

GRAFTING OF n-BUTYL ACRYLATE WITH NATURAL RUBBER LATEX FILM BY GAMMA RADIATION: A REACTION MECHANISM

K. M. Z. Hossain¹ and A. M. Sarwaruddin Chowdhury²

¹Faculty of Science and Information Technology, Daffodil International University, Dhaka 1207.

²Department of Applied Chemistry and Chemical Technology, Faculty of Engineering and Technology, University of Dhaka, Dhaka 1000, Bangladesh

E-mail: hossain015@yahoo.com

Abstract: Natural rubber latex (NRL) and n-butyl acrylate (n-BA) were blended and irradiated at various absorbed doses by gamma rays from Co-60 source at room temperature. The stabilizing effect was determined by measuring the pH and viscosity of NRL with n-BA with the storage time of five weeks. The cross-link density, swelling ratio of the radiation vulcanized rubber film were measured. The cross-link density of the n-BA grafted NRL film was found increasing and the swelling ratio of that film decreasing with the increased absorbed dose. The optimum radiation dose for better cross-linking of natural rubber latex blended with five parts per hundred rubber (phr) n-BA was found 15 kGy absorbed dose. Based on the cross-linking properties a probable cross-linking reaction mechanism for the n-BA grafted natural rubber latex film was developed.

Keywords: Natural rubber latex, n-butyl acrylate, Irradiation, Swelling ratio, Cross-link, Reaction mechanism.

1 Introduction

Natural rubber latex (NRL) is a dispersion of natural rubber particles in water. It comes from *Hevea Brasiliensis* plantation. Rubber hydrocarbon is a polymer of isoprene. The number average molecular weight of natural rubber varies from 1.6×10^5 to 7.0×10^5 while the weight average molecular weight varies from 5.0×10^5 to 10.0×10^5 . The properties of natural rubber can be improved by vulcanization. Vulcanization is an important chemical reaction of rubber. NRL can be vulcanized [1, 2] by irradiation without and with radiation vulcanization accelerator. Polymer blend is a mixture of two or more

polymers. This technique has gained much attention as an alternative to meet the steadily increasing demands of polymer materials with new exploitation property profiles in parallel to the synthesis of new polymer [3]. Methyl methacrylate (MMA) grafted natural rubber latex film [4] has been developed for the improvement of the tensile properties of the rubber film. The modulus and hardness of irradiated rubber latex are low. This drawback can be eliminated by incorporation of hard segment like poly (methyl methacrylate) (PMMA). The incorporation of hard segment can be carried out either by grafting or by blending technique. Thermoplastic elastomer (TPE) has been prepared [5] by blending radiation vulcanized natural rubber latex (RVNRL) or sulfur pre-vulcanized NRL with un-vulcanized NRL at the dry rubber content ratio of 1:2 followed by grafting with methyl methacrylate (MMA). The TPE obtained from blend of MMA grafted RVNRL/MMA grafted NRL shows good processability [6]. Blending between non-irradiated NRL and RVNRL improves the tensile strength with a low absorbed dose [7]. In this study we developed a probable cross-linking reaction mechanism for n-BA grafted NRL film by using radiation vulcanization process.

2 Materials and Methods

2.1 Natural Rubber Latex (NRL)

The natural rubber field latex was collected from the Atomic Energy Research Establishment (AERE) rubber garden, Savar. Immediately after collection of NRL from

rubber tree, it was preserved with ammonia solution obtained from BDH, England. NRL was concentrated to 60% total solids content (TSC) using a laboratory scale centrifuge machine model SPL-100, Saito Separator Ltd., Japan.

2.2 Irradiation of NRL

The concentrated NRL was diluted to 50% TSC by adding 1.5% dilute ammonia solution. A five parts per hundred rubber (phr) *n*-butyl acrylate (n-BA) obtained from Kanto Chemical Co. Inc., Japan was added dropwise to diluted NRL as radiation vulcanization accelerator (RVA) and stirred with a magnetic stirrer for one hour. The RVA mixed NRL was irradiated [8] by Co-60 gamma source.

2.3 Preparation of Rubber Films

Irradiated n-BA blend natural rubber latex was cast on raised rimmed glass plates to make rubber films. They were leached with distilled water for 24 hours at room temperature and then air dried until transparent [9] film was obtained. Then the films were dried in an oven at 70°C for one hour.

2.4 Measurements of pH and Viscosity

In this study pH was measured by a digital pH meter (Model PW9409, Philips, England) by direct immersion of the electrode into the n-BA blended natural rubber latex. Viscosity was measured by digital viscometer Visconic ELD 'R' with viscometer controller E-2000 (Toki Sangyo Co. Ltd, Japan). About 0.5 gm. of sample was taken in the groove of the spindle guard and immediately attached the guard securely. The viscometer was then switched on and the value of viscosity was obtained in milipascal second (mPa.s) directly.

2.5 Measurements of swelling ratio of Rubber

British standard (B.S 1673: part 4, 1953) was followed to measure swelling ratio of rubber latex film. The natural rubber centrifuged latex films was cut into small round shape pieces and the weight was measured and then immersed into toluene for 24 hours. After this period, the

film was taken out from the solvent and excess solvent was removed by wiping it with a filter paper and then weight of the swelled film was measured immediately.

The swelling ratio (Q) was calculated as follows:

$$\text{Swelling ratio, } Q = \frac{W_0 - W_i}{W_i}$$

Where, W_0 = Final weight of film after swell in gm, W_i = Initial weight of film in gm

2.6 Measurements of Cross-linking density of Rubber

The cross-link density i.e. degree of cross-link of irradiated centrifuged rubber latex was measured by using swelling ratio (Q) and was calculated on the basis of FLORY and REHNER equation as follows [10]:

$$\text{The degree of cross-linking, } V = K \times Q^{.5/3}$$

Here, $K = 4.71 \times 10^{20}$ for solvent of toluene. Q = Swelling ratio.

The FT-IR spectrum of the grafted rubber film was measured by using calibrated FT-IR 8900, Shimadzu, Japan (Software – Hyper IR).

3 Results and Discussions

The pH and viscosity of NR latex containing 5 phr n-BA is used as a measure of stability of NR latex against n-BA. Table 1 presents pH and Viscosity of NR latex blended with five phr n-BA changes with storage time at room temperature. During the five weeks storage period the pH of the natural rubber latex decreases a little and this is due to the escape of some ammonia solution, which was previously used for the preservation of filed latex. And for the same reason the viscosity of the latex is also increased slightly.

A sharp decrease in pH may disrupt the electrical charge in the surface layer of NR particles and rapid increase in viscosity may badly affect the NR latex properties. From the Table 1 we find that the NR latex blended with 5 phr n-BA remains quite in a good condition during the five weeks storage time at room temperature (27°C).

Table 1 Effect of storage time of radiation vulcanized n-BA blend natural rubber latex

Natural rubber latex	pH						Viscosity (mPa.s)					
	0 week	1 week	2 week	3 week	4 week	5 week	0 week	1 week	2 week	3 week	4 week	5 week
With 5 phr n-BA	10.21	10.15	9.98	9.81	9.67	9.55	60.78	61.14	61.32	61.54	61.65	61.8

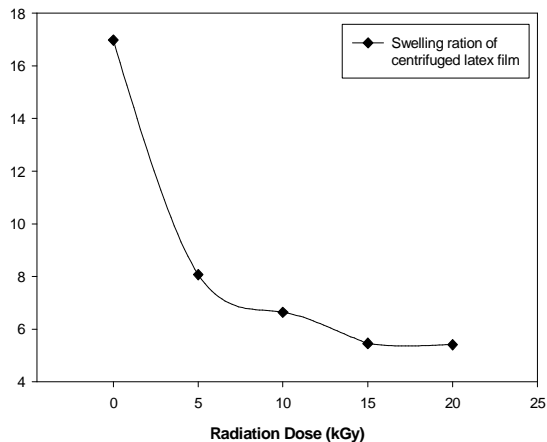


Fig. 1 Effect on swelling ratio of centrifuged latex film with various radiation doses, sensitized with 5 phr n-BA.

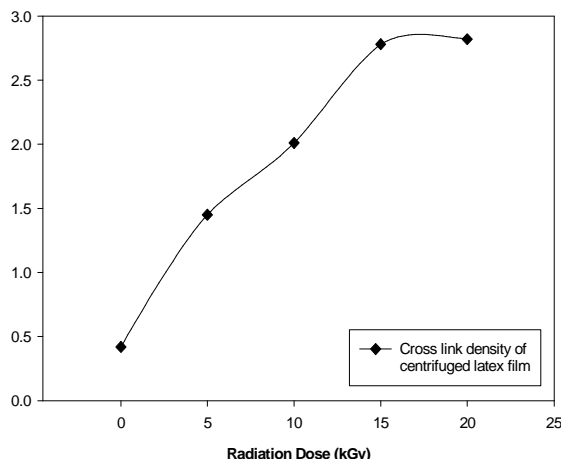


Fig. 2 Effect on Cross-link density of centrifuged latex film with various radiation doses, sensitized with 5 phr n-BA

For various radiation dose causes variation of swelling ratio. Swelling ratio decreases with the increases of radiation dose due to the higher cross linking attained by the natural rubber and n-BA.

The Fig. 1 reveals that the swelling ratio is decreased sharply with the increasing radiation dose up to 5 kGy and this is due to the maximum number of cross-linking is observed in this stage. After this absorbed dose the decreasing trend of

swelling ratio becomes slow with the additional radiation dose. But after 15 kGy radiation dose the variation of swelling ratio was not remarkable i.e. about 15 kGy radiation dose is considered to be optimum. Without radiation the swelling ratio of the centrifuged latex film is 16.98 and at 5 kGy, 10 kGy, 15 kGy and 20 kGy radiation dose the swelling ratio of the centrifuged latex film is 8.07, 6.64, 5.46 and 5.41 respectively.

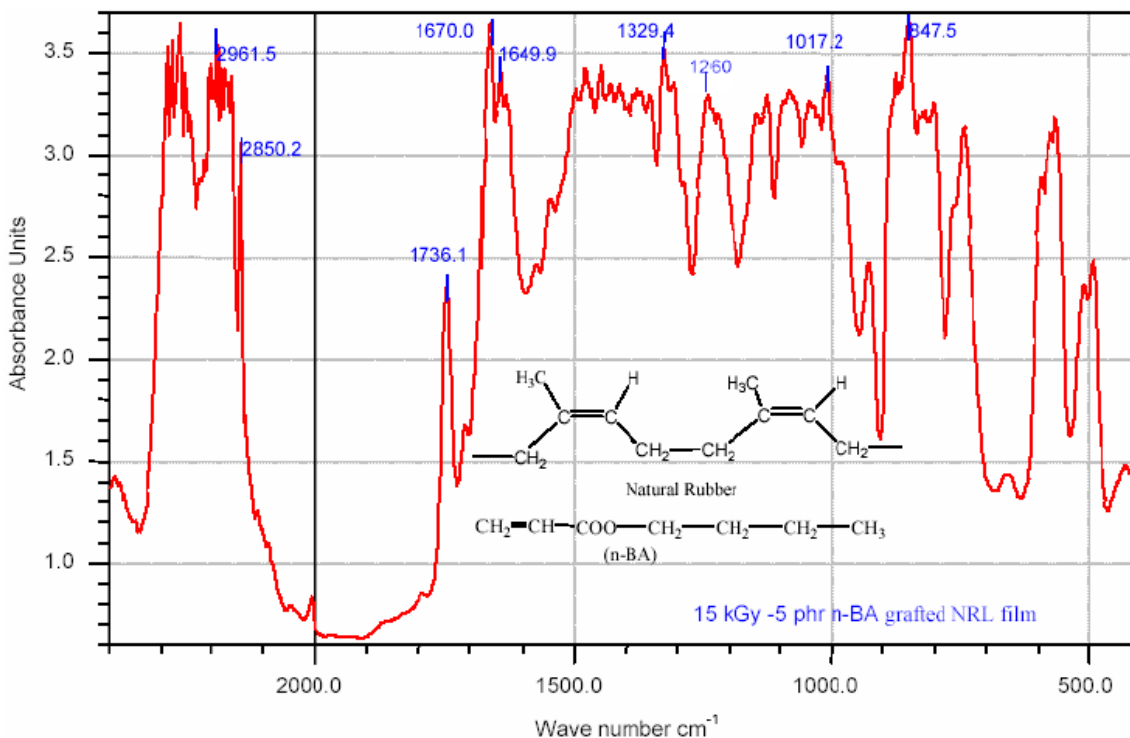


Fig. 3 FT-IR spectrum of radiation vulcanized natural rubber latex film grafted with 5 phr n-BA sensitizer (15 kGy)

The natural rubber latex is subjected to radiation vulcanization to gain induced cross-linking. The homogeneous cross-link density increases with the radiation dose.

But after reaching at saturation point or maximum cross-link density, the irradiated centrifuged latex film is not affected remarkably by further additional radiation doses. The Fig. 2 shows that the cross-link density of the centrifuged latex film without radiation is very low (0.42×10^{19}). With the additional radiation doses the cross-link density within the rubber molecule is increases sharply. Up to 15 kGy radiation dose the increasing rate of the cross-link density is remarkable. At 5 kGy, 10 kGy and 15 kGy radiation dose the cross-link density of centrifuged latex film is 1.45×10^{19} , 2.01×10^{19} and 2.78×10^{19} respectively. After that for higher radiation dose (20 kGy) the cross-link density does not increase remarkably (2.82×10^{19}). So, 15 kGy radiation dose is the optimum dose for getting radiation induced cross-link natural rubber film.

The FT-IR spectrum of radiation vulcanized natural rubber film is shown in the Fig. 3.

From the Fig. 3 we identify the functional

groups of the n-BA grafted natural rubber latex film by detecting the major absorbance peaks.

C-H stretching vibration from CH_3 shows peak at 2961.5 cm^{-1}

[Range: $3000 - 2850 \text{ cm}^{-1}$]

C-H stretching vibration from CH shows peak at 2850.2 cm^{-1}

[Range: $3000 - 2850 \text{ cm}^{-1}$]

C-H deformation shows peak at 1329.74 cm^{-1}

[Range: $1450 - 1375 \text{ cm}^{-1}$]

C=C stretching vibration shows peak at 1670.0 cm^{-1}

[Range: $1680 - 1600 \text{ cm}^{-1}$]

C=C stretching vibration (n-BA) shows peak at 1649.9 cm^{-1}

[Range: $1650 - 1635 \text{ cm}^{-1}$]

C=O conjugation for n-BA shows peak at 1736.1 cm^{-1} [Range: $1740 - 1715 \text{ cm}^{-1}$]

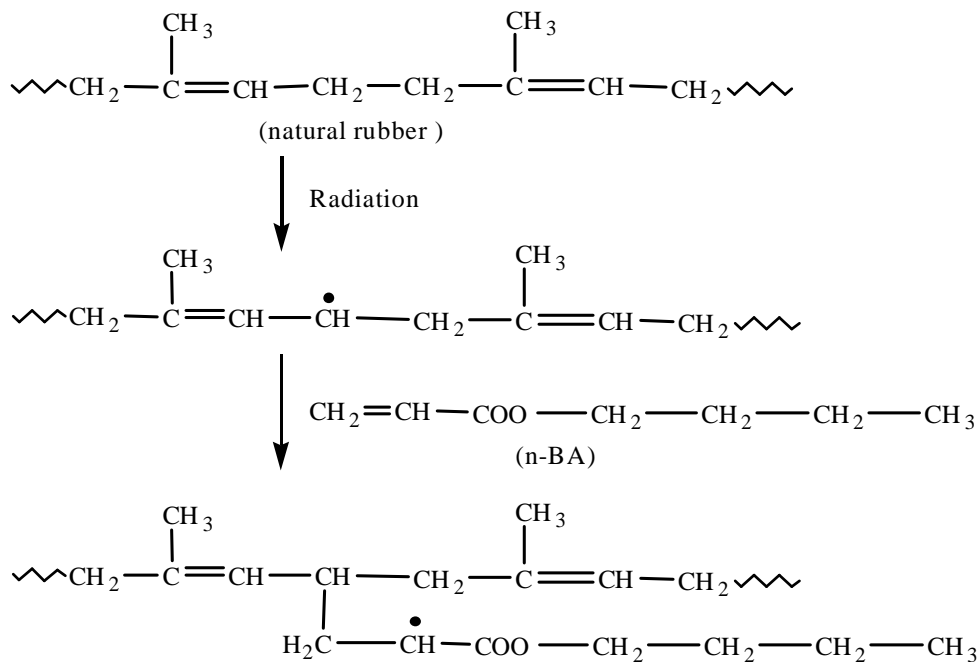
C-H out of plane deformation shows peak at 847.5 cm^{-1}

[Range: $1000 - 650 \text{ cm}^{-1}$]

C-O stretch of ester group (1260 cm^{-1})

The probable reaction mechanism for cross-linking of natural rubber with n-butyl acrylate (n-BA) during the radiation vulcanization is shown in the next sub-sections:

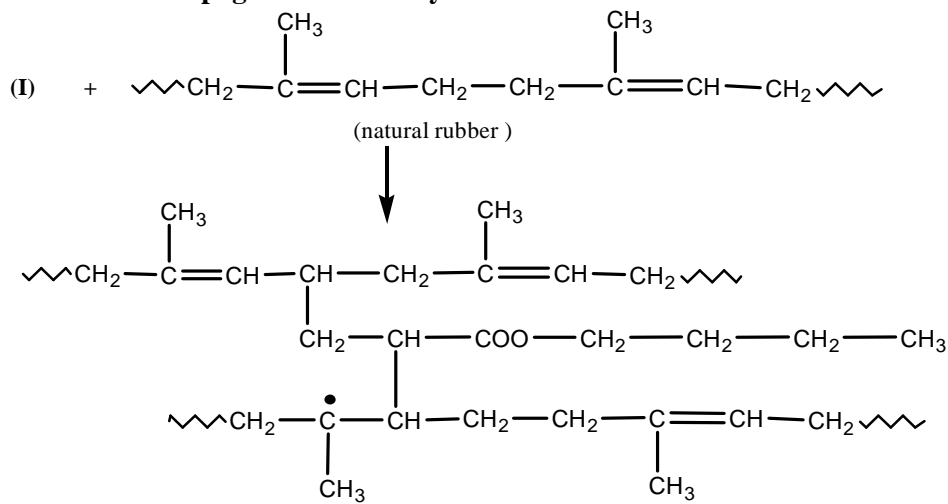
3.1 Free Radical Formation and Chain Initiation



(I)

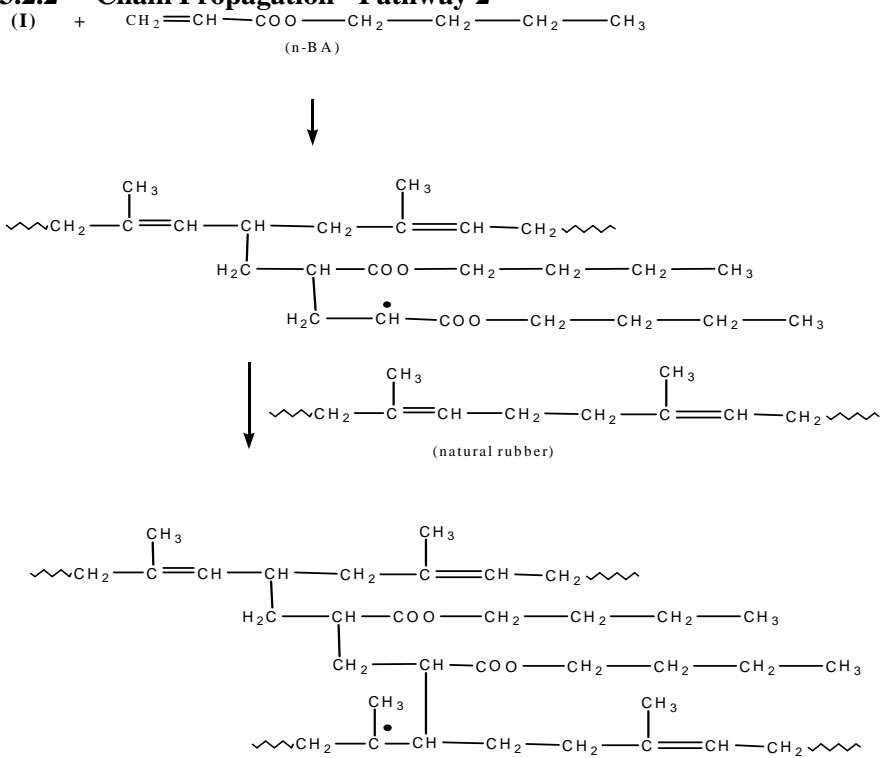
3.2 Chain Propagation

3.2.1 Chain Propagation - Pathway 1



(II)

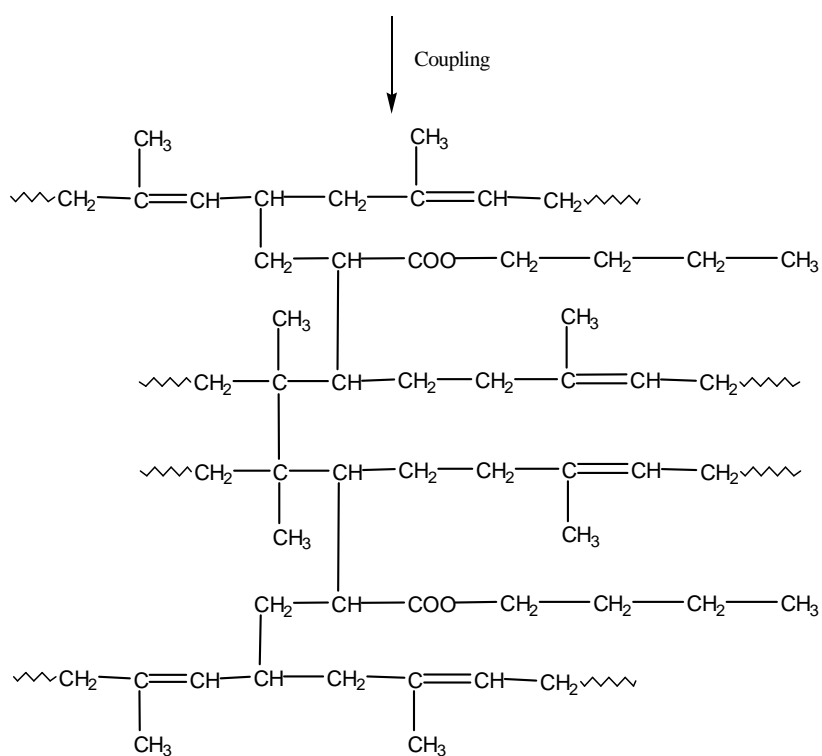
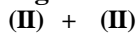
3.2.2 Chain Propagation - Pathway 2



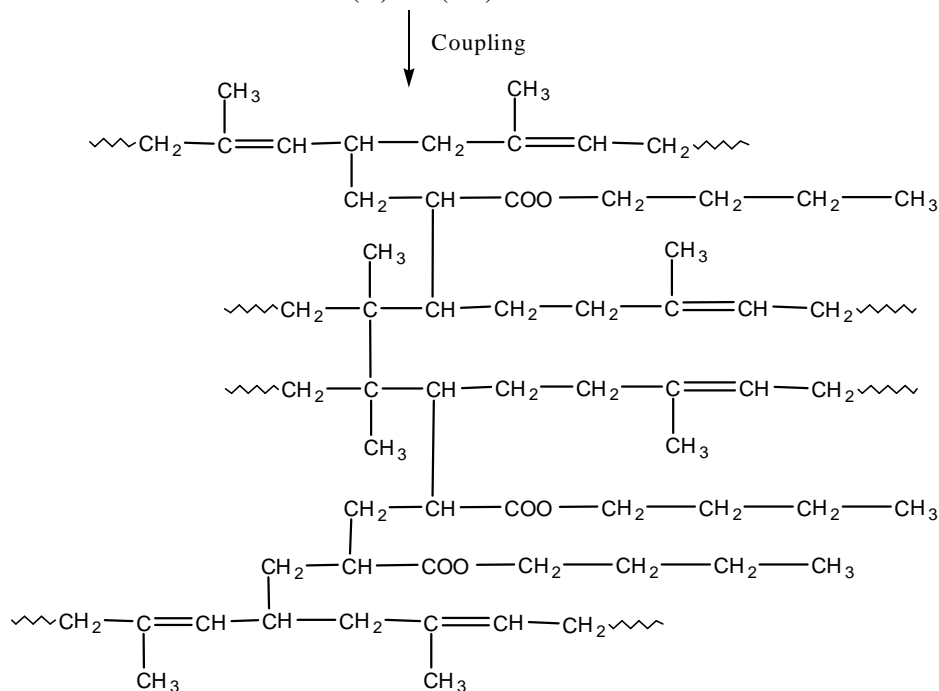
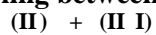
(III)

3.3 Chain Termination

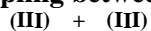
3.3.1 Termination by Coupling between (II) and (II)



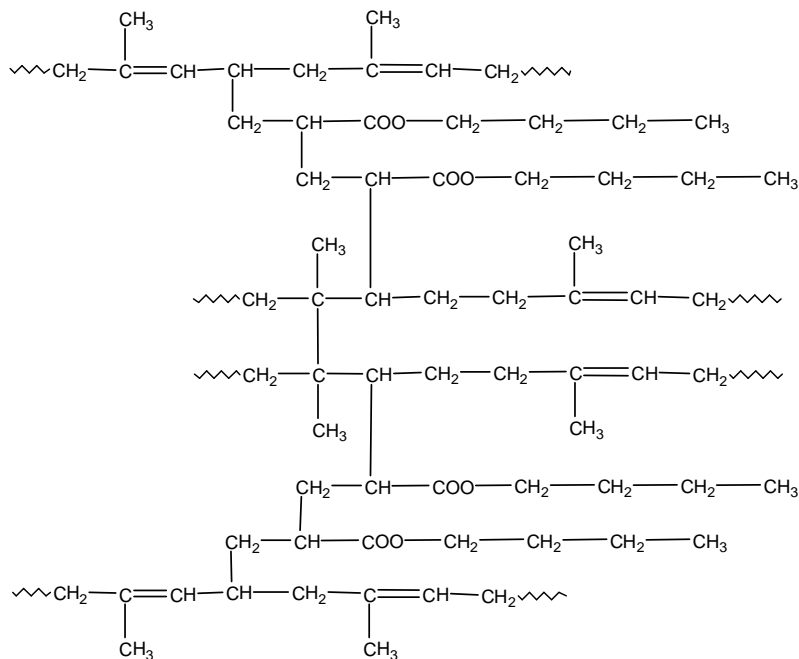
3.3.2 Termination by Coupling between (II) and (III)



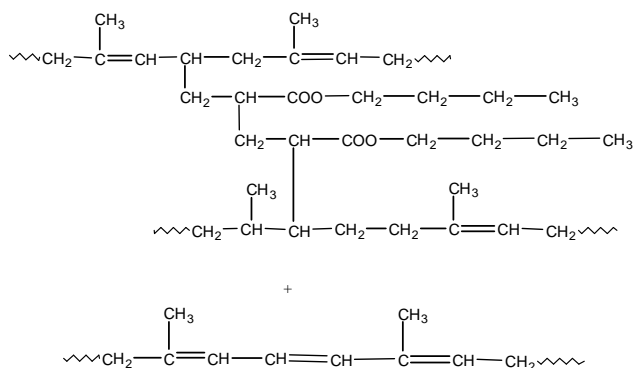
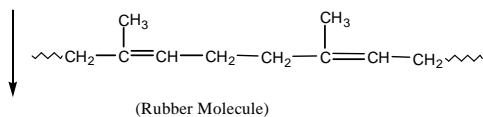
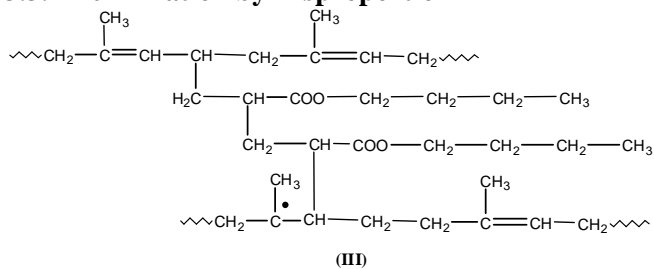
3.3.3 Termination by Coupling between (III) and (III)



Coupling
↓



3.3.4 Termination by Disproportionation



Termination through disproportion between (III) and the rubber molecule is shown.

4 Conclusion

The blend of n-BA grafted rubber latex was prepared by gamma radiation exposure. The stability of NR latex can be improved by using five phr n-BA grafted with NR latex film. The value of maximum cross-linking of n-BA blend rubber is obtained at the absorbed dose of 15 kGy, which is optimum. Swelling ratio of the radiation vulcanized natural rubber film decreases with increased absorbed dose and consequently cross-link density of the rubber film is increased. So from this study it has been proved that the cross-linking of the n-BA grafted NR latex film can be done by gamma radiation through the proposed probable cross-linking reaction mechanism.

References

- [1] Y. Minoura, and M. Asao, *J. Appl. Polym. Sci.*, 1961, 5(14): p. 233.
- [2] Y. Minoura, and M. Asao, *J. Appl. Polym. Sci.*, 1961, 5(16): p. 401.
- [3] D. R. Paul, and C. B., Bucknall, "Polymer blends", Vol. 1 and 2, John Wiley & Sons Inc., New York, 2000, p. 477.
- [4] N. C. Dafader, M. E. Haque, and F. Akhtar, *Chinese Journal of polymer Science*, 2007, 25(5): pp. 519-523.
- [5] C. Siri-Upathum, K. Suchiva, and M. Sonsuk, "A study of methyl methacrylate grafting on natural rubber by gamma radiation", In: "Proceedings RadTech Asia'95 Symposium and Workshop, Bangkok, 1995", ed. by S. Kiatkamjornwong, Chulalongkorn University, Bangkok, Thailand, 1995, p. 423.
- [6] M. T. Razzak, F. Yoshii, K. Makuuchi, and I. Ishigaki, *J. Appl. Polym. Sci.*, 1991, 43(5): p. 883.
- [7] M. A. Haque, M. U. Ahmad, F. Akhtar, N. C. Dafader, and M. E. Haque, *Polym. Plast. Technol. Eng.*, 2004, 43(5): p. 1345.
- [8] M. F. Mina, A. K. M. M. Alam, M. N. K. Chowdhury, S. K. Battacharia, and F. Balta Calleja, *J. Polym. Plast. Technol. Eng.*, 2005, 44(4): p. 523.
- [9] C. V. Chaudhari, Y. K. Bhardwaj, N. D. Patil, K. A. Dubey and S. Sabharwal, *Radiat. Phys. Chem*, 2005, 72(5): p. 613.
- [10] Y. Minoura and M. Asao, Studies on gamma rays irradiation of natural rubber latex. The effect of organic halogen compound on crosslinking by gamma irradiation, *J. Appl. Polym. Sci.*, 5, 401 (1961)
- [11] M. Utama, Y. S. Soebianto, M. T. Razzak, S. Kusumawati and H. Tungawiharja, "Rubber thread made from a mixture of RVNRL and NR-g-PMMA", In: "Proceeding, The Second International Symposium on Radiation Vulcanization of Natural Rubber Latex, Kuala Lumpur, 1996", ed. by W. Z. Wan Manshol, Malaysian Institute for Nuclear Technology Research (MINT), Kuala Lumpur, 1996, p. 159.
- [12] D. E. El-Nashar, *Polym. Plast. Technol. Eng.*, 2004, 43(5): p. 1425.
- [13] N. C. Dafader, M. E. Haque, F. Akhtar, and M. U. Ahmad, *Polym. Plast. Technol. Eng.*, 2006, 45(7): p. 889.
- [14] N. C. Dafader, F. Akhtar, Y. N. Jolly, M. E. Haque, and M. U. Ahmad, *J. Bangladesh Chem. Soc.*, 2001, 14(1): p. 55.
- [15] M. E. Haque, N. C. Dafader, F. Akhtar, and M. U. Ahmad, *Radiat. Phys. Chem.*, 1996, 48(4): p. 505.
- [16] N. C. Dafader, M. E. Haque, F. Akhtar, and M. U. Ahmad, *Radiat. Phys. Chem.*, 2006, 75: p. 168.
- [17] S. S. Mahfuza, M. E. Haque, N. C. Dafader, F. Akhtar and M. U. Ahmad, *Macromolecular Reports*, 1996, A33(Suppl. 3&4): p. 175.