

Effect of gamma radiation on the tensile properties of epoxidized natural rubber latex

Chee Keong **Chai**^{*1}, ChantaraThevy **Ratnam**¹, Luqman Chuah **Abdullah**²,

Mohamed Syafiq Shaik **Mohamed Amin**¹, Wan Manshol **Wan Zin**¹

¹Malaysian Nuclear Agency, Bangi, 43000 Kajang, Malaysia

²Department of Chemical and Environmental Engineering, Faculty of Engineering,

Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia

*Corresponding author's phone: +603-89112000

E-mail: chai@nuclearmalaysia.gov.my

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ABSTRACT

Gamma irradiation on epoxidized natural rubber latex, of 25 and 50 mole% epoxidation levels (ENRL-25 and ENRL-50), was carried out with particular attention to the effect of gamma radiation on tensile properties of ENRL. ENRL was irradiated as received with gamma radiation doses ranging from 20 to 160 kGy. Cast films were prepared from irradiated ENRL which were used for determination of tensile properties and gel fraction. Significant increment of modulus and tensile strength, and gradual reduction of elongation at break of ENRL films were observed. ENRL-25 and ENRL-50 showed optimum radiation dose at 80kGy and 60kGy respectively. The gel fraction was found to increase with irradiation. ENRL-25 showed higher tensile properties and gel fraction values than ENRL-50. Such observation was attributed to the presence of more unreacted double bonds in ENRL-25 which participated in the irradiation-induced crosslinking.

Keywords: Epoxidized natural rubber latex, Irradiation, Irradiation-induced crosslinking

1.0 INTRODUCTION

Epoxidized natural rubber (ENR) is a chemically modified natural rubber (NR) by adding oxygen atom to the carbon-carbon double bonds of rubber molecule chains, thereby converting them to oxirane (epoxide) ring. Epoxidation of NR can be done by treating natural rubber latex (NRL) with preformed peroxyacetic or *in-situ* generated peroxyformic acid [1]. The epoxidation level can achieve over 75 mole% without the formation of secondary ring-opened structures if performed under controlled conditions [2]. ENR is claimed to exhibit improved oil resistance, gas impermeability and good wet grip comparable to synthetic rubber [3]. Various studies have been conducted on ENR which include curing [4-8], thermal oxidation [9], reversion [10], and gas permeability [11]. Most studies on ENR that involved vulcanization are based on sulfur vulcanization. Some works on electron beam irradiation of ENR have been reported and found evidence of irradiation-induced crosslinking in ENR [12-13].

All work mentioned above are based on ENR. There are relatively very few studies on ENR in latex form, e.g. epoxidized natural rubber latex (ENRL). Findings of a study on sulfur vulcanization and coagulant dipping of ENRL show that ENRL can be sulfur-vulcanized and coagulant dipping can be used to produce rubber films from compounded ENRL [14]. However, to date, no information has been published on the radiation vulcanization of ENRL to the best knowledge of the authors. In this present work, ENRL was subjected to high-energy irradiation, and followed by determination of tensile properties and gel fraction. The main objective is to determine the effect of high-energy radiation, e.g. gamma radiation, on the tensile properties of ENRL.

2.0 EXPERIMENTAL

2.1 Materials

ENRL with 25% and 50% epoxidation level (ENRL-25 and ENRL-50) were obtained from Malaysian Rubber Board (MRB). The total solid contents of ENRL-25 and ENRL-50 were 47.28% and 35.88% respectively.

2.2 Irradiation and sample preparation

About 1000 g of ENRL-25 and ENRL-50 were sieved with wire mesh and poured into high density polyethylene (HDPE) bottles of 1000 ml capacity. The bottles were irradiated at a gamma irradiation facility in Malaysian Nuclear Agency at a dose range of 20 – 160 kGy at temperature range of 33°C – 37°C. Dose rate was 25Gy/minute. Irradiated ENR latices were poured into glass plate with dimension of 100 mm x 220 mm and left to dry to form cast ENR films with thickness of about 1 mm. ENR films were conditioned in desiccator for at least 16 hours before testing. Dumbbell-shaped samples were cut from the cast ENR films according to ASTM D412.

2.3 Tensile tests

Tensile tests were carried out with a universal testing machine Instron model 5564 in accordance with ASTM D412. Crosshead speed was 500 mm/minute. All the tests were conducted at a controlled temperature of $25 \pm 2^\circ\text{C}$. Tensile tests conducted were modulus at 300% elongation (M300), tensile strength (TS) and elongation at break (EB).

2.4 Gel fraction

ENR films weighing about 0.2 g each were extracted by refluxing with tetrahydrofuran (THF) for 24 hours. Extracted samples were dried to constant weight. Gel fraction was calculated as followed:

$$\text{Gel fraction, \%} = (W_1/W_0) \times 100 \quad \text{- Equation (1)}$$

where W_1 and W_0 are the weight of extracted sample and the weight of sample before extraction respectively.

3.0 RESULTS AND DISCUSSION

3.1 Tensile properties

The effect of gamma radiation on modulus at 300% elongation (M300) of ENRL is shown in Figure 1. It is clear from Figure 1 that M300 of ENRL-25 and ENRL-50 increases with gamma radiation dose. Modulus is an indicator to the stiffness of rubber films, which is directly proportional to crosslink density [15]. Hence, the increase of M300 with radiation dose indicates the increase of crosslink density of ENRL upon irradiation. This shows the evidence of occurrence of irradiation-induced crosslinking in the ENRL. However, ENRL-25 was found to be more brittle than ENRL-50 at radiation dose beyond 100 kGy where ENRL-25 films broke before its elongation reached 300%. Such observation indicates the embrittlement of the ENRL-25 samples due to formation of high extent of radiation-induced crosslinks implying a higher degree of crosslink density was achieved in ENRL-25 as compared to ENRL-50.

The effect of gamma radiation on tensile strength (TS) of ENRL is shown in Figure 2. In general, the TS of both ENRL-25 and ENRL-50 increased with radiation dose, and

declined after reaching a maximum value at an optimum dose. The optimum dose of ENRL-25 and ENRL-50 was 80 kGy and 60 kGy respectively. The increase in TS is attributed to the occurrence of irradiation-induced crosslinking in the latex. The decline of TS beyond the optimum dose is believed to be the consequence of embrittlement of ENRL due to high extent of crosslinking [16]. It was observed that, within the dose range of this experiment, the overall tensile strength of ENRL-25 was higher than ENRL-50. Again, similar to the case of M300, it shows that ENRL-25 is more radiation-sensitive than ENRL-50. Such observation is believed to be attributed to the presence of more unreacted double bonds in ENRL-25 which participated in the irradiation-induced crosslinking.

The effect of gamma radiation on elongation at break (EB) of ENRL is shown in Figure 3. The EB of ENRL reduced gradually with radiation dose. Again, this is associated with radiation-induced crosslinking. As the radiation dose increases, the increasing crosslinks formed in the ENRL reduce segmental mobility of the rubber chain, causing the rubber films to be more brittle [12]. Hence, it causes a gradual reduction of EB with increasing radiation dose.

3.2 Gel fraction

Similar to modulus, gel fraction measurement can be used to estimate the extent of radiation crosslinking of polymers [17]. The effect of gamma radiation on gel fraction of ENRL is shown in Figure 4. It is apparent from Figure 4 that the gel fraction of ENRL increased with radiation dose, where it increased marginally beyond 100 kGy. These results imply the existence of irradiation-induced crosslinking in ENRL. The gel fraction measurements agree with the trend observed for M300 in Figure 1. It is clear from Figure 4 that the gel fraction of irradiated ENRL-25 was higher than irradiated ENRL-50, indicating that a higher crosslink density is achieved in ENRL-25 compared to ENRL-50. This

observation is in agreement with the earlier statement that ENRL-25 is more radiation-sensitive than ENRL-50, which is believed to be attributed to the presence of more unreacted double bonds in ENRL-25 which participated in the irradiation-induced crosslinking.

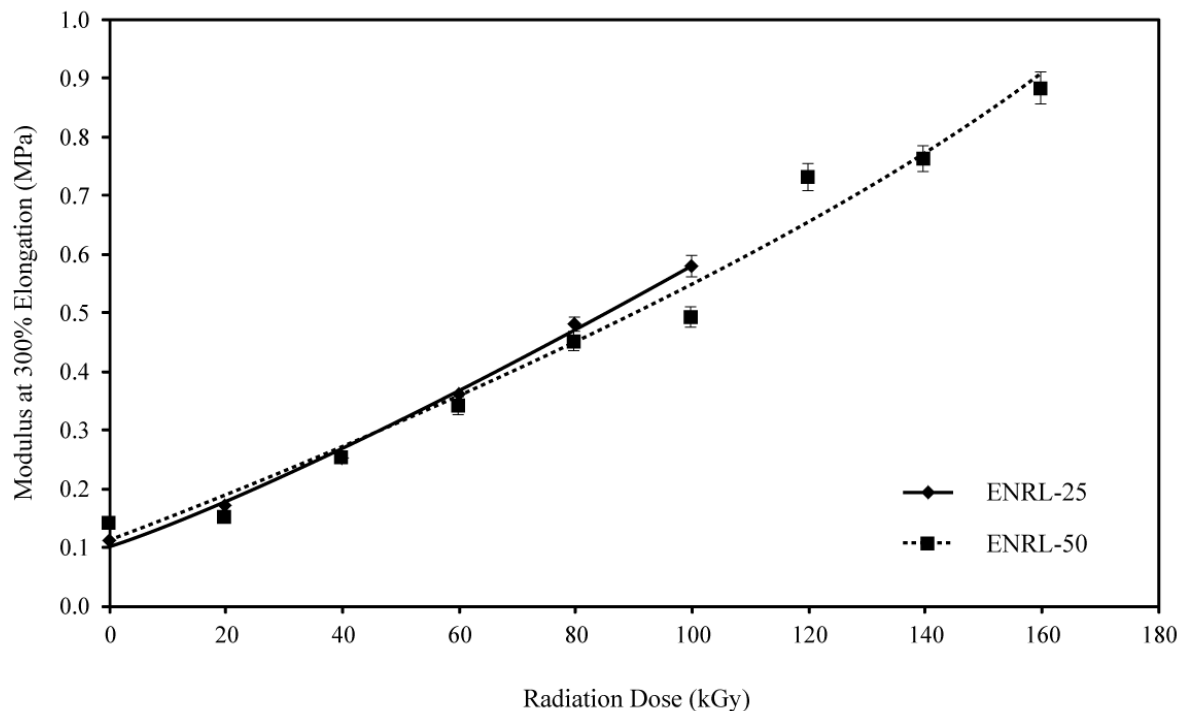


Figure 1: Effect of gamma radiation on modulus at 300% elongation of ENRL

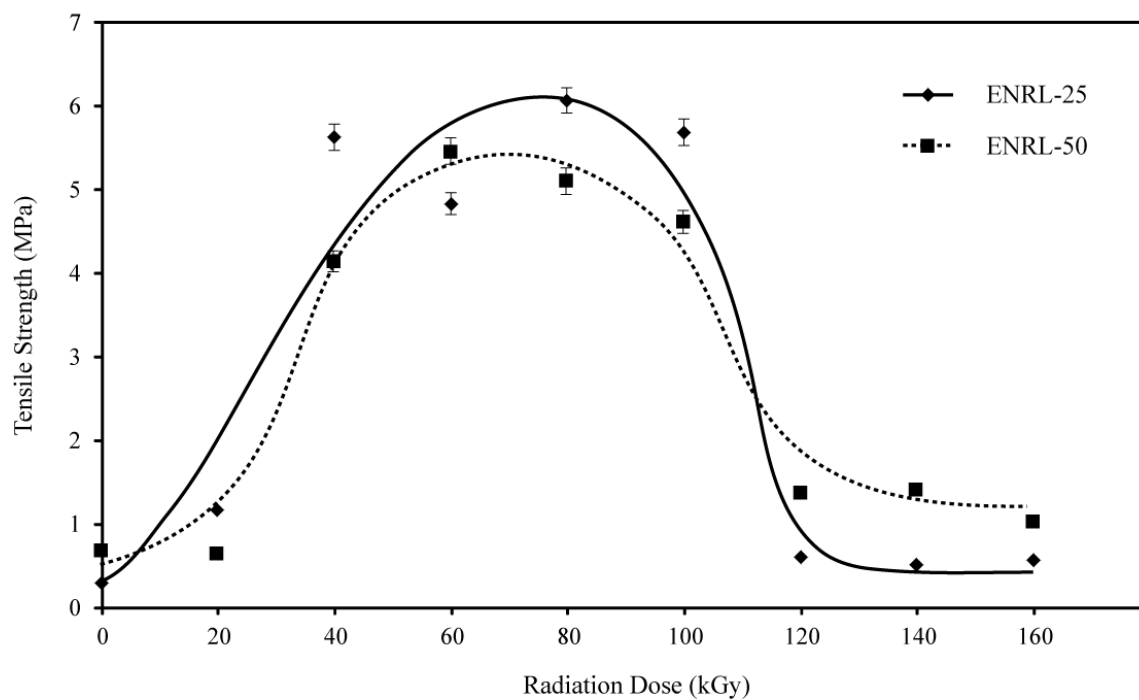


Figure 2: Effect of gamma radiation on tensile strength of ENRL

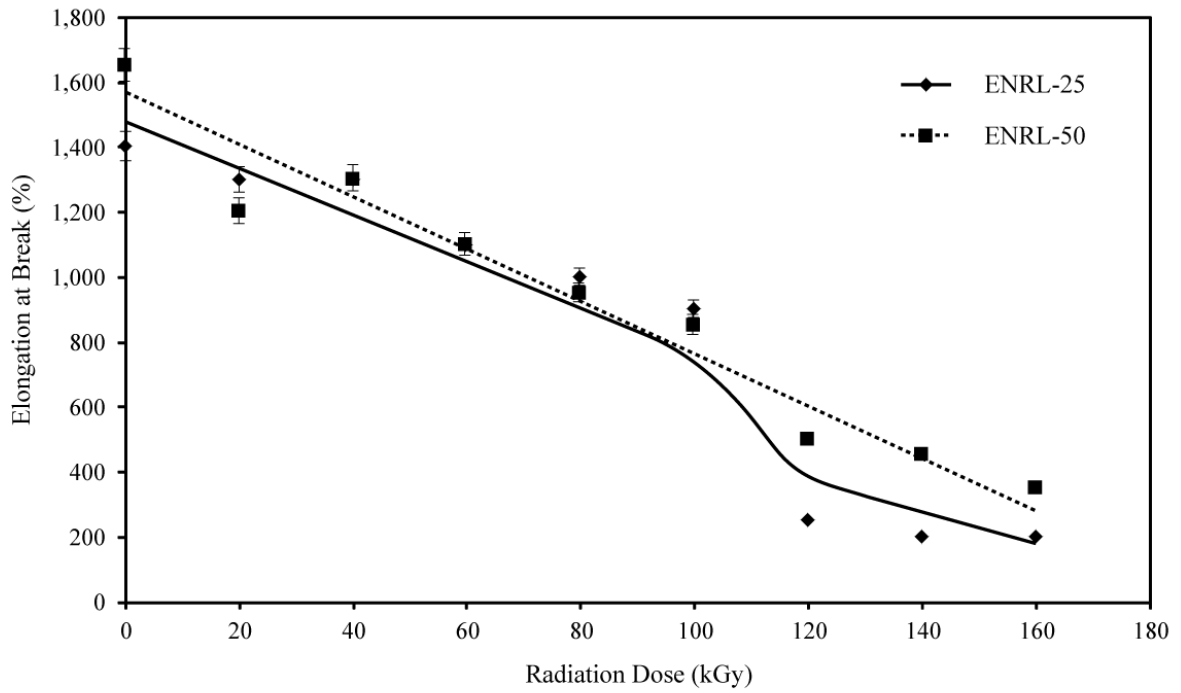


Figure 3: Effect of gamma radiation on elongation at break of ENRL

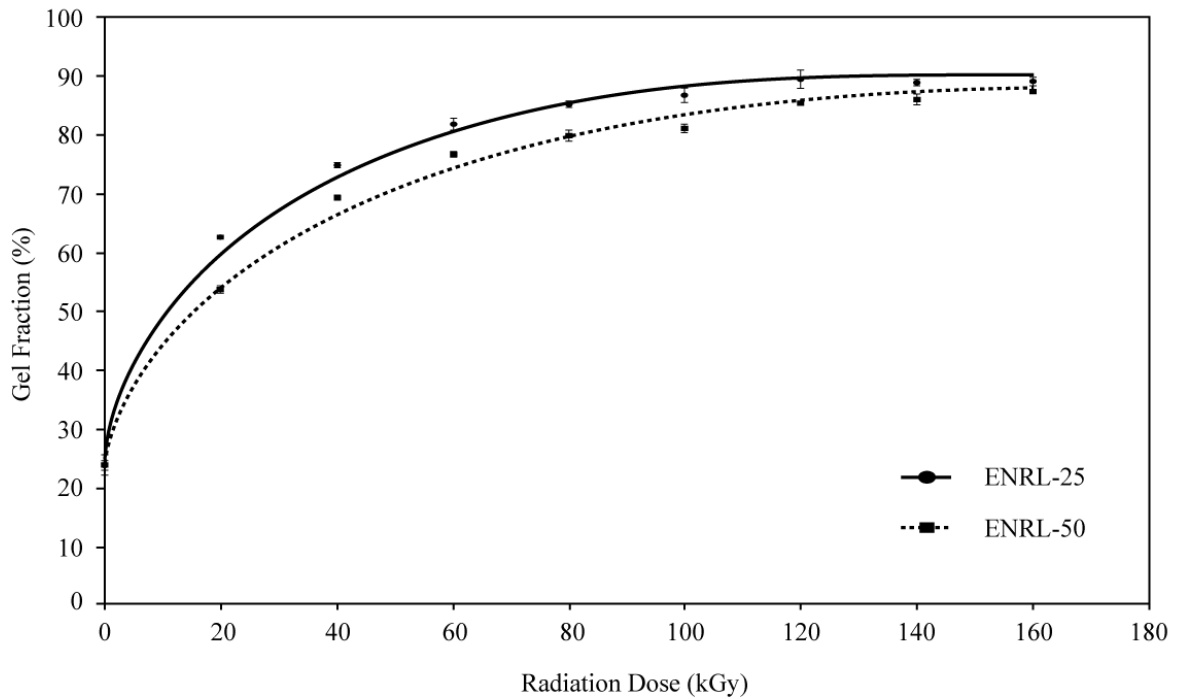


Figure 4: Effect of gamma radiation on gel fraction of ENRL

4.0 CONCLUSIONS

Gamma radiation is found to enhance the tensile properties of ENRL-25 and ENRL-50, which is believed to be the consequence of irradiation-induced crosslinking within the latex. ENRL-25 is found to be more radiation-sensitive than ENRL-50, which is believed to be attributed to the presence of more unreacted double bonds in ENRL-25 which participated in the irradiation-induced crosslinking.

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REFERENCES

1. S.C. Ng, L.H.Gan. Reaction of natural rubber latex with performic acid from *European Polymer Journal*, 1981. 17: 1073-1077.
2. I.R. Gelling. Epoxidized natural rubber from *Journal of Natural Rubber Research*, 1991 6(3): 184-205.
3. C.S.L. Baker, I.R. Gelling, R. Newell. Epoxidized natural rubber from *Rubber Chemistry and Technology*, 1985. 58(1): 67-85.
4. Y.Y. Luo, C.J. Yang, Y.Q. Wang, C.Z. He, J.P. Zhong, S.Q. Liao, Z. Peng, X.X. Liu. Effect of neodymium stearate on cure and mechanical properties of epoxidized natural rubber from *Journal of Rare Earths*, 2012. 30(7): 721-724.
5. G.W. Liau. Dynamic mechanical relaxation of lightly cross-linked epoxidized natural rubber from *Polymer*, 1999. 40: 599-605.
6. A.M. Sadequl, U.S. Ishiaku, B.T. Poh. Cure index and activation energy of ENR 25 compared with SMR L in various vulcanization systems from *European Polymer Journal*, 1999. 35: 711-719.
7. A.M.Sadequl, U.S. Ishiaku, B.T. Poh. The effect of accelerator/sulfur the scorch time of epoxidized natural rubber from *European Polymer Journal*, 1998. 34(1): 51-57.
8. M. Nasir, B.T. Poh, P.S. Ng. The effect of γ -mercaptopropyltrimethoxysilane coupling agent on t_{90} , tensile strength and tear strength of silica-filled ENR vulcanizates from *European Polymer Journal*, 1989. 25(3): 267-273.
9. B.T. Poh, K.S. Lee. FTIR study of thermal oxidation of ENR from *European Polymer Journal*, 1994. 30(1): 17-23.
10. B.T. Poh, C.P. Kwok, G.H. Lim. Reversion behavior of epoxidized natural rubber from *European Polymer Journal*, 1995 31(3): 223-226.

11. J.A. Barrie, M. Becht, D.S. Campbell. Gas transport in epoxidized natural rubber from *Polymer*, 1992. 33(11): 2450-2451.
12. C.T. Ratnam, M. Nasir, A. Baharin, K. Zaman. Electron beam irradiation of epoxidized natural rubber from *Nuclear Instruments and Methods in Physics Research B*, 2000. 171: 455-464.
13. C.T. Ratnam, M. Nasir, A. Baharin, K. Zaman. The effect of electron beam irradiation on the tensile and dynamic mechanical properties of epoxidized natural rubber from *European Polymer Journal*, 2001. 37: 1667-1676.
14. D. Darji, M. Md Said. Vulcanization and coagulant dipping of epoxidized natural rubber latex from *Pertanika Journal of Science & Technology*, 2010. 18(2): 421-425.
15. G. Alliger, I.J. Sjothun. *Vulcanization of Elastomers*. New York: Robert E. Krieger Publishing Company, 1978.
16. C.T. Ratnam. Irradiation crosslinking of PVC/ENR blend: a comparative study with the respective homopolymers from *Macromolecular Materials and Engineering*, 2001. 286(7): 429-433.
17. E. Menzibal, L. Cruz, C.F. Jasso, G. Burillo, V. I. Dakin. Radiation crosslinking of highly plasticized PVC from *Radiation Physics Chemistry*, 1996. 47(2): 305-309.