcanised natural rubber latex dipped films via hybrid radiation and peroxidation vulcanisations obtained showed tensile strength of 26.7 MPa, an increment of more than 15% compared to controlled film (22.5 MPa). Besides, the crosslink percentage of the rubber films also showed around 5% increment from 90.7% to 95.6%.

Keywords: RVNRL, vulcanisation, irradiation, latex

I. INTRODUCTION

One of the major contributors to Malaysia's national income is rubber and latex-based products. Based on Natural Rubber Statistics 2017 report (Malaysian Rubber Board, January-March 2017), Malaysia's manufactured rubber goods sales from year 2008 to 2017 showed a very encouraging increment, especially on rubber gloves product (Figure 1). From the data, it is shown that in 2016 the sale of rubber gloves alone contributed RM10.49 billion to national income, an increment of 1.2% from previous year. Therefore, a continuous research and development in latex technology is essential to guarantee the expansion of this positive sales performance.

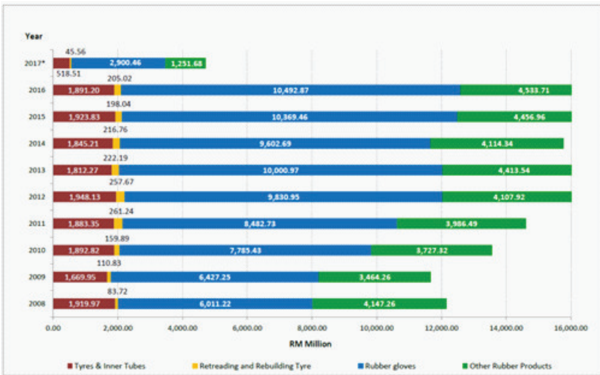

Figure 1. Sales value of Malaysia manufactured rubber goods from 2008-2017 (RM million)

In rubber glove production, it is known that natural rubber latex needs to be vulcanised prior to use in rubber glove production. At present, there are three major types of vulcanisation

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methods being used in natural rubber latex industries; sulphur, radiation, and peroxide vulcanisations. Generally, rubber goods produced from sulphur vulcanised latex possess the most superior tensile strength among the three vulcanisation methods. However, sulphur vulcanisation has a major drawback in regards to its by-products, i.e. nitrosamines and nitrosatables. These unwanted by-products are carcinogenic materials which may cause cancer and chemical allergies (Makuuchi, 2003; Sofian *et. al.*, 2015a).

Meanwhile, radiation vulcanisation of natural rubber latex (RVNRL) and peroxides vulcanisation of natural rubber latex (PVNRL) have several advantages over the conventional sulphur vulcanisation such as less or absence of toxicity, free from nitrosamines and accelerator induced allergies, low in cytotoxicity, and cleaner process (Makuuchi, 2003; Pairu *et. al.*, 2016; Sofian *et. al.*, 2015a; Wan Manshol, 2004). These are crucial properties to be possessed by many healthcare related rubber products, particularly protective gloves, catheters and other medical and hospital supplies. For such uses, it is important that products are free of contaminants, toxic and carcinogenic components to avoid harmful effects in human beings.

Being sulphur-free, only RVNRL is currently made fully utilised for commercial production of finger cots and finger stalls of sulphur-free grade. Though many other potential products like examination gloves, surgical gloves, balloons, dental dams, and condoms could be made from RVNRL and PVNRL, the up scaling activity for commercialisation has not been initiated. This is mainly due to the inferior tensile strength of RVNRL and PVNRL products (<22 Mega Pascal, MPa) compared to SPVL products (>24 MPa). ASTM D3577-01a (Standard Specification for Rubber Surgical Gloves) clearly stated that minimum requirement of tensile strength for surgical glove has to be 24 MPa. The strength factor of surgical gloves is important for its quality and performance. Tensile strength testing of surgical gloves is performed as per the international standards of ASTM D412 for its acceptance worldwide. The standardisation ensures that the surgical glove will not tear or fail, and has sufficient stretch. Intensive research and development work on RVNRL by Malaysian Nuclear Agency and PVNRL by Malaysian Rubber Board (MRB) has been carried out since 1980's to achieve perfection in both processes. However, all the efforts have been in vain when the tensile strength of end products failed to achieve a minimum of 24 MPa (Sofian *et. al.*, 2015b). It is believed that the inferiority in mechanical properties of RVNRL and PVNRL is due to the difference in vulcanisation structure and its bond energy (Makuuchi, 2003).

Since tensile value of RVNRL and PVNRL is quite low and still inferior compared to the SPVL, it has attracted many interests on the latex modification to improve the properties of these lattices. Hybrid vulcanisation method which consists of radiation and peroxidation vulcanisation is one of the modification systems proposed to improve the properties of the vulcanised latex (Sofian *et. al.*, 2007; Chyagrit, 1996). It is the aim of the present study to investigate the effect of organic peroxide as a co-sensitizer system in hybrid radiation and peroxidation vulcanisation on mechanical properties and gel content of the resulted latex dipped films. The outcome of this study may help to diversify and encourage the use of radiation pre-vulcanised natural rubber latex in Malaysia and abroad, and also likely to support the Economic Transformation Program (ETP) since one of the Entry Point Projects (EPPs) in ETP is the commercialisation of new generation latex grades.

II. MATERIALS AND METHODS

A. Materials

The latex utilised in this work was of a high ammonia type (HA latex) supplied by Revertex (M) Sdn. Bhd., Malaysia. The sensitisers used were Hexanediol diacrylate (HDDA) supplied by Allnex, China, and tert-butyl hydroperoxide (*t*-BHPO) supplied by Fluka. The stabiliser used was potassium laurate supplied by Tiarco Chemical (M) Sdn. Bhd., Malaysia and the antioxidant used was Aquanox Lp supplied by Aquaspersion (M) Sdn. Bhd., Malaysia. These materials were used as received.

B. Sample preparation

A typical latex compounding formulation for RVNRL (Wan Manshol *et. al.*, 1993) preparation using a co-sensitiser system is given in Table 1. The sensitiser, stabiliser, antioxidant, and water were first prepared into an emulsion before slowly added into the latex with gentle stirring (Sofian *et. al.*, 2007; Wan Manshol *et. al.*, 1993). Once the addition of the emulsified materials was completed, the latex mixture was left stirring for a couple of hours. It was then transferred into 1 litre capacity screw capped plastic container and irradiated with gamma rays from a cobalt-60 source for a dose of 12 kGy. After irradiation, the latex is now called RVNRL was made into film by coagulant dipping method.

The experiment was repeated by preparing an emulsion from t-BHPO (co-sensitiser) together with the sensitiser, stabiliser, antioxidant, and water as formulated in Table 2.

C. Irradiation

The latex formulations were irradiated using gamma rays from Co-60 isotope at MINTec-Sinagama Plant, Malaysian Nuclear Agency. The activities of Co-60 are 447000 Curie with dose rate of 2.08 kGy/hr.

D. Measurement of tensile properties

Specimens for tensile testing were prepared using the coagulant dipping method (Pairu *et al.*, 2016). A glass plate was immersed in the coagulant and then placed in an oven at 100^{o}C to partially dry the coagulant. It was then immersed in the latex compound for 20s. The wet gel was allowed to consolidate at 100^{o}C for 1 minute, and followed by leaching in distilled water at 60^{o}C for 5 minutes. The latex film was finally dried at 100^{o}C for 30 minutes and subjected to tensile test using Universal Testing Machine Instron 5564 in accordance to ASTM D412. The latex films samples were cut into dumbbell shape test pieces (Figure 2). Five samples were used for tensile test and a median value was taken as the final result.

E. ATR spectroscopy

In this study, FTIR spectroscopy analysis was carried out using Bruker's Tensor II Platinum Attenuated total reflection (ATR) spectropho-

Table 1. Compounding formulation of standard RVNRL (control)

Materials	Part per hundred rubber (PPHR)
NR Latex (62% TSC)	100
Stabilizer	0.06
HDDA	2.50
Antioxidant	2.50
Water	Add to 52% TSC

Table 2. Compounding formulation of RVNRL with co-sensitiser

Materials	Part per hundred rubber (PPHR)
NR Latex (62% TSC)	100
Stabilizer	0.06
HDDA	2.50
t-BHPO*	0.10
Antioxidant	2.50
Water	Add to 52% TSC

*0.1, 0.3 and 0.5 pphr of *t*-BHPO

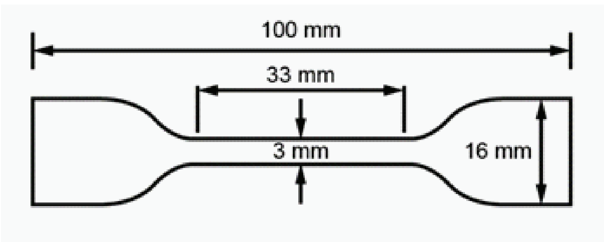


Figure 2. Dimension of dumbbell cut

tometer. Range of wavenumber employed was 4000 – 500 cm^{-1}.

F. Determination of gel content

Gel content of the radiation crosslinked samples were determined by extracting the samples in boiling samples in the extraction of samples in toluene for 8 hours using Soxhlet apparatus (Jayasuria *et. al.*, 2001; ASTM D3616-95, 2014). The extracted samples were dried in an oven at 70^{o}C till constant weight was achieved. The gel fraction was calculated as Eq. 1:

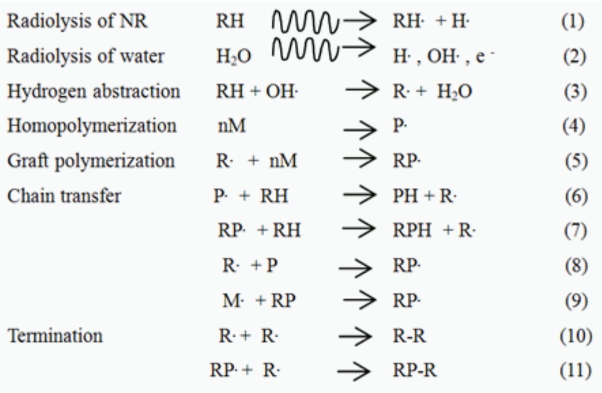
$$Gel\ Content, \% = \frac{w_1}{w_0} x100 \qquad (1)$$

where w_0 and w_1 are the weights of the dried samples before and after extraction, respectively.

III. RESULTS AND DISCUSSION

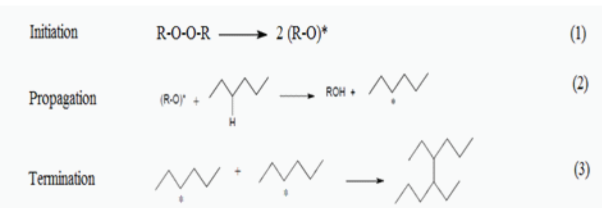
Makuuchi (2003) has proposed a general mechanism of acceleration of monomer in the process of radiation vulcanisation of natural rubber latex as shown in Scheme 1. In such a mechanism, RH, M and P will represent natural rubber, monomer and polymer respectively.

As for the peroxide vulcanisation, van der Hoof (1963) has proposed a general mechanism of initiation, propagation and termination of peroxide species as shown in Scheme 2. Initiation is induced by homolytic decomposition of a peroxide species, which engenders the radical re-



Scheme 1. General mechanism acceleration of monomer in the process of radiation vulcanisation of natural rubber latex (Makuuchi, 2003)

action. The peroxide decomposition is normally triggered by heat; however, in this experiment irradiation has been used for that purpose. During the propagation step, alkoxy radical abstracts a hydrogen atom from a polymer chain leading to a radical on the polymer molecule. This reaction is bimolecular as two species are involved, i.e. the alkoxy radical and the polymer chain. Finally, in the termination step two radicals on adjacent polymer chains couple to form a carbon-carbon covalent crosslink.



Scheme 2. General mechanism of peroxide vulcanization

Modulus and tensile strength values are considered as the commercial importance parameter, typically in gloves production. Modulus values are always referred as the degree of crosslinking in the films whilst tensile strength value is referred to the extent of the film undergo stress (Roslim *et. al.*, 2015). Figure 1 shows the median value for tensile strength, modulus at 500% and modulus at 700% from four different samples with 0.0 (control), 0.1, 0.3 and 0.5 pphr of *t*-BHPO respectively. From the diagram, it is obvious that RVNRL sample with 0.1 pphr *t*-BHPO gives higher tensile strength (26.69 MPa) compared to the control (22.54 MPa). The increment in tensile strength, modulus at 500% and modulus at 700% is due to the enhancement of the intra-particle crosslink density (chemical crosslinking) induced by radiation and monogeneity of the vulcanisation from the radiation and peroxide vulcanisation (Chyagrit, 1996; Makuuchi, 2003; Ma'zam *et. al.*, 2006).

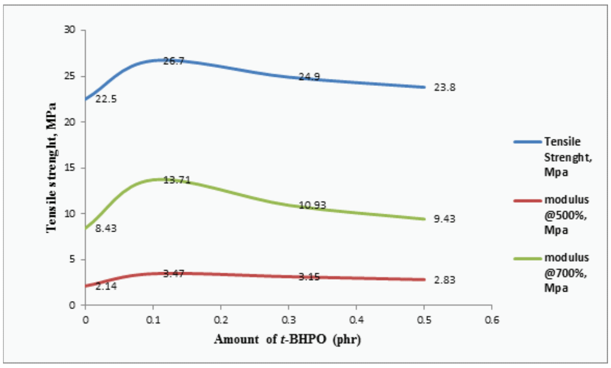


Figure 3. Mechanical properties of hybrid RVNRL-peroxide (median value from tensile test)

Figure 4 shows the relationship between samples with different amounts of t-BHPO with elongation at break value for RVNRL films. As shown, the extent of elongation at break value decreased with the increasing amount of t-BHPO, indicating increases in crosslink density of the polymer. Alliger (1978) described that elongation at break value will decrease with the increasing of crosslink density and it can be determined via gel fraction experiment. The results for this experiment were shown in Figure 6.

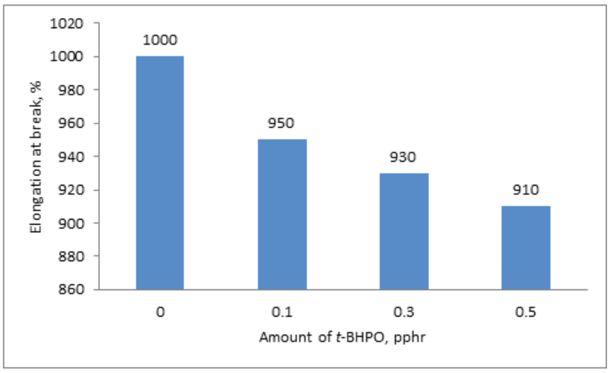


Figure 4. t-BHPO effect on elongation at break of RVNRL films

It is also observed that upon reaching the highest value of tensile strength and modulus at 0.1 pphr of t-BHPO, tensile properties of the irradiated samples started to decrease with higher level of t-BHPO. It is believed that there are several factors leading to this observation. One of the identified factors is irradiation period. The gamma irradiation facility used in this study was equipped with Cobalt-60 source that has a dose rate of 2.058 kGy/hour. It took about 6 hours to irradiate the samples in order to achieve absorbed dose of 12 kGy. It is believed that, besides vulcanisation or crosslinking, both HDDA and peroxide will also be consumed by radiation polymerisation and hydrolysis upon irradiation. Thus, for a longer irradiation period, the actual concentration of HDDA and peroxide decreases during irradiation and rate of vulcanisation become lower as not all of both substances are fully utilised for radiation vulcanisation (Sofian *et. al.*, 2015b).

Another factor is the inter-particle entanglement (physical crosslinking) that is decrease with the increasing dose. The inter-particle entanglements are depending on the free rubber chain ends at the surface of each latex particle. These chains interpenetrate during film formation and contribute to the strength of the film by means of entanglements. The length of free rubber chain ends decreases with the increasing of irradiation dose because it is equivalent to molecular weight between crosslink (Makuuci, 2003). Thus, the tensile strength, modulus at 500% and modulus at 700% of the hybrid RVNRL-peroxide latex film increase up to maximum level and then decrease with the increasing dose.

This above claim is supported by infra-red spectroscopy in Figure 3a to 3d, which showed that there is no sign of residue HDDA and/or peroxide found in RVNRL samples because they are believe to be consumed by radiation polymerization and hydrolysis during the radiation vulcanisation process. According to Diagram 3b and 3c, it can be clearly observed the presence of functional groups of $C-O$ and $C=O$ at wavelength ranges 1181-1192 and 1719 cm^{-1} respectively. However, there is no sign of functioning group of $C-O$ and $C=O$ in the RVNRL spectrums in Figure 3d.

According to Figure 6, it is observed that the addition of 0.1 pphr t-BHPO as co-sensitizer helped to achieve higher crosslink percentage; 95.5% compared with the controlled sample which is 90.7 %. However, it also showed that the crosslink percentage starts to decrease as the amount of t-BHPO increase. Explanation for this observation is similar to tensile properties above.

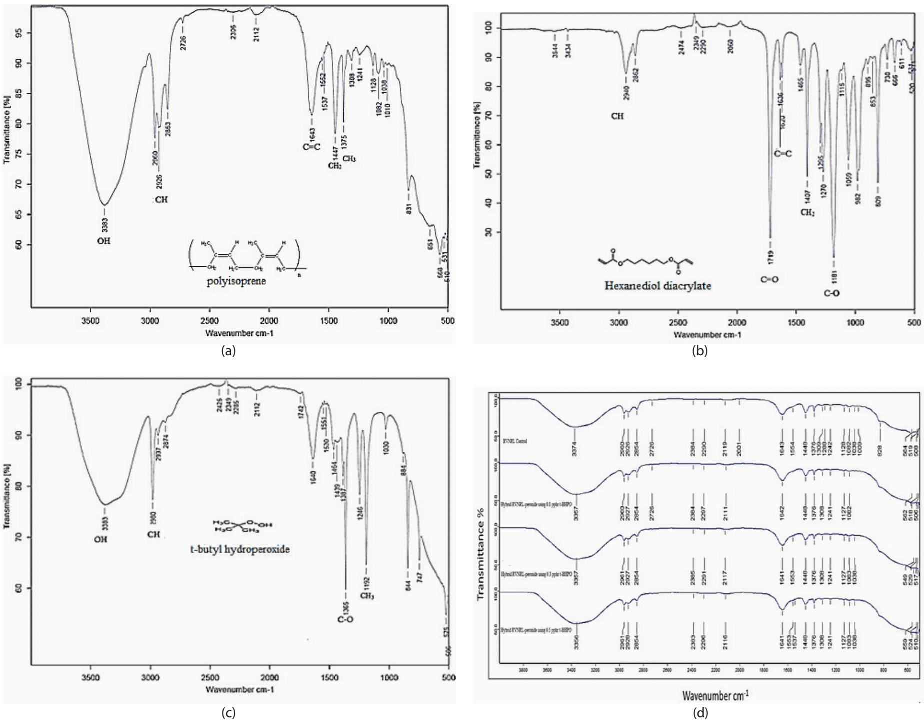


Figure 5. (a) Infra-red spectrum for polyisoprene (b) Infra-red spectrum for hexanediol diacrylate (c) Infra-red spectrum for tert-butyl hydroperoxide (d) Infra-red spectrums for RVNRL at various amount of t- BHPO

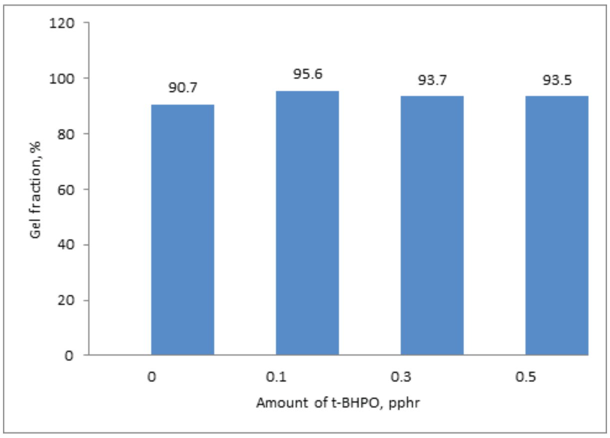


Figure 6. Gel fraction of RVNRL with different amount of *t*-BHPO

IV. CONCLUSION

Organic peroxide, i.e. *t*-BHPO, was found to be an effective co-sensitiser in hybrid radiation and peroxide vulcanisations. It is due to higher level of monogeneity in the hybrid vulcanisation. Irradiation of latex formulations based on 2.5 pphr of hexanediol diacrylate (HDDA) as sensitiser, 0.1 pphr of tert-butyl hydroperoxide (*t*-BHPO) as co-sensitiser and 2.5 pphr of Aquanox LP as an antioxidant at radiation dose of 6 kGy can produced rubber film with tensile strength of 26.7 MPa with crosslink percentage of 95.6 % and elongation at break of 950%.

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VI. REFERENCES

[1] Alliger, G. & Sjothun, I. J. (1978) Vulcanization of Elastromers. New York, *Robert E. Krieger Publishing Company.*

[2] ASTM D3577-01a. (2001) Standard Specification for Rubber Surgical Gloves, *ASTM International*, West Conshohocken, PA.

[3] ASTM D3616-95 (2014) Standard Test Method for Rubber—Determination of Gel, Swelling Index, and Dilute Solution Viscosity, *ASTM International*, West Conshohocken, PA.

[4] B.M.E. van der Hoff (1963) Reactions between Peroxide and Polydiolefins, *Ind. Eng. Chem. Prod. Res. Dev.* 2 (273).

[5] Chyagrit, S. U. (1996) Development of An Efficient Process For Radiation Vulcanization Of Natural Rubber Latex Using Hydroperoxide With Sensitizer. *The Second International Symposium On RVNRL*, Malaysia, pp. 46-49.

[6] Hossain, K. M. Z., Sharif, N. C, Dafader, M. E., Haque & Chowdhury, S. (2013) Physicochemical, Thermomechanical, and Swelling Properties of Radiation Vulcanised Natural Rubber Latex Film: Effect of Diospyros peregrina Fruit Extracts. Hindawi Publishing Corporation, *Polymer Science*, Volume 2013, Article ID 621352.

[7] Jayasuria, M. M., Makuuchi, K. & Yoshi, F. (2001) Radiation vulcanization of natural rubber latex using TMPTA and PEA. *European Polymer Journal*, 37, pp. 93-98.

[8] Makuuchi, K. (2003) An Introduction to Radiation Vulcanization of Natural Rubber Latex. *Bangkok T.R.I. Global Co., Ltd.*

[9] Malaysian Rubber Board (2017) Natural Rubber Statistics 2017 (January- March). Credible Rubber Pricing Systems. viewed 15 June 2017. <www.lgm.gov.my/nrstat/nrstats2017_(Jan-Mar)_pword.pdf>.

[10] Ma'zam, M. S. & Wan Manshol, W. Z. (1996) Extractable Protein Content of Radiation Vulcanised Natural Rubber Latex Films. A Paper Presented at the Second International Symposium on RVNRL, Kuala Lumpur, Malaysia.

[11] Ma'zam, M. S., Darji, D. & Mok, K. L. (2006) Recent development of peroxide prevulcanized NR latex. *Proceeding of 3rd International Rubber Conference & Exhibition 2006*, pp. A3 1-35.

[12] Pairu, I., Rusli, D. & Wan Manshol, W. Z. (2016) Thermal and mechanical properties of gamma-irradiated prevulcanized natural rubber latex/low nitrosamines latex blends. *Radiation Effects and Defects in Solids*, 171(11-12).

[13] Pairu, I., Wan Manshol, W. Z., Chai, C.K. & Mohd, N. M. L. (2011) Radiation Vulcanization of Natural Rubber Latex (RVNRL): A Potential Material for Nuclear Power Plant Gloves. *International Nuclear Information System (INIS)*, 44(50), Report no. INIS-MY—2013-150.

[14] Roslim, R., Jefri, J., Manroshan Singh, J. S., Siti Noor Suzila, M. U. H., Amir Hashim, M. Y. (2015) Characterizing Physical Properties of Peroxide Vulcanized Natural Rubber Latex Films. Trans Tech Publications Ltd., Switzerland, 1134, 236-242.

[15] Sofian, I., Mohd, N. M. L., Syuhada, R., Chai, C. K., Muhammad, K. M. Y., Saiful, O., Najib, M. Z., Hafizuddin, M. & Hasni, M. A. (2015 a) Analysis of Aqueous Extractable Protein in Radiation Prevulcanized Natural Rubber Latex (RVNRL) And Sulphur Prevulcanized Natural Rubber Latex (SVNRL). *International Nuclear Information System (INIS)*, 47(45), Report no. INIS-MY—2016-006.

[16] Sofian, I., Mohd, N. M. L., Syuhada, R., Chai, C. K., Muhammad, K. M. Y., Saiful, O., Najib, M. Z., Hafizuddin, M. & Hasni, M. A. (2015b) Effect of Dose Rate on Radiation Prevulcanized Natural Rubber Latex Tensile Strength and Physical Properties. *International Nuclear Information System (INIS)*, 47(45), Report no. INIS-MY—2016-042.

[17] Sofian, I., Wan Manshol, W. Z., Chai, C.K. & Pairu, I. (2007) Improving on Tensile Strenght and Modulus of Radiation Vulcanization Natural Rubber Latex (RVNRL) by Using *t*-butyl hydroperoxide (BHPO) as Co-sensitizer. *Research Note Malaysian Nuclear Agency* 04/07.

[18] Wan Manshol, W. Z. & Chai C. K. (2000) Preparation and Mechanical Properties of Low Proteins Radiation Vulcanised Natural Rubber Latex. A Paper Presented at MINT R&D Seminar 2000, MINT, Bangi, Selangor, Malaysia.

[19] Wan Manshol, W. Z. & Othman, N. (1996) Determination of Soluble Protein Contents from RVNRL. A Paper Presented at the Second International Symposium on RVNRL, Kuala Lumpur, Malaysia.

[20] Wan Manshol, W. Z.(1992) Radiation Processing of Natural Rubber. A Paper Presented at Kongres dan Seminar Sains dan Teknologi, Kuala Lumpur, Malaysia.

[21] Wan Manshol, W. Z. (1995) Radiation Vulcanisation of Natural Rubber Latex: Applications and Advantages. A Paper Presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, USA.

[22] Wan Manshol, W. Z. (2004) Radiation Vulcanization of Natural Rubber Latex for Environmentally Friendly Latex Products. An Invited Paper Presented at Malaysia Chemical Congress 2004 – International Conference & Exhibition on Macromolecular Science & Its Impact on Industries, Bandar Sunway, Selangor.

[23] Wan Manshol, W. Z., Hafizzuddin, M. & Mohid, N. (1996) Stability of RVNRL upon Storage and the Degradability of its Film Vulcanisates. A Paper Presented at the Second International Symposium on RVNRL, Kuala Lumpur, Malaysia.

[24] Wan Manshol, W. Z., Mohid, N. & Razali, M. Y. (1995) RVNRL A Potential Material In Latex Dipped Products Manufacturing. *Radiat. Phys. Chem.*, 46(4-6), pp. 1019-1023.

[25] Wan Manshol, W. Z., Mohid, N., Hassan, J. & Ma'zam. M. S. (1993) Preparation, Properties and Processability of RVNRL Using Malaysian-Produced Latices. A Paper Presented at the National Executive Management Seminar on Radiation Vulcanisation of Natural Rubber Latex, Bangi, Malaysia.

[26] Wan Manshol, W. Z., Mohid, N., Hasan, J., Noor, W. K. A. M. & Jaafar, Z. (1993) The Preparation of RVNRL Using Malaysian-Produced Latices. *Radiat. Phys. Chem.*, 42(1-3), pp. 101-103.

[27] Woo, J. (2014) Prevulcanised NR Latex – Vulcanization, Advantages and Applications. viewed 25 March 2017. <https://www.linkedin.com/pulse/20140626053655-109089520-prevulcanised-nr-latex-vulcanization-advantages-and-applications>.