RADIATION VULCANIZATION OF NATURAL RUBBER LATEX

Wan Manshol bin W. Zin and Norjanah bte Mohid.
Kementerian Sains Teknologi dan Alam Sekitar,
Unit Tenaga Nuklear,
Komplek PUSPATI, Bangi 43000,
Selangor Darul Ehsan

Abstract

This paper describes the experimental techniques and the results of radiation vulcanization of natural rubber latex carried out on several high ammonia latices available in the country. The efficiency of various sensitisers and stabilisers used were evaluated in terms of the gamma radiation dose required to produce the maximum tensile strengths. The extent of crosslinking of RVNRL sample films were estimated by equilibrium swelling ratio measurements. The stability of pre-irradiated and post-irradiated samples were monitored using viscosity measurements as the parameter.

Abstrak

Kertas kerja ini menerangkan mengenai teknik-teknik eksperimen dan keputusan eksperimen pemvulkanan lateks getah asli menggunakan sinaran yang telah dilakukan keatas beberapa lateks beramonia tinggi yang terdapat di negara ini. Efisiensi beberapa jenis bahan pemeka dan penstabil dinilaikan berdasarkan dos sinaran gama yang diperlukan bagi menghasilkan kekuatan regangan yang maksima. Anggaran ukuran pertautan silang sampel filem dapat diperolehi daripada nisbah pembengkakan. Kestabilan sampel sebelum dan selepas disinarkan dikaji dengan menggunakan kelikatan sebagai parameter.

INTRODUCTION

The main aim of the project is to obtain a cleaner vulcanised natural rubber latex which is carcinogen-free and enviromentally-friendly.

The properties of RVNRL are particularly suited to applications requiring a material with neither has toxic ingredients nor residues (1,2) , and where the products will be in contact with skin. Its potential is seen in medical uses such as optical laser balloons, catheters , examination and surgical gloves and in other uses like baby-bottles teats , condoms and toy balloons (3-6).

The technology involved in RVNRL has been developed by not just one country but by many i.e. the natural rubber producing countries in the Asia/Pacific regions and with Japan being the key country. The program has been undertaken within the RCA/UNDP/IAEA Industrial Project.

Vulcanization is achieved through the use of gamma radiation (7-9). The attraction lies in the simplicity of the process , in that it only requires the latex to be the first mixed with the sensitizer such as n-butyl acrylate before being subjected to gamma radiation (10,11). The RVNRL thus formed can then be processed into dipped products according to standard techniques already available.

The promising results on the work being carried out have geared us up to promoting further the use of RVNRL. This has been done through seminars , workshop and any opportunities available for discussions with latex dipped product manufacturers. Extensive efforts are afoot towards improving further RVNRL to a level where it can be safely commercialised on a grander scale. The time could well be ripe for these manufacturers, being in the best position, to exploit the merits of RVNRL.

MATERIALS AND METHOD OF PREPARATION OF RVNRL.

MATERIALS

1. Latex

Concentrated natural rubber latex of high ammonia type were used in carrying out the research work (12). The latices studied were those supplied by Golden Hope, Dunlop, Guthrie, Felda, Lee Rubber and Mardec. Before further work, this latices were analysed for their total solid content (TSC) and dry rubber content (DRC). The mechanical stability test measurements were done and the pH values were recorded.

As in the conventional sulphur compounding the amount of sensitiser, stabiliser and water (as a diluent to reduce the TSC to 50%) used were calculated based on parts per hundred part of rubber.

2. Sensitisers

Sensitisers are used to increase the efficiency of vulcanization and to reduce the radiation dose required for maximum vulcanization (13-17). Among the sensitisers investigated were carbon tetrachloride (CCl_4) and the acrylic monomers, i.e. 2-ethyl hexyl acrylate (2-EHA) and n- butyl acrylate (n-BA). These sensitisers were used as received.

3. Stabilisers

Certain sensitisers have been found to affect the stability of certain latices. The major differences among latices lie in the non-rubber components. Thus the destabilisation has been attributed to certain non-rubber present in the latices (18,19). This effect was more pronounced when the sensitiser used was n-BA. To overcome this problem, the used of a stabiliser is thus a prerequisite. Potassium hydroxide solution of 10% concentration, potassium laurate solution of 20% concentration and potassium laurylic acid were employed for the purpose.

4. Diluent

The concentrated natural rubber latex was diluted to 50% TSC. Distilled water was used as the diluent.

5. Co-60 source

The source of gamma-rays is from Co-60 radioisotope, latex samples were irradiated in polyethylene bottles placed infront of Co-60 source. At a fixed irradiation time various radiation doses were obtained by varying the distances between the samples and the source.

Prior to actual work , the dose mapping of each sample position was carried out using ceric-cerous dosimeters. This was used as a guideline for further works. Although this was done for every subsequent irradiation , dosimeters were placed at the samples to assure of the absorbed doses actually received. This was thus reported as the actual doses.

Formulation and Method

A typical latex formulation for preparing RVNRL is shown in Table 1. The addition of the chemicals into the latex was carried out with gentle stirring and in the order given in Table 1. The latex mixture was diluted with distilled water and stirred for a couple of hours before allowing to mature at room temperature for about 16 hours. The latex mixture was then placed into one-litre screw-capped bottles and irradiated at the dose ranging between 0.84 to 2.45 KGy per hour depending on the position of the sample. After irradiation at which stage the latex now known as RVNRL were tested and evaluated for their properties.

TEST AND EVALUATIONS OF RVNRL

RVNRL films were cast from the samples. These were prepared on glass plates and dried at room temperature. Leaching in distilled water was done overnight at room temperature, followed by drying at room temperature before the films were given heat treatment in an air convention oven at 70 C for an hour. The films were kept in dessicators until required. Five dumb bell shaped test pieces were cut from each samples according to BS 6746. Tensile tests were carried out with the use of a Universal Testing Machine , Instron , Model 4301 , at a crosshead speed of 500 mm per minute according to ASTM D413-80.

The mechanical stability tests (MST) were carried out using a Klaxon Natural Rubber Lattices Mechanical Stability apparatus. Equilibrium Swelling Ratio , Q was obtained after immersing a weighed sample in hexane for 72 hours. The ratio is obtained by the following :-

$$Q = \frac{\text{Wt. of swollen sample} - \text{wt. of sample}}{\text{wt. of sample}}$$

The pH readings were determined using a Schott Gerate pH-Meter , Model CG820.

The samples viscosities were monitored with the use of a Brookfield Digital Viscometer , Model LVTD. The measurements were carried out at 25 C. The stability of RVNRL upon storage can be determined by the changes in mechanical stability , viscosity , pH, colour and tensile properties.

Table 1 : Latex formulation.

Material	Amount phr	Part by weight, g.
Concentrated NR latex (60% DRC)	100	167
Stabiliser	0.2	2
Sensitiser	5.0	5.0
Water	Add to 50% TSC	26.4

Figure 1

GRAPHS OF TENSILE STRENGTH VS IRRADIATION DOSE

Formulation NRL A + KOH + CCl_4 + H_2O

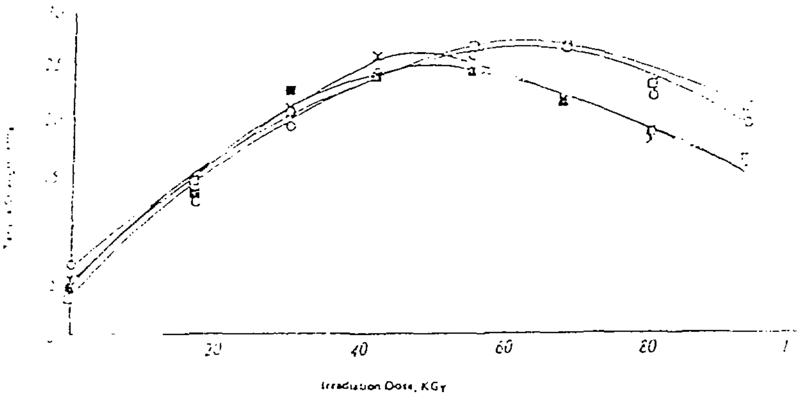


Figure 2

GRAPHS OF TENSILE STRENGTH VS IRRADIATION DOSE

Formulation. NRL A + KOH + 2-EHA + H_2O

(2-EHA concentrations : ○ 2 phr, ■ 3 phr, ◇ 4 phr, x 5 phr)

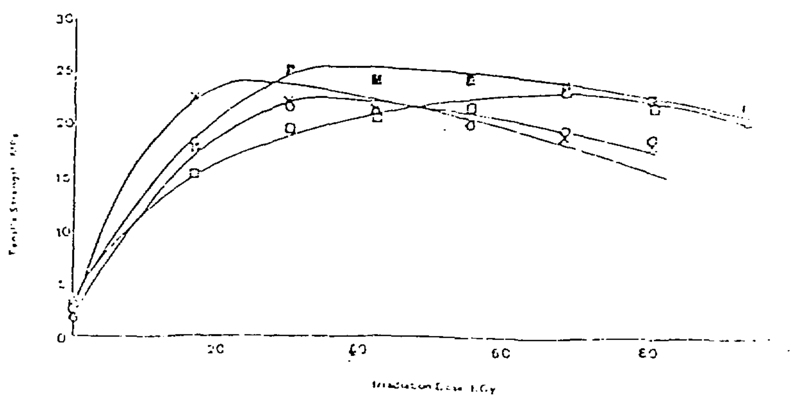


Figure 3

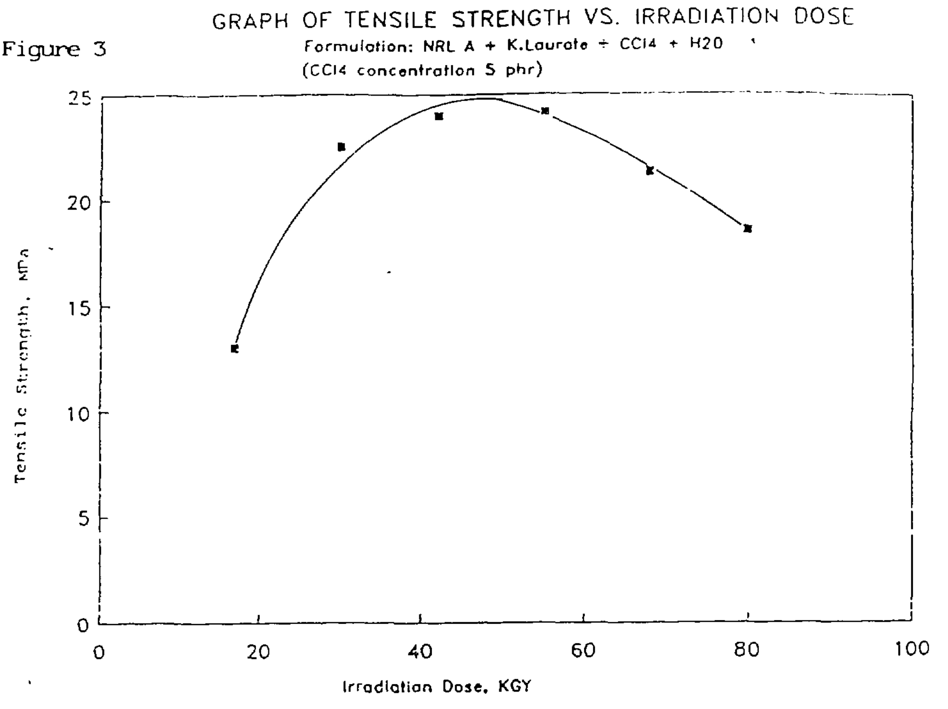


Figure 4

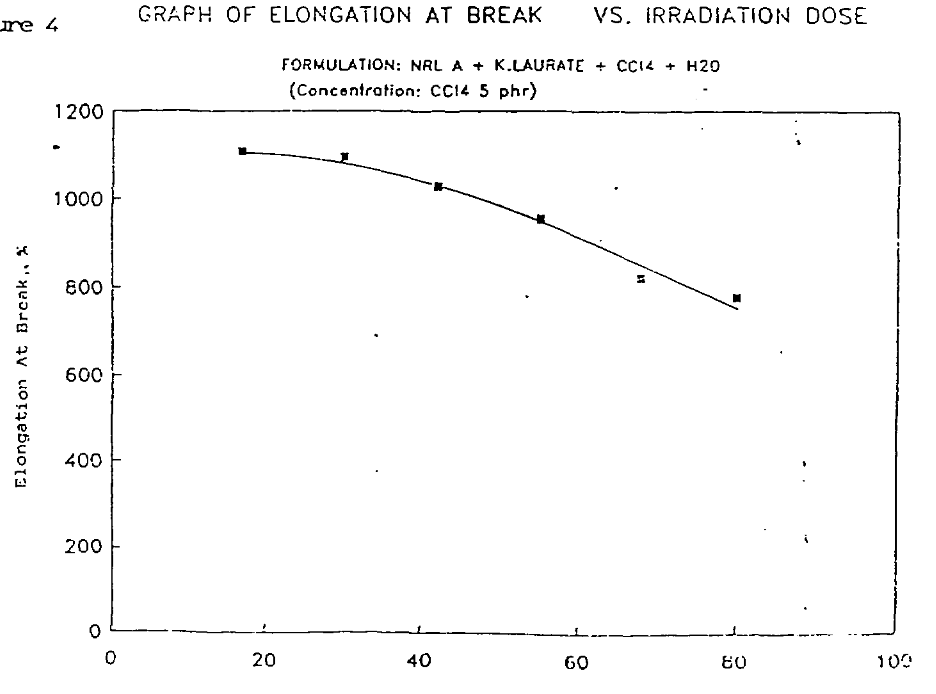


Figure 5

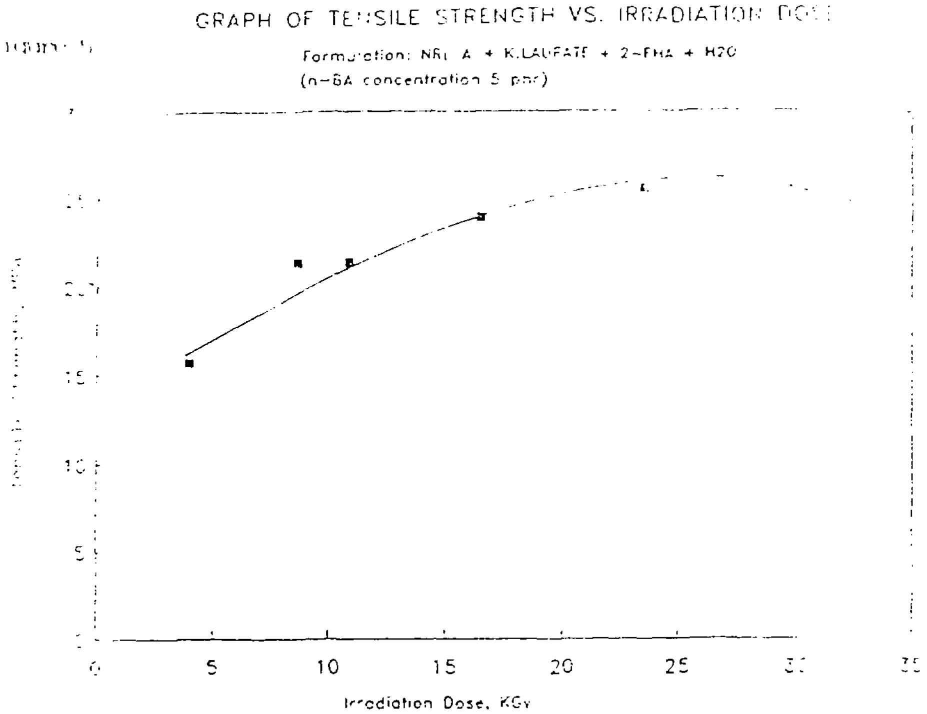


Figure 6

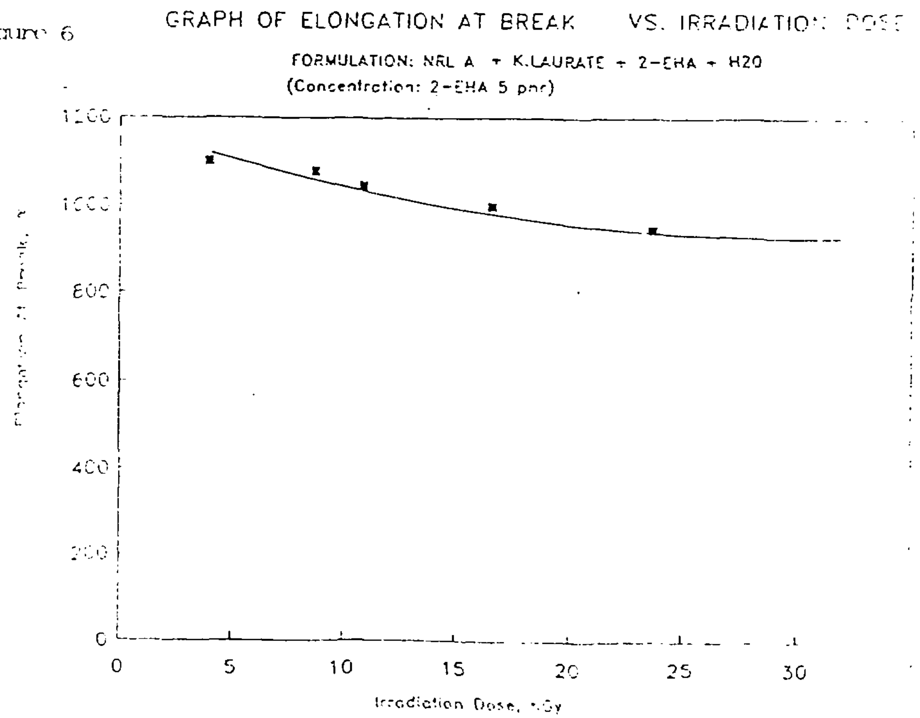


Figure 7

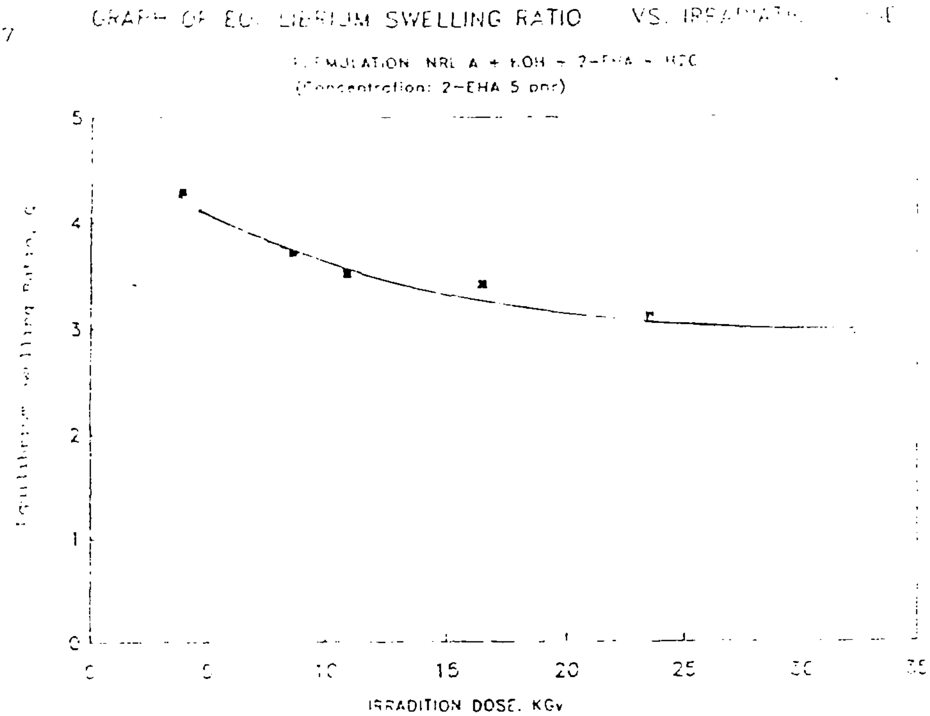


Figure 8

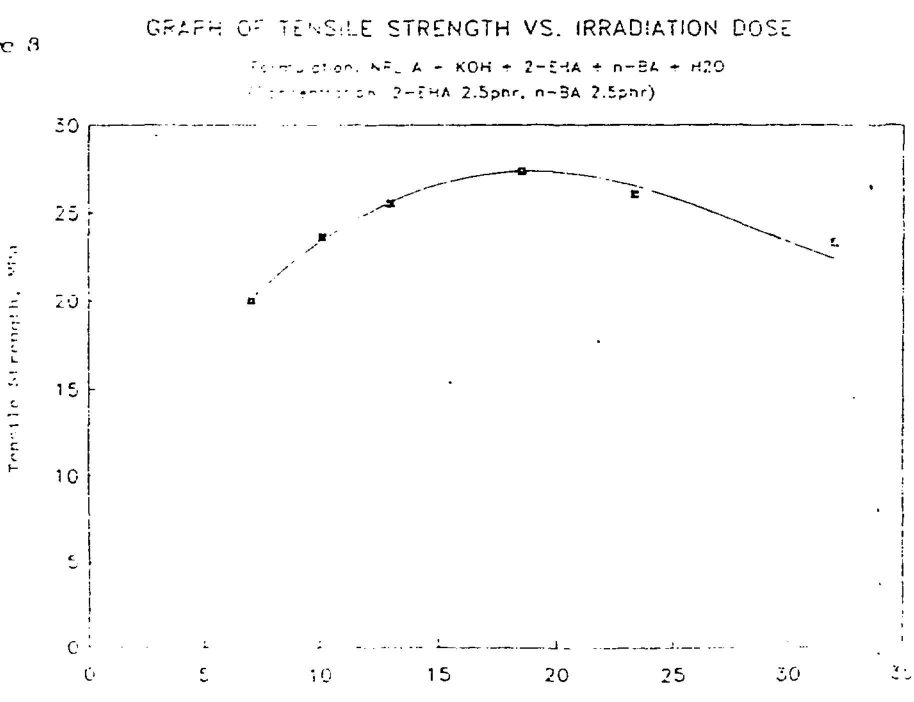


Figure 9

GRAPH OF ELONGATION AT BREAK VS. IRRADIATION DOSE

FORMULATION: NRL A + KOH + 2-EHA + n-BA + H2O
(Concentration: 2-EHA 2.5 phr, n-BA 2.5 phr)

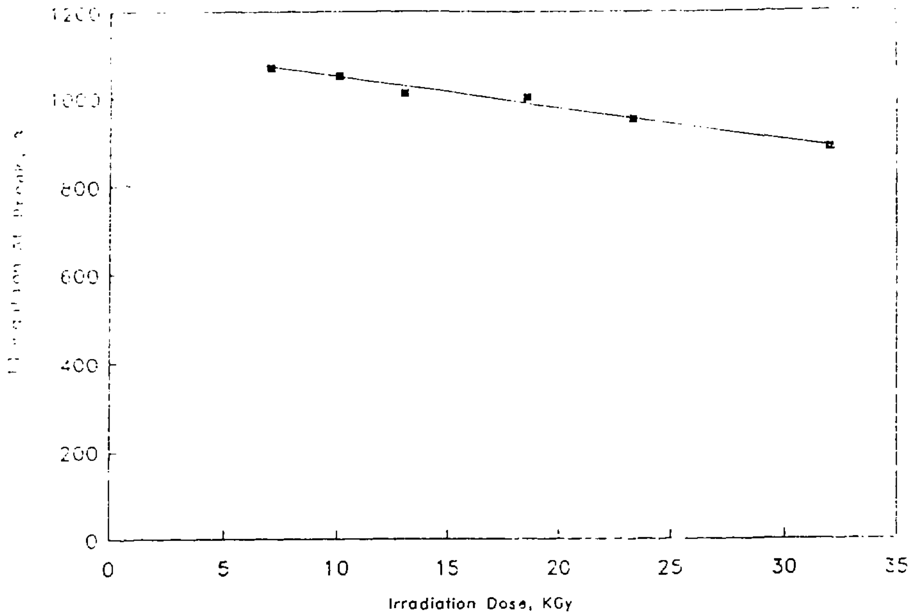


Figure 10

GRAPH OF EQUILIBRIUM SWELLING RATIO VS. IRRADIATION DOSE

FORMULATION: NRL A + KOH + 2-EHA + n-BA + H2O
(Concentration: 2-EHA 2.5phr, n-BA 2.5 phr)

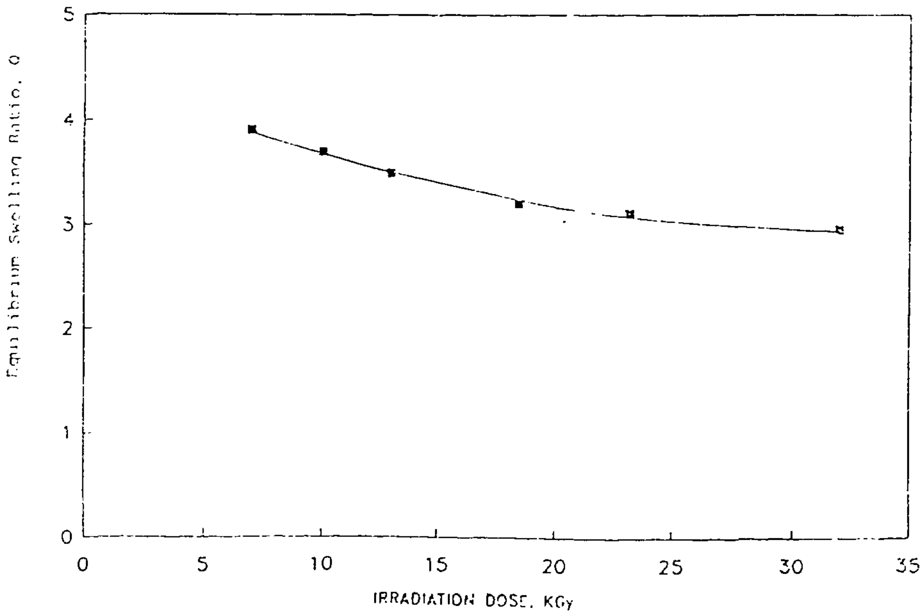


Figure 11

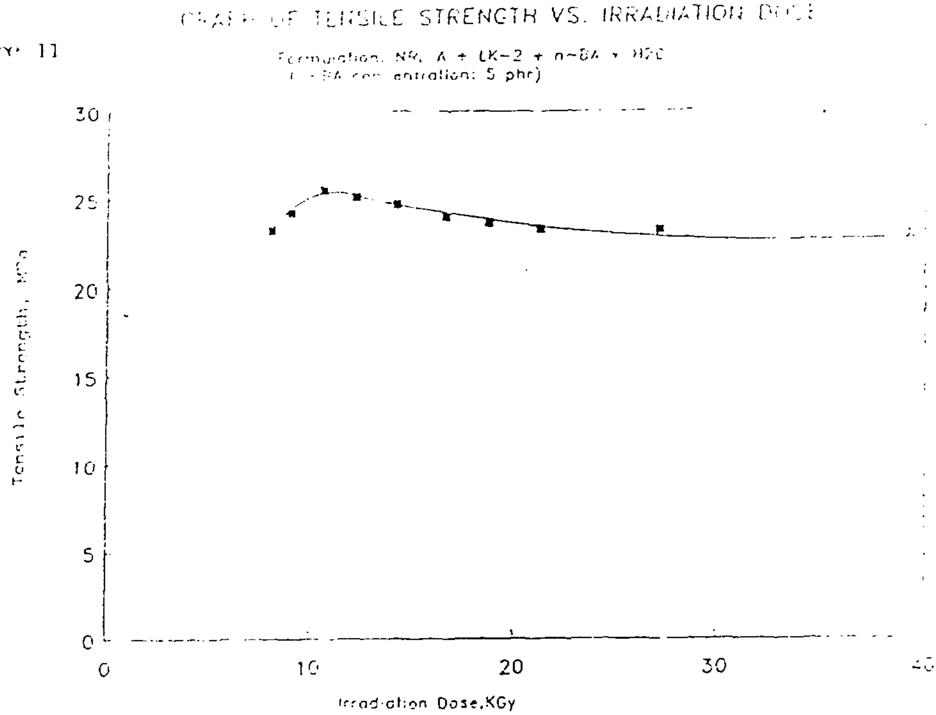


Figure 12

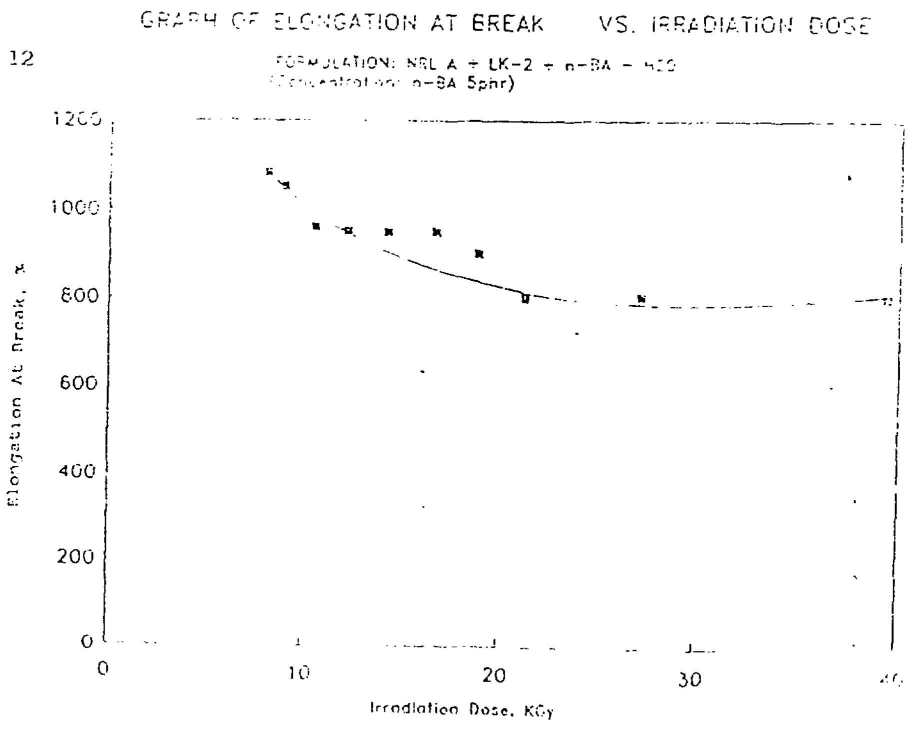


Figure 13

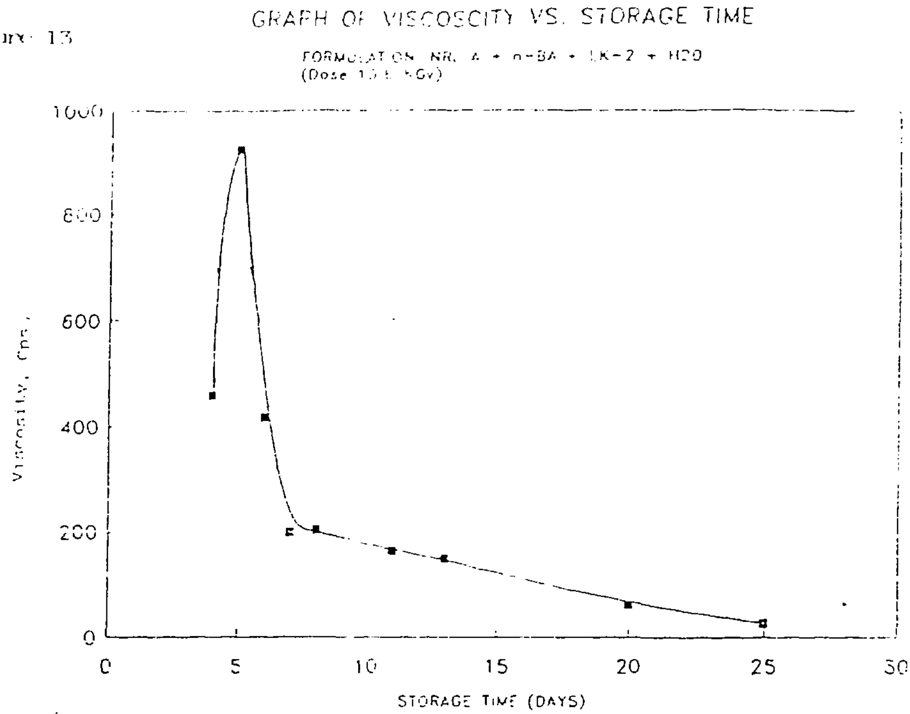


Figure 14

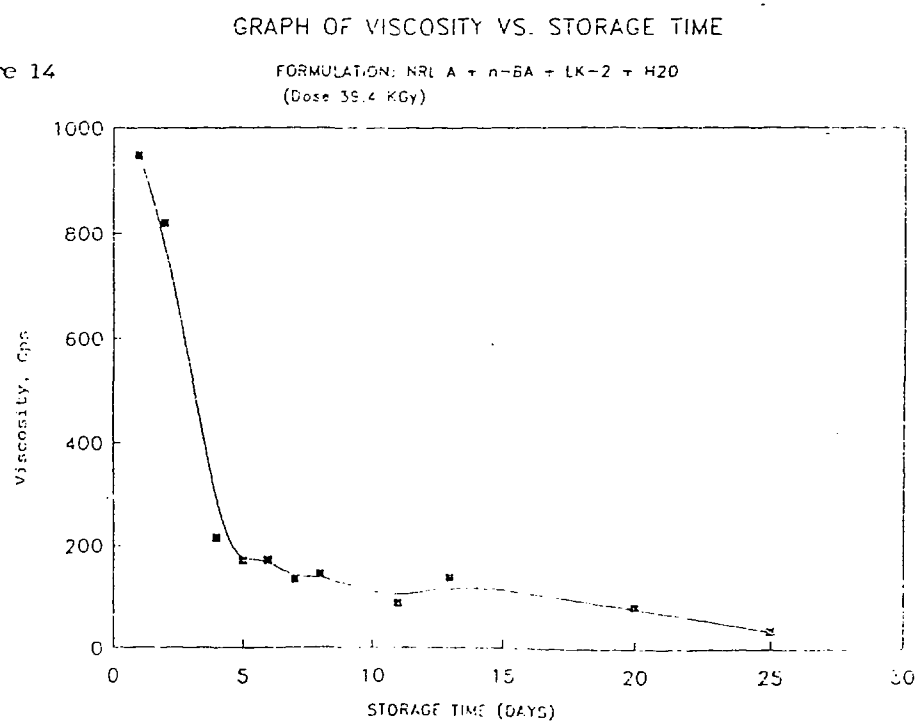


Figure 15

GRAPHS OF TENSILE STRENGTH VS IRRADIATION DOSE

Formulation : NRL C + KOH + 2 EHA + H_2O

(2 EHA concentrations: ○ 5 phr, □ 4 phr, ■ 3 phr and ● 2 phr)

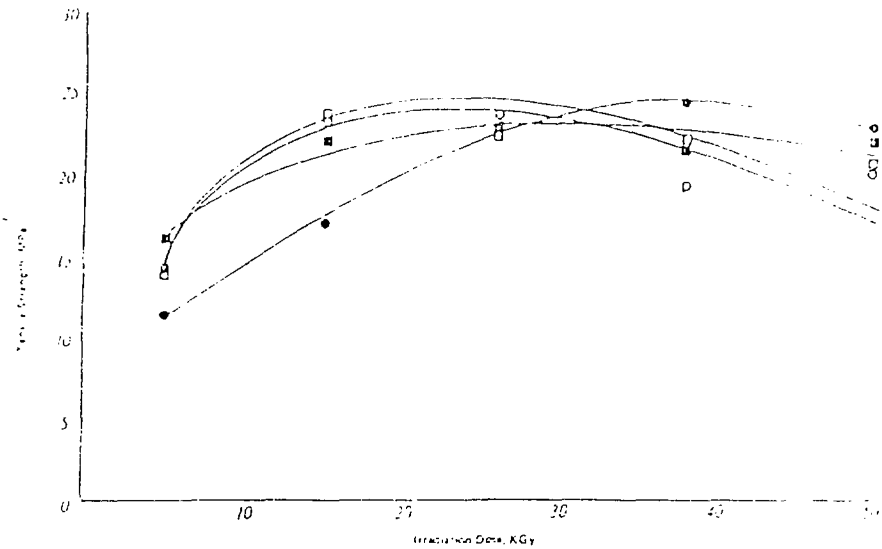


Figure 16

GRAPHS OF TENSILE STRENGTH VS IRRADIATION DOSE

Formulation : NRL C + KOH + nBA + H_2O

(nBA concentrations: ● 2 phr, ■ 3 phr and □ 4 phr)

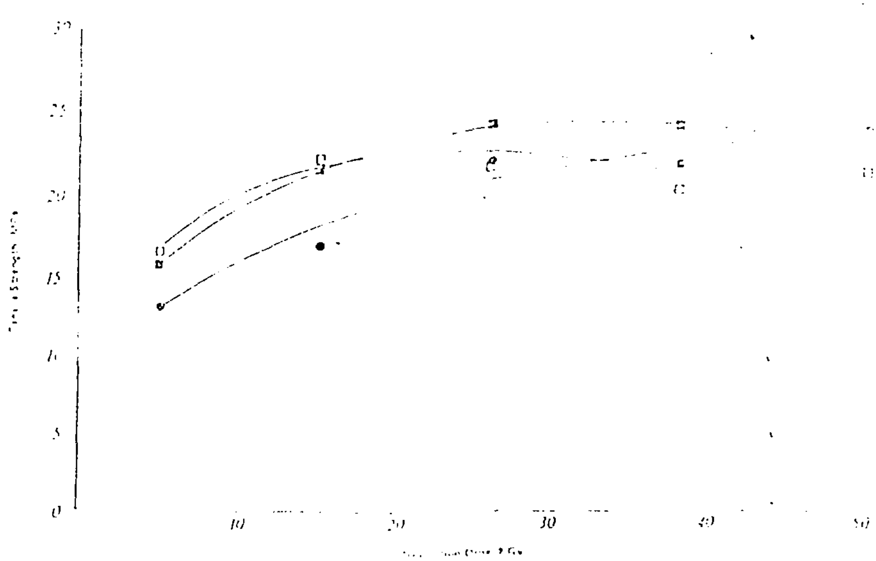


Figure 17

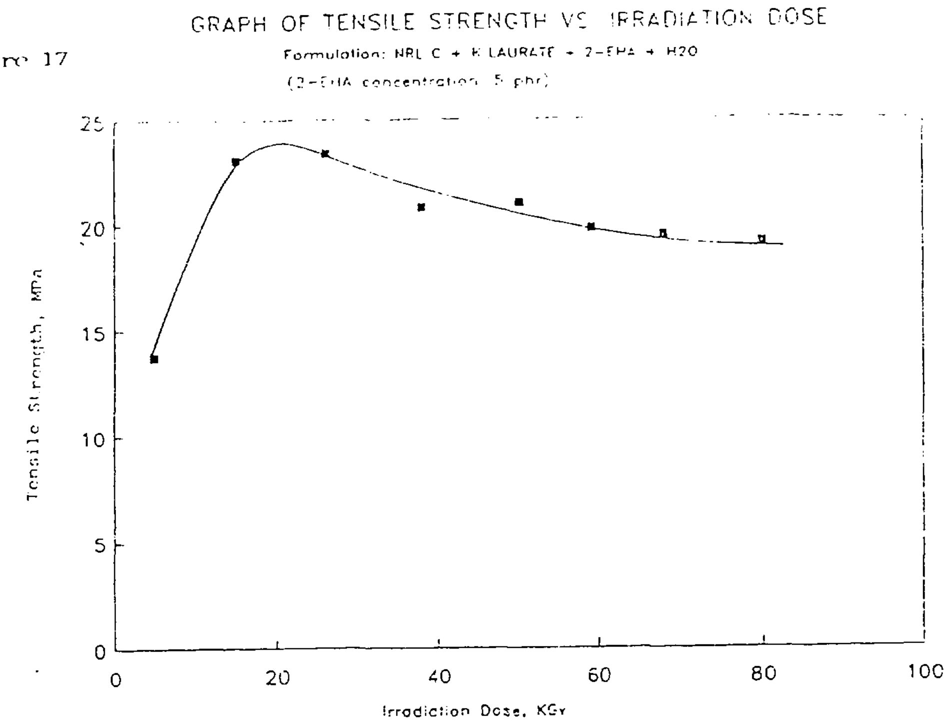


Figure 18

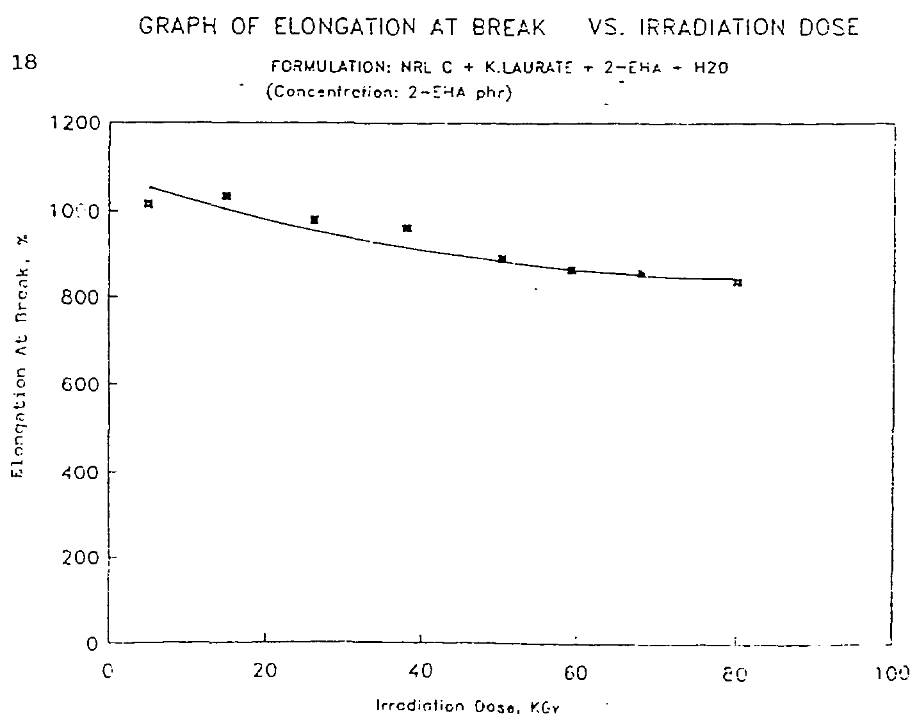


Figure 19

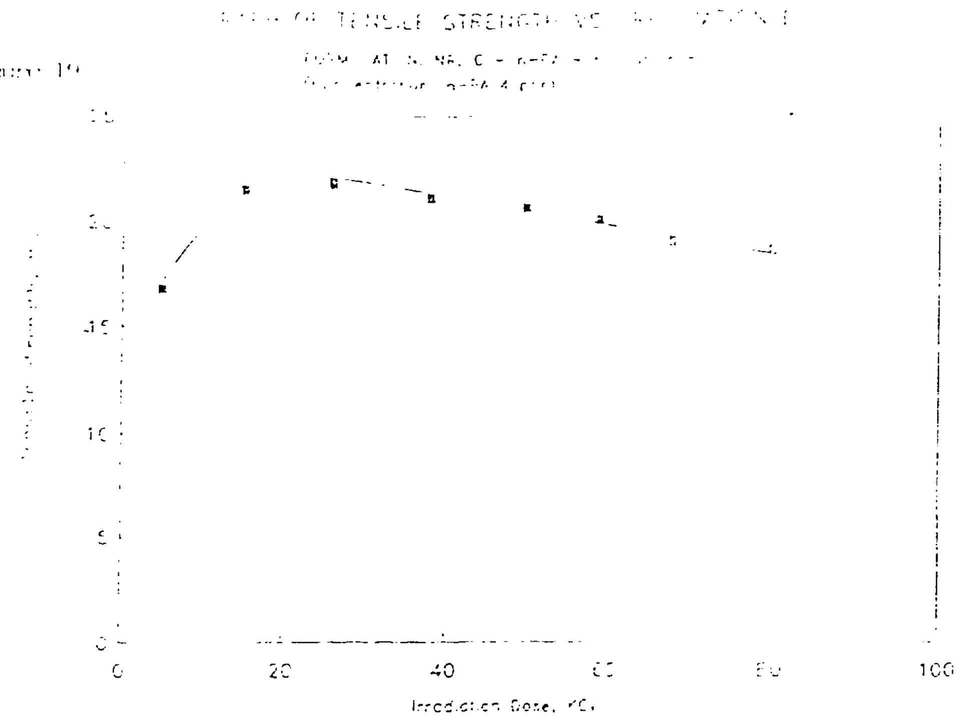


Figure 20

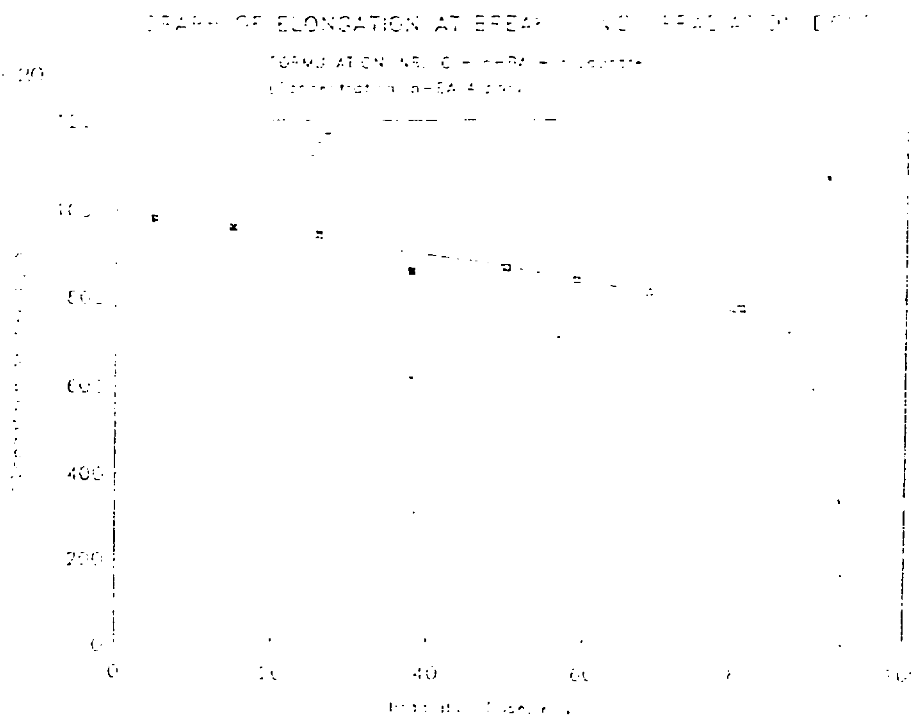


Figure 21

GRAPH OF TENSILE STRENGTH VS. IRRADIATION DOSE

Formulation: NRL C + LK-2 + n-BA + H20
(n-BA concentration 5 phr)

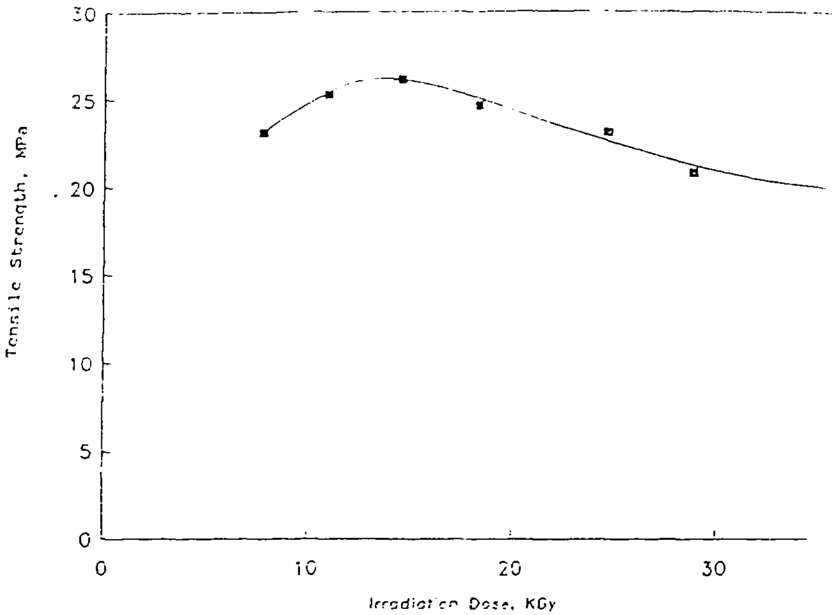
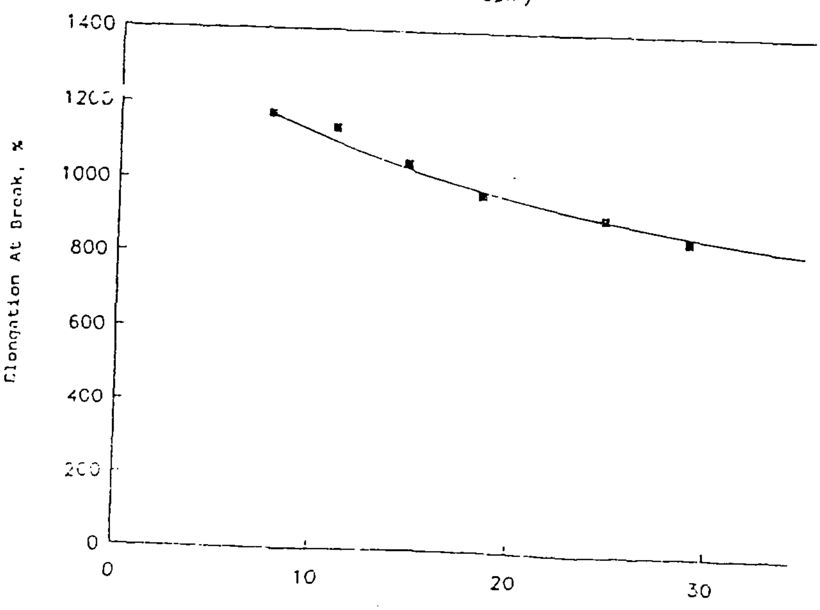


Figure 22

GRAPH OF ELONGATION AT BREAK VS. IRRADIATION

FORMULATION: NRL C + LK-2 + n-BA + H20
(Concentration: n-BA 5phr)

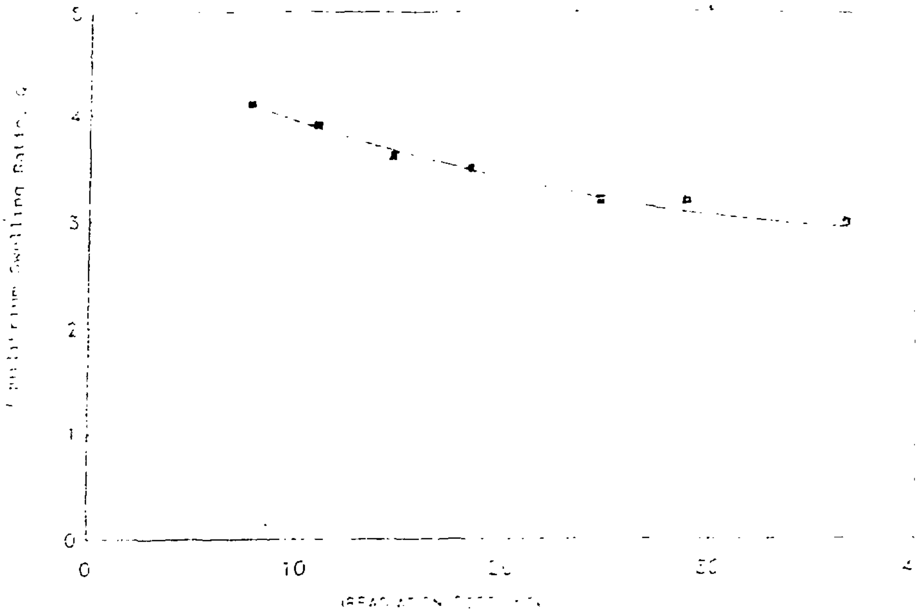


GRAPH OF EQUILIBRIUM SWELLING RATIO VS IRRADIATION DOSE

Figure 25

FORMULATION NO ...

(Concentration ...)



GRAPH OF ...

Figure 26

FORMULATION ...

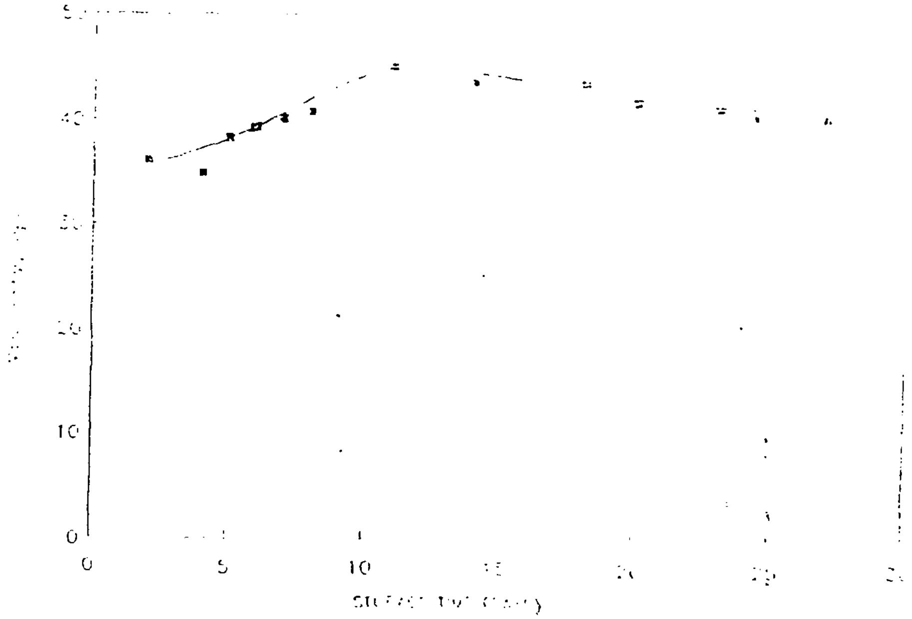


Figure 25

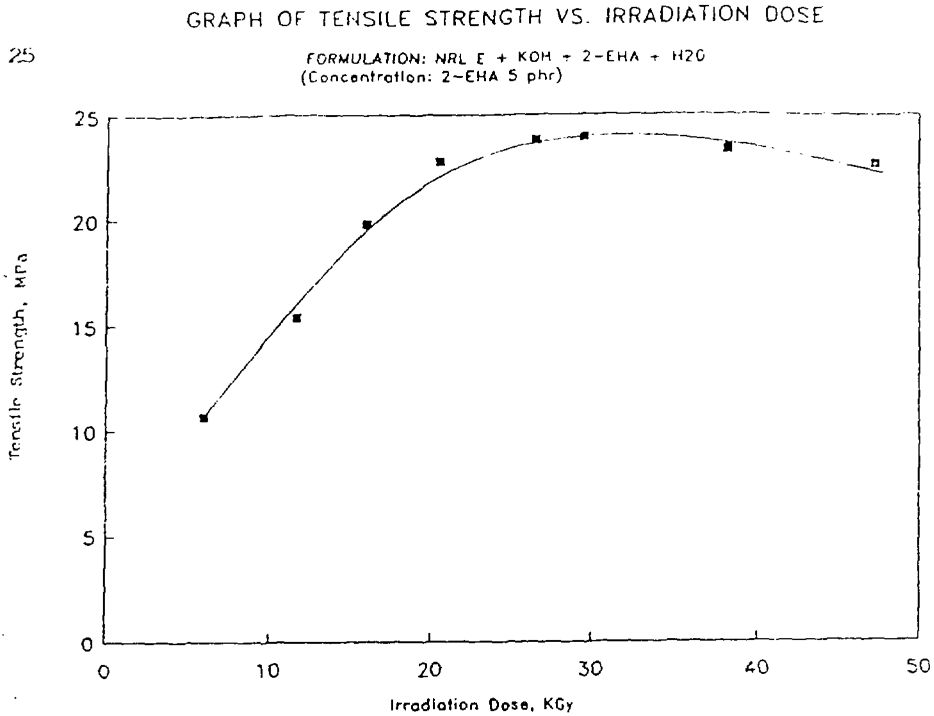


Figure 26

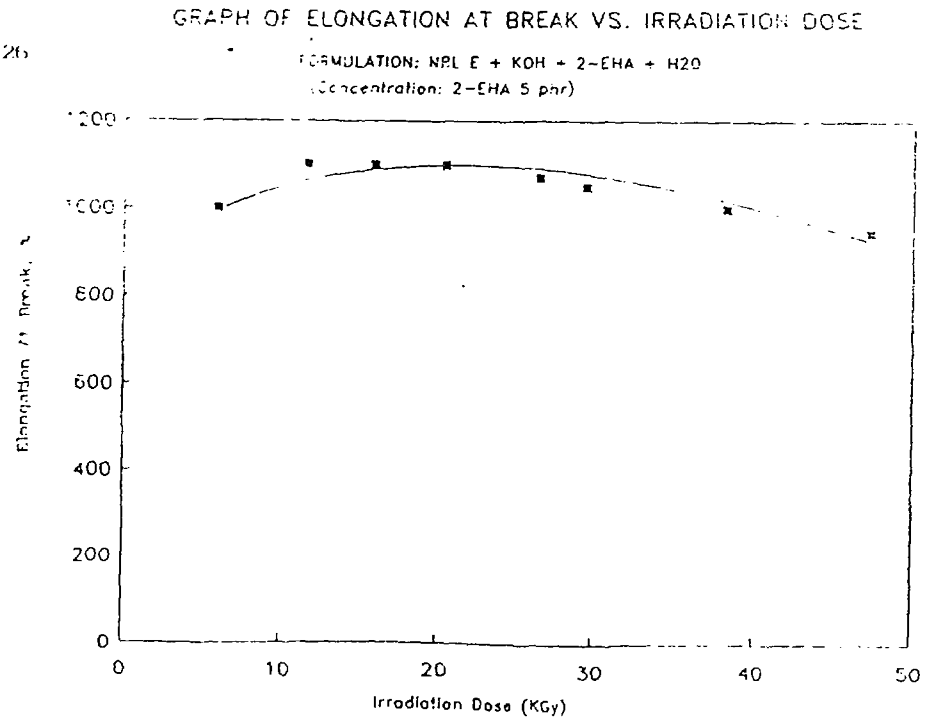
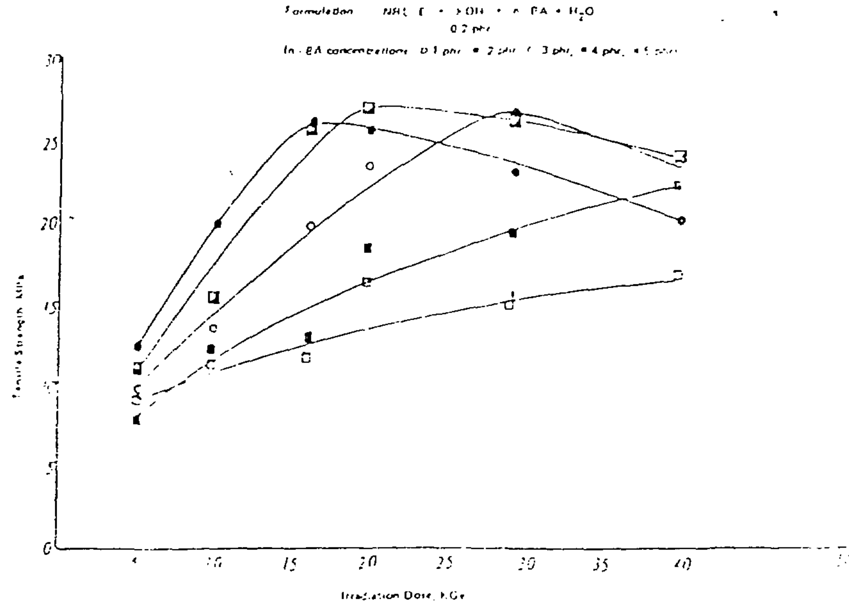


Figure 27

GRAPHS OF TENSILE STRENGTH VS IRRADIATION DOSE



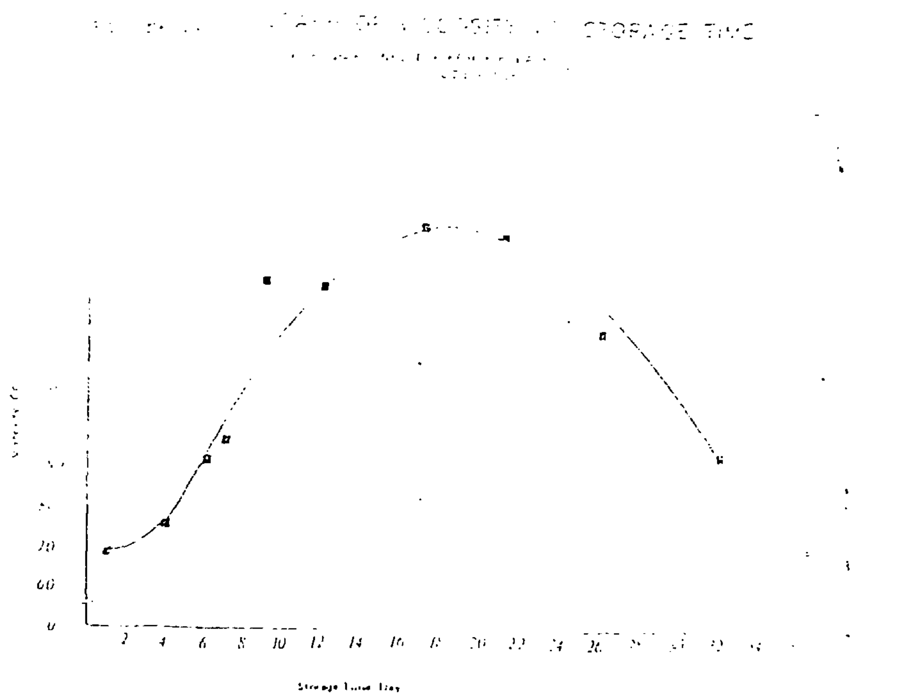


Figure 29

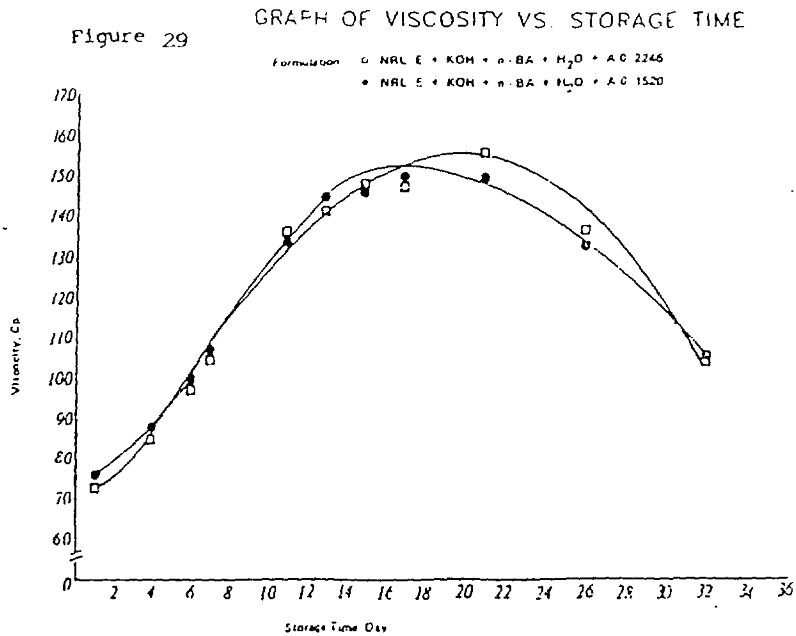

GRAPH OF VISCOSITY VS. STORAGE TIME
Formulation
□ NRL E + KOH + n-BA + H2O + AC 2246
• NRL E + KOH + n-BA + H2O + AC 1520
Viscosity, Cp
170
160
150
140
130
120
110
100
90
80
70
60
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
Storage Time Day

Figure 30

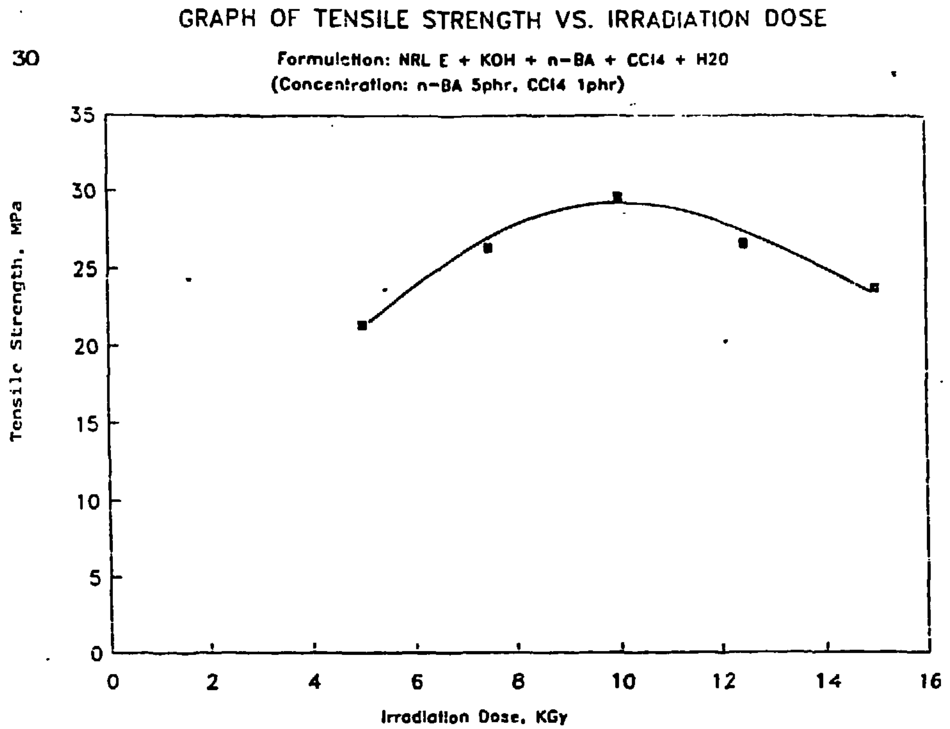
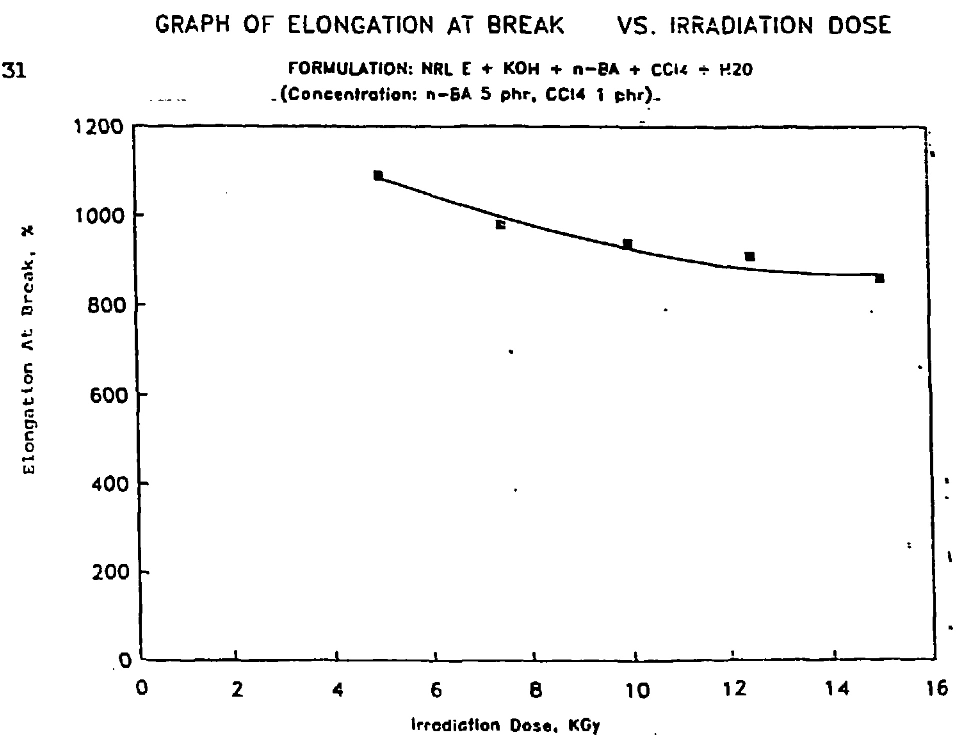


Figure 31



REFERENCES

1. NAKAMURA, A., IKARASHI, Y., TSUCHIYA, T. and KANIWA, M., Radiation Vulcanized Natural Rubber Latex is Not Cytotoxic , Proc. Int. Symp. On Radiation Vulcanization Of NR Latex , Japan , 79 Jan 1990.

2. CHYAGRIT SIRI-UPATHUM , PROPERTIES OF RVNRL , A Paper Presented at National Workshop On Radiation Vulcanization of Natural Rubber Latex , Kompleks Puspati , Bangi , Sept., 1990.

3. SHIMAMURA, Y., Development of Optical Laser Balloon and Drainage from Radiation Vulcanized Natural Rubber Latex , Proc. Int. Symp. On Radiation Vulcanization of NR Latex , Japan , 88 Jan 1990.

4. TSUSHIMA , K., MAKUUCHI, K., YOSHII , F and ISHIGAKI , I., Commercialization of Protective Rubber Gloves by Radiation Vulcanization , Proc. Int. Symp. On Radiation Vulcanization of NR Latex , Japan , 127 Jan. , 1990.

5. SUNDARDI , F., UTAMA , M., ISKANDAR , S. and HERWINANI. , Development of Condoms and Gloves from Radiation Vulcanized Natural Rubber Latex , Proc. Int. Symp. On Radiation Vulcanization of NR Latex , Japan 132 Jan. , 1990.

6. MAKUUCHI , K. et. al., Development of Rubber Gloves by Radiation Vulcanization , Proc. Int. Rubb. Conf., K.Lumpur , 104,1988.

7. ASAO, M., KUNUSAWA, S. and MINOURA , Y., Gamma-ray Vulcanization of Natural Rubber Latex , Kogyu Kagaku Zasshi , 64, 2066-2071 (1961).

8. LI ZHENGGUI and HU YOUMU. , Radiation Vulcanization of Natural Rubber Latex , Atomic Energy , 7, 618-627 (1964).

9. KARTOWARDOYO , S. and SUNDARDI , F., Studies on the Preparation and the Uses of Co-60 Gamma-ray Irradiated Natural Rubber Latex , J. Appl. Polym. Sci., 21, 3077-3085 (1977).

10. MAKUUCHI,K., Introduction to Radiation Vulcanization of Natural Rubber Latex, A paper presented at National Workshop On Radiation Vulcanization of Natural Rubber Latex, Kompleks PUSPATI, Bangi, September, 1990.

11. SHUKRI AB. WAHAB., SIDEK DULNGALI and ZARIAH MOHAMED, Preparation, Processing and Potential Applications of RVNRL, A paper presented at National Workshop On Radiation Vulcanization of Natural Rubber Latex, Kompleks PUSPATI, Bangi, September, 1990.

12. PANSA, C.P., SHUKRI, A.W., DAVENDRA, R. and MAKUUCHI, K., Selection and Characterization of natural rubber latex for radiation vulcanization of natural rubber latex, Final Report to IAEA, May, 1987.

13. MAKUUCHI, K., HAGIWARA, M. and SERIZAWA, T., Radiation Vulcanization of Natural Rubber Latex With Polyfunctional Monomers-11, Radiat. Phys, Chem., 24, 203-207 (1984).

14. CHEN, Z.H and MAKUUCHI, K., n-Butyl Acrylate As a Sensitiser For RVNRL , Proc. Int. Symp. On Radiation Vulcanization of NR Latex, Japan 327 Jan., 1990.

15. MAKUUCHI, K. and HAGIWARA, M., Radiation Vulcanization of Natural Rubber Latex With Polyfunctional Monomer, J. Appl. Polym. Sci., 29 965-976 (1984).

16. MAKUUCHI, K. and TSUSHIMA, K., Radiation Vulcanization of Natural Rubber Latex With Diacrylate, J. Soc. Rubber Ind.,Japan, 61, 471-477 (1988)

17. MAKUUCHI, K. and TSUSHIMA, K., Radiation Vulcanization of Natural Rubber Latex With Monofunctional Monomers, J. Soc. Rubber Ind., Japan, 61, 478-482 (1988)

18. NORJANAH MOHID., MAKUUCHI, K., YOSHII, F. and ISHIGAKI, I., Effect of Non-Rubber Components on Sensitized RVNRL, Proc. Int. Symp. On Radiation Vulcanization Of NR Latex, Japan, 157 Jan. 1990.

19. HASMA, H., Personal Communication, Rubber Research Institute of Malaysia, 1990.

RESULTS AND DISCUSSIONS.

From the results obtained this far it is learned that within the range of irradiation dose employed in the experiments, the tensile strengths of RVNRL film samples increases with irradiation dose to reach the maximum tensile strength before it starts to decrease again. The irradiation dose require to produce the maximum tensile strength was observed to be influenced by the type of sensitiser used and their amount , Figures 1, 2, 15, 16, 27. The more sensitiser used the lower was the dose require to produce the maximum tensile strength. However no attempt was made to use more than 5 phr of any of the sensitisers , since this may defeat the main aim of the project, i.e. to produce non-cytotoxic and environmentally-friendly vulcanized natural rubber latex.

Graphs of elongation at break versus irradiation dose are presented in Figures 4, 6, 9, 12, 18, 20, 22, 26, 31. In general the graphs indicated that the elongation at break decreases with irradiation dose up to the dose employed in the experiments. Three types of sensitisers i.e. CCl_4, 2-EHA and n-BA were used in the experiments. The most promising results (evaluated in terms of the dose required to produce the maximum tensile strength) was shown when n-BA was used as the sensitiser. However, the merits of n-BA is only observed when the right stabiliser is used, otherwise it can cause coagulation to certain latices. With 2-EHA as the sensitiser no coagulation problem is encountered with whatever stabilisers or latices used. The disadvantage however lies in the higher irradiation dose requirement and the residual smell in the products. The used of CCl_4 as a sensitiser was carried out for experimental purposes only as we are aware that CCl_4 is a carcenogenic material.

Mechanical stability test measurements were carried out in the initial stage. A standard procedure is not applicable however as RVNRL is much too stable.

From the pH measurements it was abserved that the alkalinity of the latex mix is not affected by the additives.

Figures 13, 14, 24, 28, 29 are the viscosity measurements taken over a period of time. There is a general trend whereby the viscosity increases to a maximum before going down again to almost its original value. How pronounced the curve is, depends on the type of stabiliser used. Some stabilisers showed a very gradual curves whereas some gave steeper curves. This could be used to advantage for dipping operations. It allows the user to select at which viscosity he requires. The viscosity characteristic of RVNRL is not influenced by the addition of antioxidant.

CONCLUSIONS

From the results of viscosity studies it indicates that the origin of the latex has a strong influence on the stability of the latex towards the sensitizer . It is believe that the source of such differences lie in the variation of the non-rubber components. More detail studies are now being carried out to ascertain this.

Different latices will require different stabiliser system especially where n-BA is concerned.

The most significant improvement is in the radiation dose reduction with the best stabiliser-sensitiser system. For this project to take off on a commercial level , this will be a positive factor in terms of the economics.

ACKNOWLEDGEMENT

The authors would like to thank all the members of RVNRL Group for their contribution.