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Efficiency of 1,9- Nonane-diol-diacrylate as a Radiation Vulcanization Accelerator for Natural Rubber Latex

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CONTENTS

Abstract

The efficiency of 1,9- Nonane-diol-diacrylate (NDDA) as a radiation vulcanization accelerator (RVA) for natural rubber latex (NRL) was investigated. Both gamma rays and electron beam (EB) were used for vulcanizing NRL with NDDA. The radiation dose of gamma rays, concentration of NDDA required to vulcanize the latex were optimized. 20 kGy radiation dose of gamma rays and 5 phr concentration of NDDA were found optimum to get maximum tensile and related properties. NRL was vulcanized under EB to find out the optimum condition of irradiation with this RVA. The defoamer concentrations, length of irradiation time under EB, concentration of RVA were optimized by changing various parameters of the EB machine with a constant set of the others. 0.2 phr defoamer concentration, 30 minutes irradiation time and 5 phr concentration of NDDA were found optimum for irradiation of NRL under the EB machine. Effect of low EB current and optimum volume of latex charged in the reaction vessel suitable for vulcanization at a time were found out.

1. Introduction

Radiation method for the vulcanization of natural rubber latex (NRL) emerged in late fifties [1] and got popularity for some distinct advantages over the conventional one especially for its approach to cleaner environment. But it was not proved to be suitable for industrial application due to some drawbacks such as high cost in establishing a radiation source (Co-60 for gamma rays) and of course low quality of products. Radiation vulcanization of NRL is carried out with gamma rays from Co-60 source as well as under electron beam (EB) from accelerator machine. But vulcanization with EB did not become so popular because of its low penetration into the NRL. There are also possibilities of over dosing and rise of temperature of latex during irradiation. Efforts were made to overcome these critical drawbacks [2-7]. NRL can be vulcanized by ionizing radiation without any accelerator or additives [8]. But the required vulcanization dose is very high (250-300 kGy). Radiation vulcanization accelerators (RVA) are used to reduce the vulcanization dose for economic reason [9-15]. Till now normal butyl acrylate (*n*-BA) is being used as an effective RVA [16-22]. But it has bad smell and enhances the coagulation of latex. A new RVA with good characteristic properties is essential for industrial application.

In this investigation a new RVA (1,9-Nonane-diol-diacrylate, NDDA) with good characteristic properties was used. This monomer has no smell. It possesses low primary irritation index. Latex remains in a very good physical state when mixed to several phr. The monomer mixed latex does not coagulate even by storing for several days. In this work NDDA was used to optimize the irradiation condition for NRL by gamma rays as well as by electron beam (EB).

2. Experimental

2.1. Latex

NRL concentrate (Microtex and Iotex brand) obtained from Malaysia was used throughout this work. The total solids content (TSC) of these latexes was ~ 62%. Before irradiation these latexes were diluted to different extent (35-50%) by 1% aqueous ammonia.

2.2. γ- Ray source

Co-60 source for γ-rays at Takasaki Radiation Chemistry Research Establishment was used for irradiation of latex.

2.3. Mixing RVA to the latex and irradiation by γ-rays

The monomer NDDA was used as RVA. NDDA was obtained from Osaka Organic Science Industry, Japan. The RVA was used without emulsifier and / or after making emulsion with emulsifying agents. The RVA was added to the latex drop- by- drop and mixed by stirring for 30 minutes with magnetic stirrer. After mixing the latex was taken in glass or plastic container with stopper and irradiated by exposure to γ-rays at the dose rate of 10 kGy/h at room temperature with various doses. Small quantity (50-500 mL) of latex was used for irradiation by γ-rays.

2.4. Selection of emulsifier for RVA

The emulsifiers listed in Table 1 supplied by Kao Corporation, Japan were investigated to find out the best ones. Each of the emulsifiers was mixed with RVA and water at the emulsifier, water, monomer ratio of 1: 99: 100. The mixture was stirred for 1 hour with a ball mixer, FRITSCH Pulvurisette, Germany. The resulted emulsions were stored and lengths of time needed for phase separation were recorded. The phase separation took place after different extent of time for each emulsifier. For Emulgen 420 more then 48 hours were needed for phase separation. Emulgen 420 was selected as the best emulsifier for this purpose.

Table 1. List of emulsifier

Ser. No.	Trade name	Chemical name
1.	EMUL 10 POWDER	Sodium lauryl sulfate
2.	NEOPELEX F-65	Sodium dodecyl benzene sulfonate
3.	LATEMUL S-180	Special anionic surfactant
4.	LATEMUL ASK	Special carboxylic acid type surfactant
5.	EMULGEN 147	Polyoxyethylene lauryl ether
6.	EMULGEN 420	Polyoxyethylene oleyl ether
7.	EMANON 1112	Polyethylene glycol monolaurate
8.	RHEODOL TW – P120	Polyoxyethylene sorbitan monopalmitate

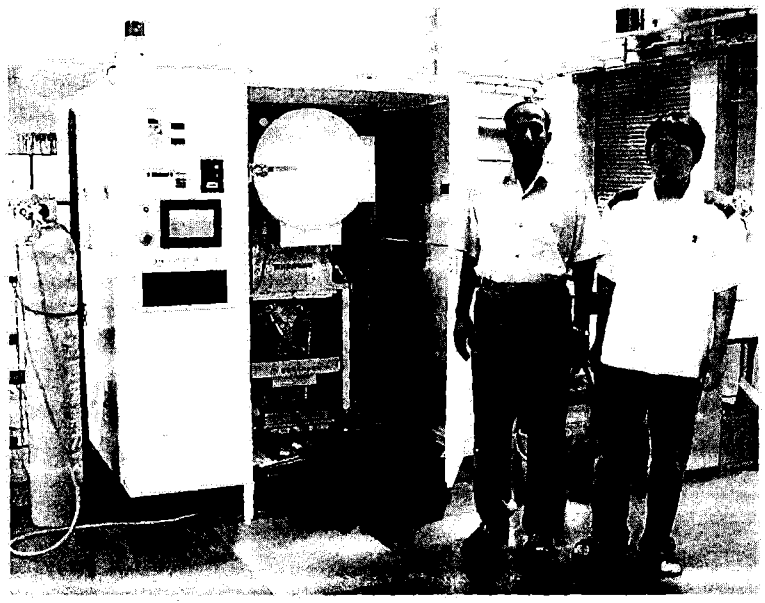
2.5. Preparation of emulsion of RVA

The emulsion of RVA was prepared by mixing the emulsifier, Emulgen 420 with RVA and water in the ratio mentioned in section 2.4 for 1 hour using the ball mixer.

2.6. The EB pilot plant and irradiation of latex under EB

2.6.1. The EB pilot plant

The front view of the EB pilot plant is shown in Photograph 1. It has a reaction vessel with the capacity of 18 liters latex to irradiate at a time. The accelerating voltage and beam current of the plant are 250 kV and 10 mA respectively. The length and width of the beam window are 20 and 6 cm respectively. The latex irradiation vessel under EB is a cylindrical stainless steel vessel (29 cm Φ and 30.5 cm height) containing four baffle plates onto the inner wall at 90° intervals and fitted with a propeller type stirrer and outer jackets. The vessel is covered with a cooling plate having titan film (thickness = 0.0015 cm) window (20 cm × 8 cm).



Photograph 1. Front view of EB pilot plant

2.6.2. Irradiation of latex under EB

The latex was irradiated under EB after mixing with RVA (NDDA with constant stirring at a fixed rpm. RVA was used after mixing with an emulsifier or without emulsifier. An antifoam, BYK022, from BYK-Chemie GmbH Co. Ltd., Germany was mixed with latex to suppress the foam formation. The mixing of RVA was done for 30 minutes in the reaction vessel with 150 rpm. The length of irradiation time, volume of latex, EB current, total solids content in the latex, RVA were varied to have a proper setting of the plant for latex irradiation.

2.7. Preparation of cast films

Spreading 25-35 mL latex on each of several raised rimmed glass plates made cast films of latex. They were allowed to air dry till transparent (for about 24 hours). The films were heated in an oven at 80-100°C for 1 hour after leaching.

2.8. Preparation of dipped films

Dipped films were made by dipping cleaned glass plates into the latex for a definite length of time. The films were air dried up to gel formation and leached in wet-gel condition. They were then heated in an oven at 80°C for 40 minutes.

2.9. Leaching of the films

Leaching of the cast films was done with 1% ammonia in most of the cases. Hot water was also used for leaching in specific cases. The wet-gel leaching for the dipped film was done with hot water at 56°C for various lengths of time. The length of leaching period varied from 2 minutes to 24 hours.

2. 10. Measurement of swelling ratio and cross-link density

A weighed amount of rubber film was immerged into toluene for 24 hours. The rubber film was taken out from the solvent and the adherent solvent was soaked from the swelled film. The swelling ratio was calculated from the weight of the films before and after swelling. The cross-link density was calculated from Flory and Rehner equation[23] as follows:

Cross-link density (number of cross-link/mL) = $K \times Q^{-5/3}$ where,
K = constant (4.71×10^{20} for a system of toluene-natural rubber), Q = swelling ratio.

3. Results and Discussion

3.1. Optimization of irradiation condition by γ-rays.

3.1.1. Optimization of radiation dose for vulcanization

NRL with 50% TSC was mixed with 5 phr NDDA for 30 minutes and irradiated for various doses at the dose rate of 10 kGy/h. Cast films were made, dried, leached for 10 minutes with 1% ammonia and heated at 80°C for 1 hour in an oven. The tensile strengths (Tb) obtained from the films corresponding to their doses are shown in Fig. 1.

It is found that the Tb of the rubber film increases with the increase in radiation dose. Tb of the film without irradiation i.e. green strength is ~7 MPa but by the application of radiation Tb increases up to ~30 MPa which corresponds to 20 kGy beyond which it decreases. The elongation at break (Eb) decreases almost linearly with the increased radiation dose. During irradiation cross-linking between the rubber chains occurs which ultimately leads to improve Tb. Fig. 2 shows the swelling ratio and corresponding cross-link density of RVNRL films at various doses. Cross-link density increases up to 20 kGy. By further increase in the radiation dose the cross-link density remains more or less similar. So by 5 phr NDDA the optimum radiation dose for obtaining maximum Tb of RVNRL film is 20 kGy.

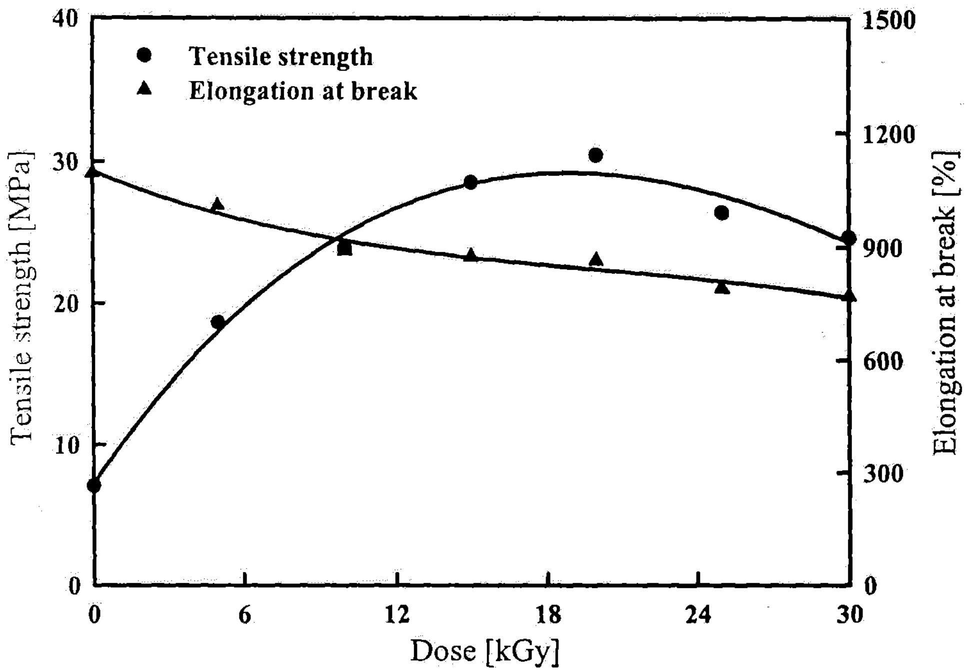


Fig. 1. Tensile properties of gamma ray irradiated latex films versus doses.

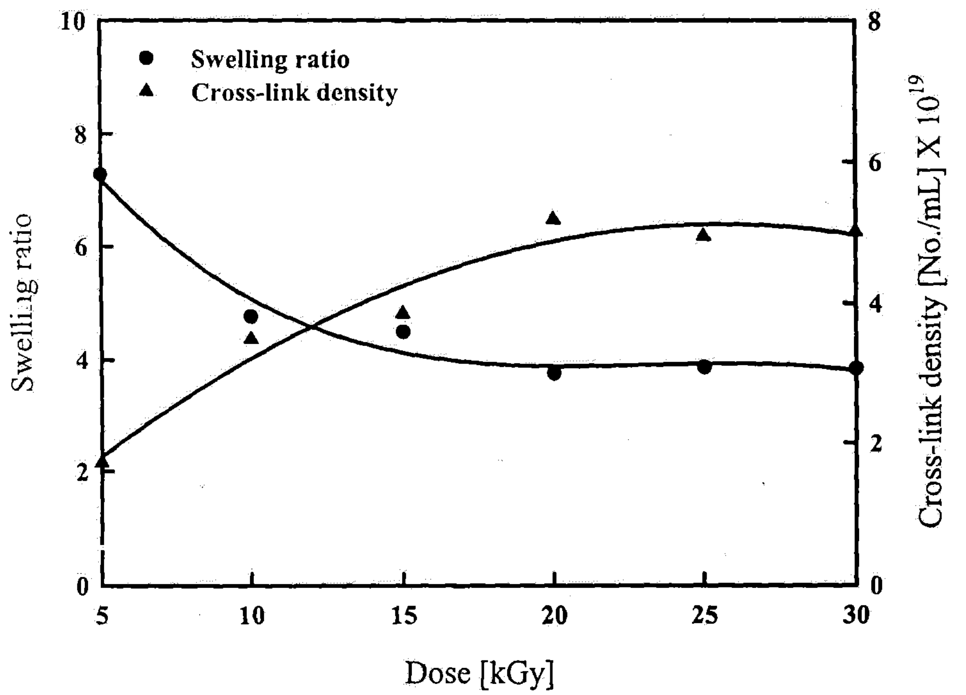


Fig. 2. Swelling ratio and cross-link density of gamma-ray irradiated NRL films against radiation doses.

3.1.2. Optimization of NDDA concentration

In order to optimize the concentration of NDDA, NRL with 50% TSC was irradiated after mixing with varying amount of NDDA separately. The Tbs obtained with various concentrations of NDDA are plotted against the corresponding doses. Fig. 3 shows the Tb versus dose curve for 2.5, 5 and 10 phr concentrations of NDDA. The data for 5 phr NDDA (Fig. 1) is used in this graph for comparison. It is evident that Tb increases up to certain dose in each case. By further increase in radiation dose the Tb curve either goes down or remains virtually constant. With lower concentration (2.5 phr) of NDDA the maximum tensile strength of ~31 MPa is obtained at the cost of higher doses (25-30 kGy). At higher concentration of NDDA (10 phr) maximum Tb is achieved with low dose (5 kGy) but the maximum value of Tb (~24 MPa) is not as high as that for higher doses.

Fig. 4 shows the plot of Eb of these films versus dose. It is evident that the Eb decreases almost linearly with increased radiation dose in each case. The highest values of Eb are obtained from the films with lowest concentration of NDDA (2.5 phr) and the lowest values of Eb are obtained from the films with highest concentration (10 phr). Very high and very low Eb is not suitable for dipped products. The elongation with 5 phr NDDA possesses medium level elongation that may be suitable for hand gloves. The Eb depends on the cross-link density in the rubber film.

Fig. 5 shows the swelling ratio and the corresponding cross-link density versus various doses. Cross-link density is the reciprocal of swelling ratio i.e. if cross-link density increases swelling ratio decreases. The cross-link density increases with the increased applied dose and it possesses maximum at about 20 kGy radiation dose beyond that it remains almost similar. The cross-link density also varies with the concentration of NDDA. The RVNRL film with highest concentration of NDDA gets highest cross-link. Similarly the RVNRL films with lowest NDDA concentration gets lowest cross-link. This pattern is reciprocally similar to the swelling ratio values. This also corresponds to the Eb values of the RVNRL films. But this pattern does not correspond to the Tb values. The cross-link density continues to increase with the increase of applied dose although the increment is not so significant but the Tb decreases after certain optimum radiation dose. So it can be inferred that to obtain maximum Tb there should be an optimum number of cross-link and that number is spread over a range.

From the plot (Fig. 6) of maximum Tb at optimum doses against the corresponding concentration of NDDA it is found that maximum Tb of ~31 MPa is obtained with 30 kGy radiation dose using 2.5 phr NDDA. But this dose is high enough. On the other hand similar value of Tb is obtained by 20 kGy dose if 5 phr NDDA is used. Also the Eb with 2.5 phr NDDA is high. So considering these facts 20 kGy radiation dose and 5 phr concentration of NDDA can be considered optimum for Microtex latex in this condition of latex irradiation.

3.2. Optimization of various parameters of EB pilot plant for the vulcanization of NRL

The EB pilot plant has been installed under the consideration that RVNRL with this type of low energy accelerator would reduce the initial investment and irradiation cost. In order to obtain a suitable setting of experimental condition for radiation vulcanization of latex under EB various parameters were optimized.

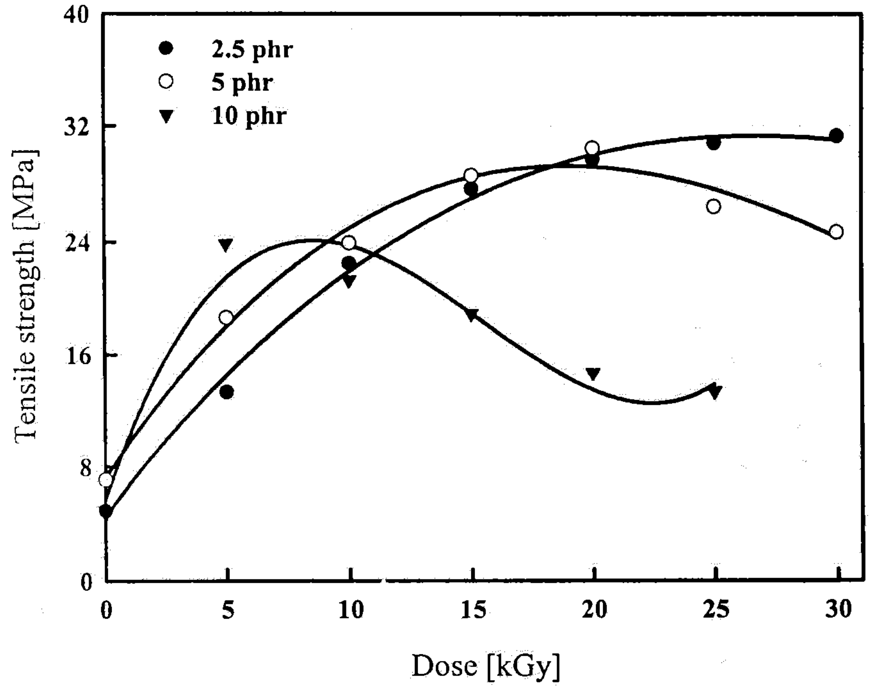


Fig. 3. Tensile strength of RVNRL films versus radiation doses with various concentrations of RVA.

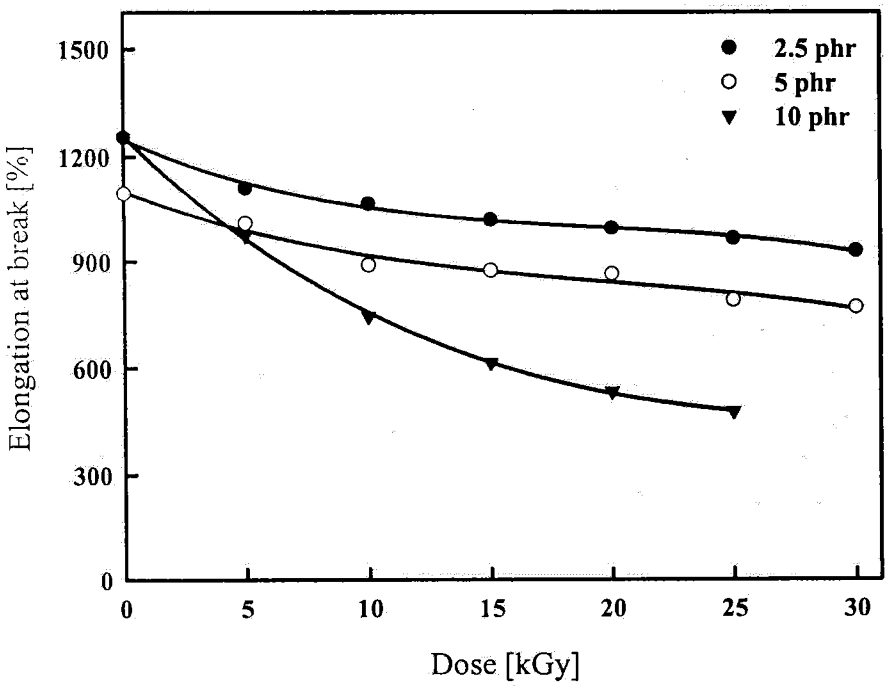


Fig. 4. Elongation at break of RVNRL films versus radiation doses with various concentrations of RVA.

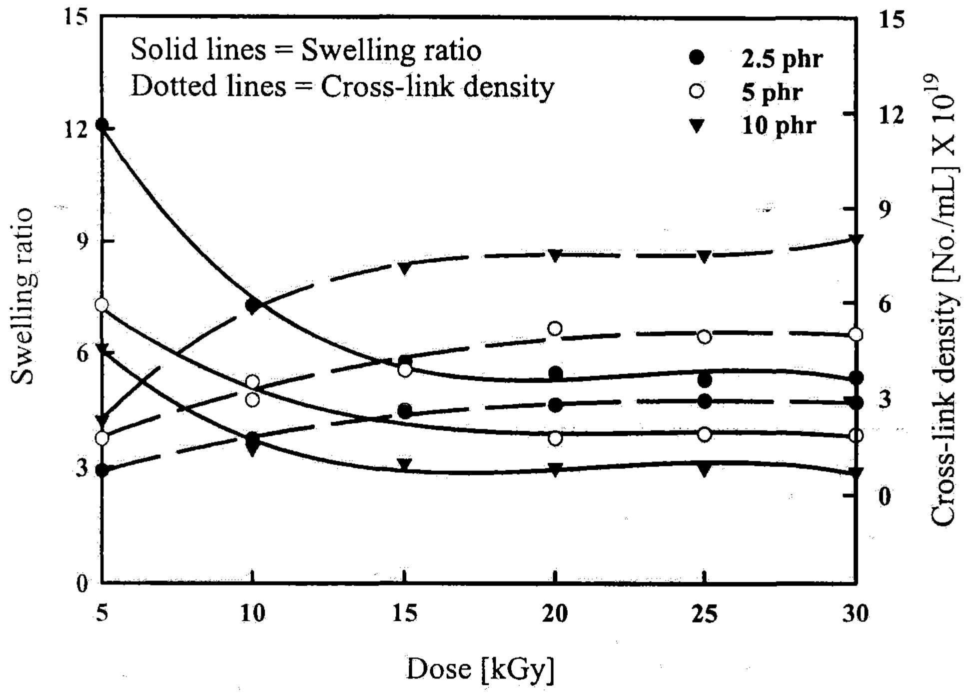


Fig. 5. Swelling ratio and cross-link density of RVNRL films versus doses of radiation with various concentrations of RVA.

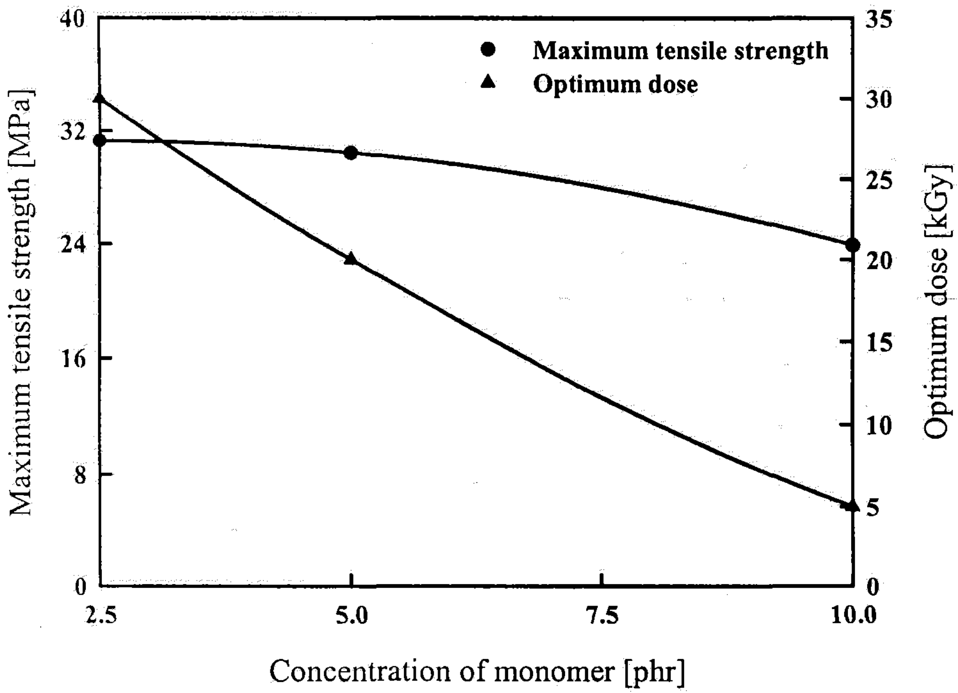


Fig. 6. Concentration of RVA versus maximum tensile strength of RVNRL films for optimum doses of radiation

3.2.1. Optimization of defoamer concentration

By vigorous stirring of the latex many bubbles are formed and create problem during irradiation. So a defoamer (BYK022) is used to suppress the bubble formation. To optimize the defoamer concentration varying quantities (0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 phr) of defoamer were added to the 5 phr NDDA impregnated latex separately and stirred with low to high speed for 20 minutes with a magnetic stirrer. It was found that 0.2 phr concentration of defoamer was sufficient to suppress the bubble formation when latex was stirred at 360 rpm. The maximum rotational speed of the stirrer in the EB reactor vessel is 360 rpm. So 0.2 phr of defoamer concentration could be used at any stirring speed of the stirrer. The foam formation in the EB reactor vessel was examined by taking 16 liters of latex and stirring at 210 rpm. No bubbles were formed.

3.2.2. Length of irradiation time for maximum Tb

(I) Irradiation with maximum EB current: For this purpose latex (Microtex brand) was irradiated under EB for various lengths of time using fixed volume, stirring speed, concentration of RVA and antifoam. 14 liters of latex with 50% TSC was taken for irradiation at a time. Speed of stirring was fixed at 210 rpm. 5 phr NDDA was used as an RVA. 0.2 phr of antifoam was used for suppression of foam. Tensile properties were measured after making cast film from the irradiated latex. Fig. 7 shows the Tb and Eb plotted against the irradiation time. It is found that maximum Tb is ~ 26 MPa for the film prepared from the latex irradiated for 30 minutes. Eb however decreases gradually with increased irradiation time. Fig. 8 shows the swelling ratio and corresponding cross-link density of the RVNRL films against the length of irradiation time. The swelling ratio goes down to a minimum value (that corresponds to maximum value of cross-link density) for the film obtained from the latex irradiated for 40 minutes. But maximum value of Tb is obtained for 30 minutes irradiated sample. In this case optimum cross-link (corresponding to swelling ratio value of ~5) is obtained by irradiating the latex for 30 minutes.

(II) Irradiation with low EB current: Fig. 9 shows the Tb and Eb of the RVNRL film prepared by irradiating latex at low EB current (5 mA) fixing other conditions as stated above. At this EB current same trend in the Tb and Eb values is observed. But the maximum Tb (~26 MPa) is obtained for the RVNRL film from 40 minutes irradiated latex. Thus the length of irradiation time required to obtain maximum Tb is less at higher EB current. The swelling ratio and corresponding cross-link density of these films are shown in Fig. 10. At 40 minutes irradiation the values of cross-link have got the similar range to that of RVNRL film obtained by higher EB current.

3.2.3. Effect of volume of latex

The capacity of the reaction vessel is 18 liters. The stirring and heating effect depends on the quantity of latex used for irradiation. The distance between the upper level of latex and beam window is inversely proportional to the volume of latex used. Taking 16 liters in the reaction vessel latex was irradiated fixing other parameters. The tensile properties are shown in Fig. 11. It is seen that the Tb obtained by using higher volume (16 L) of latex is lower. If compare the tensile curve to that in Fig. 7 it is found that the curve with higher volume latex lies below all along to the curve obtained by using lower volume latex. In case of larger volume the maximum value of Tb obtained at the cost of 35 minutes irradiation. Also the maximum value is lower than the value obtained by using 14 liters latex. The cause of lower value may be due to the inhomogeneous distribution of cross-link density (which is more prominent with higher volume) or/ the heating effect (high because the level is high) that produces bubbles and small coagulant particles that prevent the rubber molecules to come closer. So 14 liter of latex was selected as the ideal volume. Further lowering of volume could not work well because the distance of the latex surface and beam window would become large that may cause delayed vulcanization.

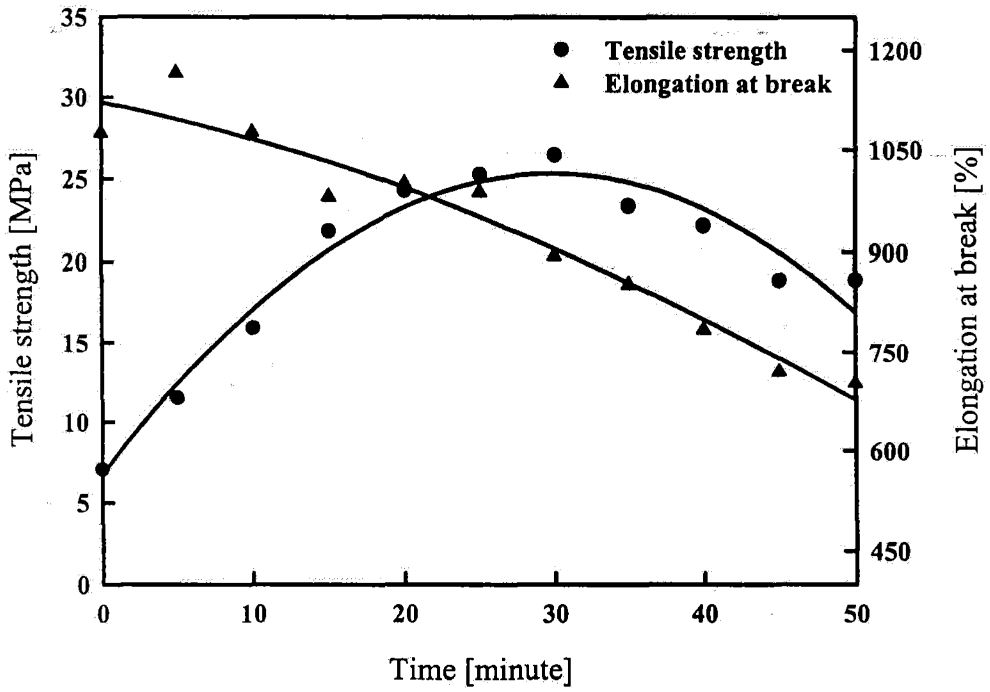


Fig. 7. Tensile properties of EB irradiated latex films versus length of irradiation time.

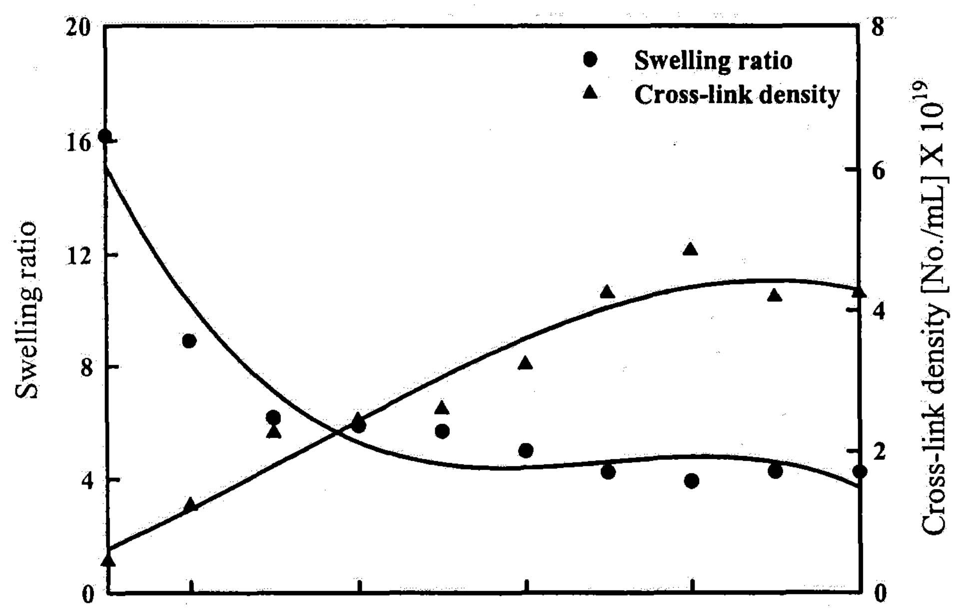


Fig. 8. Swelling ratio and cross-link density of EB irradiated latex films versus irradiation time.

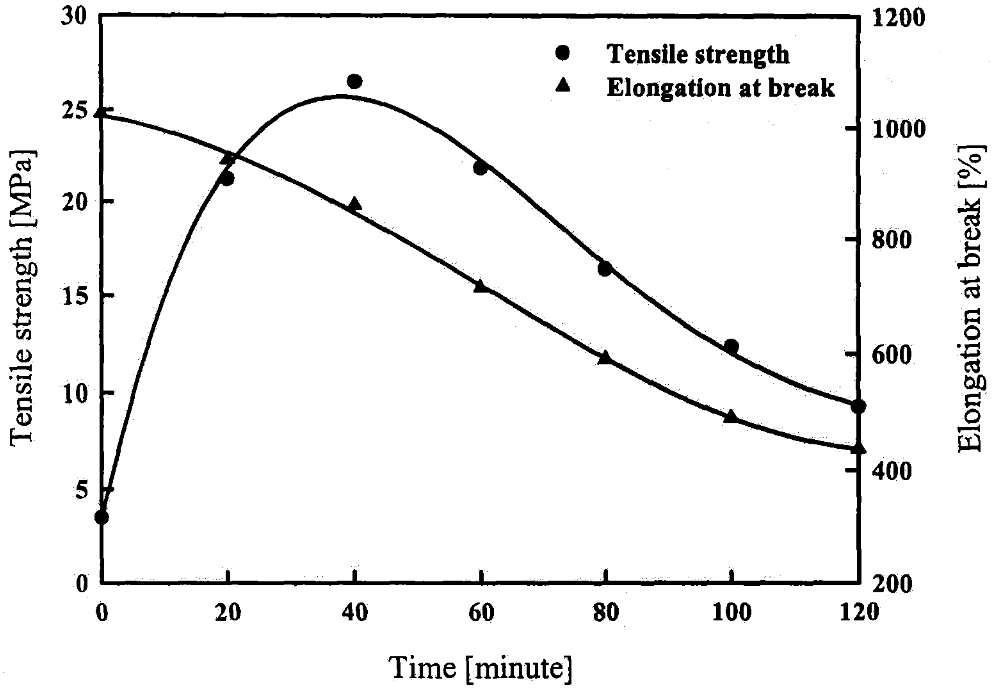


Fig. 9. Tensile properties of EB irradiated latex films vesrsus lengths of irradiation times at low EB current (5 mA).

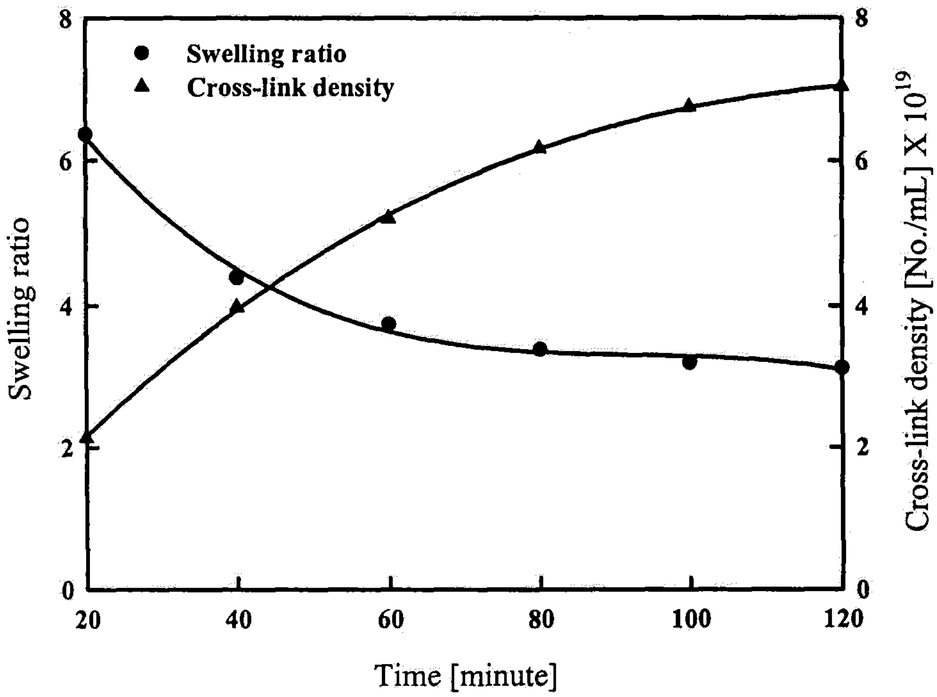


Fig. 10. Swelling ratio and cross-link density of EB irradiated latex films versus lengths of irradiation time at low EB current (5 mA).

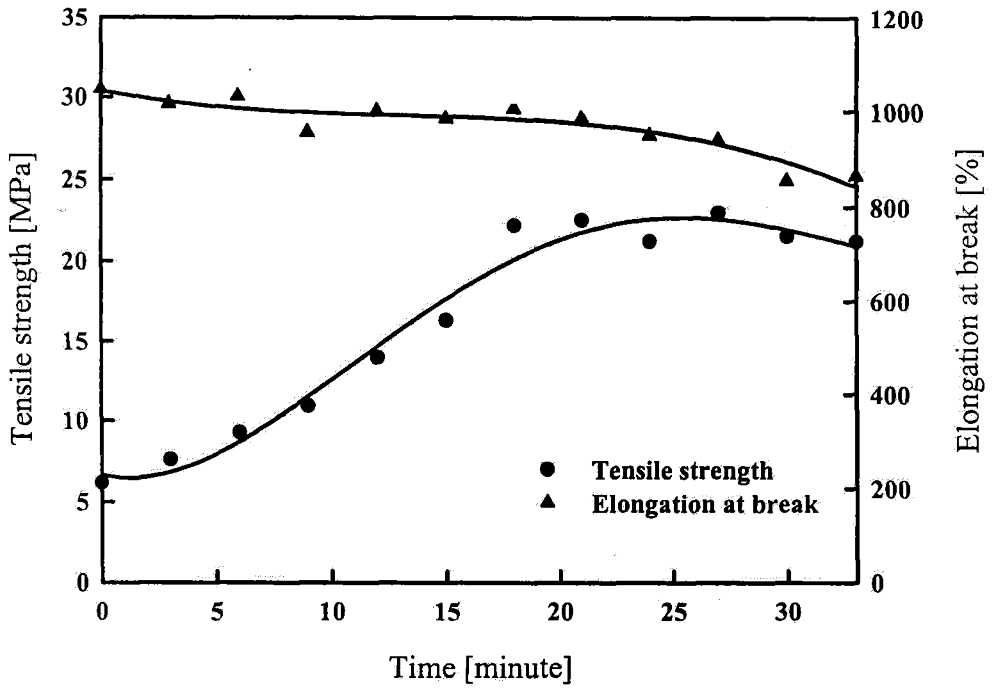


Fig. 11. Tensile propperties of rubber film obtained by irradiating latex under EB taking higher volume of latex at a time (16 L).

4. Conclusion

NDDA has very good accelerating efficiency in the radiation vulcanization process of NRL with both the gamma rays and EB. 5 phr concentration of NDDA and 20 kGy radiation doses of gamma rays are found optimum to get maximum Tb in the experimental condition. 30 minutes exposure time and 5 phr NDDA are found optimum to get maximum Tb under EB if 14 liters latexes are used with 10 mA current of EB. The maximum Tb obtained with gamma rays is significantly higher than that with EB.

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