

## **Modification of Natural Rubber Latex in the Presence of Vinyl Monomers by Gamma Radiation**

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*Glicidyl methyl methacrylate (GMA), hydroxyl ethyl methyl methacrylate (HEMA) and diethyl amino methyl methacrylate (DE) have been copolymerised in natural rubber (NR) latex by gamma radiation. Some interesting properties of the copolymers were observed. Since ammoniated latex was used, epoxide ring opening reaction of the GMA occurred. Attempts to preserve the epoxide group by addition of acetic acid or formaldehyde to remove ammonia resulted in poor radiation stability of the polymer latex. The percentage of the homopolymer formed for HEMA-NR copolymer was higher than that for DE-NR copolymer. In the case of HEMA-NR system, the percentage of homopolymer polyHEMA formed (based on the initial monomer concentration) generally increased with monomer concentration while in the DE-NR system, the percentage of homopolymer polyDE decreased with monomer concentration. The physical properties of the copolymers were compared with those of NR dry films whose latices had been irradiated at various doses. Generally, there was enhancement of the tensile strength of NR in the presence of the polymerised monomers.*

Numerous studies<sup>1</sup> have been made on the graft polymerisation of vinyl monomers onto NR. Due to certain technical reasons, the methyl methacrylate-NR copolymer has been most extensively studied<sup>2</sup>. This has led to the commercial development and exploitation of the rubber under the trade name, Heveaplus MG.

In previous studies, oil-soluble monomers were mostly used in the graft polymerisation of vinyl monomers in NR latex. Little work has been carried out on hydrophilic monomers. Burfield<sup>3</sup> *et al.* has studied the graft polymerisation of methacrylamide in NR latex by per-

sulphate initiation. Their report indicates that there are some differences in the kinetics of polymerisation between oil-soluble monomers and hydrophilic monomers in NR latex.

Few monomers (e.g. methyl methacrylate, styrene and acrylonitrile) have been investigated in radiation-induced grafting with NR latex<sup>4,5,6</sup>. In the present investigation, three hydrophilic monomers (GMA, HEMA and DE) were grafted onto NR latex by gamma radiation. The effects of monomer concentration and irradiation dose on the properties of the graft copolymer latices and copolymer dry films are discussed.

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## EXPERIMENTAL

### Materials

The NR latex used was a high ammonia (HA) centrifuged concentrate of 61.3% total solids. In all cases the latex concentrate was diluted with water to 35% total solids content. Commercial monomers of GMA, HEMA and DE were used as supplied (without purification). Other materials were of laboratory reagent grade.

### Method

To the diluted latex, a solution of 2 p.h.r. of 10% (by weight) sodium dodecyl sulphate (SDS) was added. The latex was stirred (using a magnetic stirrer) and then left to stand for at least 1 h before the addition of pH modifiers or monomers.

The latex was poured into 100 ml cylindrical sample bottles of about 2 cm radius. Acetic acid or formaldehyde (as pH modifiers) was slowly added at various levels and the pH of the latex was measured. It was then left to stand for at least 1 h before the addition of GMA. No pH modifier was added to HEMA-NR and DE-NR latices.

The polymer latices were kept standing for about 12 h or more before they were exposed (at ambient temperature of about 20°C) to a Co-60 source of nominal field intensity of 0.5 MR per hour (or otherwise stated). The percentage conversion of monomer was determined from the total solids content of the latices before and after polymerisation. The total solids content was determined by drying samples of the latex at 60°C and finally heating to a constant weight at 100°C.

The dry films of the irradiated latex were prepared on glass plates and dried at 25°C in a drying box. The dried films were then vacuum-dried for 2 h followed by 1 h heat treatment at 80°C before

carrying out the physical analysis. The gel fraction of the dried film was determined by extraction of the samples in toluene for 20 h at boiling point. The uncombined homopolymers (polyHEMA or polyDE) were extracted with methanol for five days at boiling point. The gas chromatographic analyses were carried out on the latex serum and monomer-ammonia reaction mixture, while infra-red analyses were carried out on thin dried films.

## RESULTS AND DISCUSSION

Glicidyl methyl methacrylate reacts with ammonia, resulting in the opening of the oxirane ring to produce hydroxy amines. The addition of acids or formaldehyde into the GMA-NR latex before irradiation was intended to lower the ammonia level and to see if the epoxide function could be preserved. However as shown in *Table 1*, stability of the GMA-NR latex was extremely sensitive to lowering of the pH. Increasing the level of SDS up to 4 p.h.r. did not help in improving the irradiation stability of the copolymer latex.

Using untreated latex (no pH modifier added), upto 10 p.h.r. GMA could be used without affecting the irradiation stability of the latex. The GMA-NR copolymer produced from this latex did not contain epoxide group. This was indicated by gas chromatographic analysis of the latex serum (from irradiated latex) and infra-red analysis of the dry film. *Table 2* shows the effect of GMA concentration on some colloidal properties of the latex and physical properties of the dry copolymer. The viscosity of the irradiated latex was high and it increased rapidly with increasing monomer concentration. As a result of this, the maximum GMA concentration that could be used without resulting in coagulation of the GMA-NR latex was rather low.

TABLE 1. EFFECT OF PH ON IRRADIATION STABILITY OF GMA-NR LATEX

| Condition                          | pH modifier |     |      |              |     |     |
|------------------------------------|-------------|-----|------|--------------|-----|-----|
|                                    | Acetic acid |     |      | Formaldehyde |     |     |
| Initial pH                         | 5.7         | 9.1 | 10.1 | 6.5          | 8.5 | 9.9 |
| pH before irradiation <sup>a</sup> | 6.0         | 8.9 | 9.2  | 9.6          | 9.2 | 9.1 |
| pH after irradiation               | X           | X   | 9.2  | X            | X   | 9.0 |

GMA concentration: 10 p.h.r.

Irradiation dose: 1 MR at 0.25 MR per hour

<sup>a</sup>Just after the addition of pH modifier

X: Samples coagulated

TABLE 2. EFFECT OF GMA CONCENTRATION ON COLLOIDAL PROPERTIES OF THE LATEX AND PHYSICAL PROPERTIES OF THE COPOLYMER

| Property                                     | Control | GMA (p.h.r.) |      |      |
|----------------------------------------------|---------|--------------|------|------|
|                                              |         | 2            | 5    | 10   |
| pH before irradiation                        | 10.4    | 10.2         | 10.2 | 9.8  |
| pH after irradiation                         | 10.4    | 10.2         | 10.0 | 9.5  |
| Viscosity after irradiation at 5 r.p.m. (CP) | —       | 9.0          | 23.3 | 69.1 |
| Tensile strength (kg/cm <sup>2</sup> )       | 129     | 125          | 211  | 276  |
| Elongation at break (%)                      | 1 400   | 1 150        | 890  | 860  |
| Gel fraction (%)                             | 74.3    | 65.6         | 67.1 | 72.0 |

Irradiation dose: 2.25 MR

Irradiation dose for control (without GMA): 3 MR

Tensile strength of the GMA-NR copolymer increased with monomer concentration. The tensile strength of samples with more than 5 p.h.r. GMA was higher than the control sample. The gel fraction increased (in a similar manner as tensile strength) with monomer concentration while elongation at break decreased with monomer concentration. A similar pattern of results (Table 3) was also observed for the effect of irradiation dosage on the above physical properties. No data was available to relate the above properties

TABLE 3. EFFECT OF IRRADIATION DOSE ON PHYSICAL PROPERTIES OF GMA-NR COPOLYMER

| Property                               | Irradiation dosage (MR) |      |      |
|----------------------------------------|-------------------------|------|------|
|                                        | 0.75                    | 1.25 | 2.25 |
| Tensile strength (kg/cm <sup>2</sup> ) | 151                     | 182  | 211  |
| Elongation at break (%)                | 1 210                   | 950  | 890  |
| Gel fraction (%)                       | 22.2                    | 33.3 | 67.1 |

Irradiation dose: 5 p.h.r

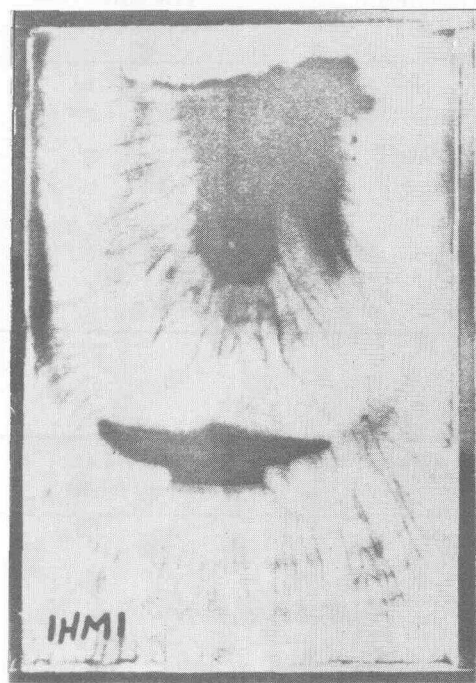
GMA concentration: 0.25 MR per hour

with graft percentage (of polymerised GMA) as characterisation work for this copolymer was difficult to carry out.

The film-forming property of DE-NR latex or that of GMA-NR latex was good. The HEMA-NR dry films produced distinct patterns as shown in *Figure 1*. These patterns disappeared on heating at 80°C for 1 h. This phenomenon could probably be explained in a similar manner as Cockbain *et al.*<sup>5</sup>'s description of MG latex (polymerised by redox catalyst), which gave a discontinuous, cracked film. An important point derived from their observation was that, for good film-forming properties, the polymerised monomer should be uniformly distributed throughout the latex particles. In the case of HEMA-NR system, the HEMA

monomer was water soluble and for this reason polymerisation would be favourable in the aqueous phase and at the surface of the latex particles. As a result the polymerised monomers were not uniformly distributed throughout the latex particles. Although GMA and DE are also hydrophilic monomers, their copolymer latices did not show similar film-forming properties as HEMA-NR latex. This was probably due to the difference in their hydrophilicities and their monomer reactivities. These factors influence the course of polymerisation and thus the distribution of the polymerised monomers.

Accurate determination of percentage monomer conversion was rather difficult. However, for all the monomer concentrations studied, 100% monomer conversion



6.1 p.h.r. HEMA



18.3 p.h.r. HEMA

*Figure 1. Surface appearance of HEMA-NR dry films. They were irradiated at 1 MR.*

was achieved when using irradiation dosage higher than 3 MR. With irradiation dosage lower than 3 MR, between 75% and 95% monomer conversion was achieved.

Table 4 shows the characterisation data of HEMA-NR copolymer. For this copolymer system, the percentage of homopolymer formed based on the total amount of monomer added was rather high. This was expected since polymerisation of HEMA largely occurred at the water phase and the surface of latex particles. As polymerisation proceeded much of it was being conducted in the polyHEMA environment, rendering it more difficult for grafting reactions onto NR to take place. Except for samples containing 5 p.h.r. HEMA, the percentage

of homopolymer polyHEMA formed increased with increasing monomer concentration.

In the case of the DE-NR system, the homopolymer formed from the monomer was probably not strictly polyethyl amino methyl methacrylate (PDE). This is because DE monomer in an alkaline state rearranges to N-hydroxy ethyl methacrylamide<sup>7</sup>. Since pH of the latex used was about 10, such a rearrangement probably has occurred.

Table 5 shows the characterisation data of the DE-NR copolymer. The percentage of the homopolymer PDE formed decreased with increasing monomer concentration i.e. the graft percentage increased with monomer concen-

TABLE 4. CHARACTERISATION DATA OF HEMA-NR COPOLYMER

| Dose (MR) | Monomer (p.h.r.) | Homopolymer polyHEMA (% of monomer) | PDE graft (% of total solids) |
|-----------|------------------|-------------------------------------|-------------------------------|
| 3         | 5                | 66                                  | 1.7                           |
| 3         | 10               | 71                                  | 2.9                           |
| 3         | 15               | 79                                  | 3.2                           |
| 4         | 5                | 100                                 | 0                             |
| 4         | 10               | 73                                  | 2.7                           |
| 4         | 15               | 86                                  | 2.1                           |
| 5         | 5                | 100                                 | 0                             |
| 5         | 10               | 49                                  | 5.1                           |
| 5         | 15               | 64                                  | 5.4                           |

TABLE 5. CHARACTERISATION DATA OF DE-NR COPOLYMER

| Dose (MR) | Monomer (p.h.r.) | PDE homopolymer (% of monomer) | Graft polyHEMA (% of total solids) |
|-----------|------------------|--------------------------------|------------------------------------|
| 3         | 5                | 60                             | 2.0                                |
| 3         | 10               | 45                             | 5.5                                |
| 3         | 15               | 22                             | 11.7                               |
| 4         | 5                | 100                            | 0                                  |
| 4         | 10               | 46                             | 5.4                                |
| 4         | 15               | 24                             | 11.4                               |
| 5         | 5                | 96                             | 0.2                                |
| 5         | 10               | 45                             | 5.5                                |
| 5         | 15               | 20                             | 12.0                               |

tration. This kind of behaviour is rather different from many copolymer systems. Comparatively, the DE-NR copolymer had a much higher percentage graft than HEMA-NR latex. Except for samples containing 5 p.h.r. DE, the percentage of homopolymer PDE formed seemed

to be independent of irradiation dose.

Figure 2 shows the infra-red spectra of NR, HEMA-NR and DE-NR copolymers. The shapes of the HEMA-NR and DE-NR spectra were generally similar to that of the NR spectrum. For the HEMA-NR copolymer, the strong and

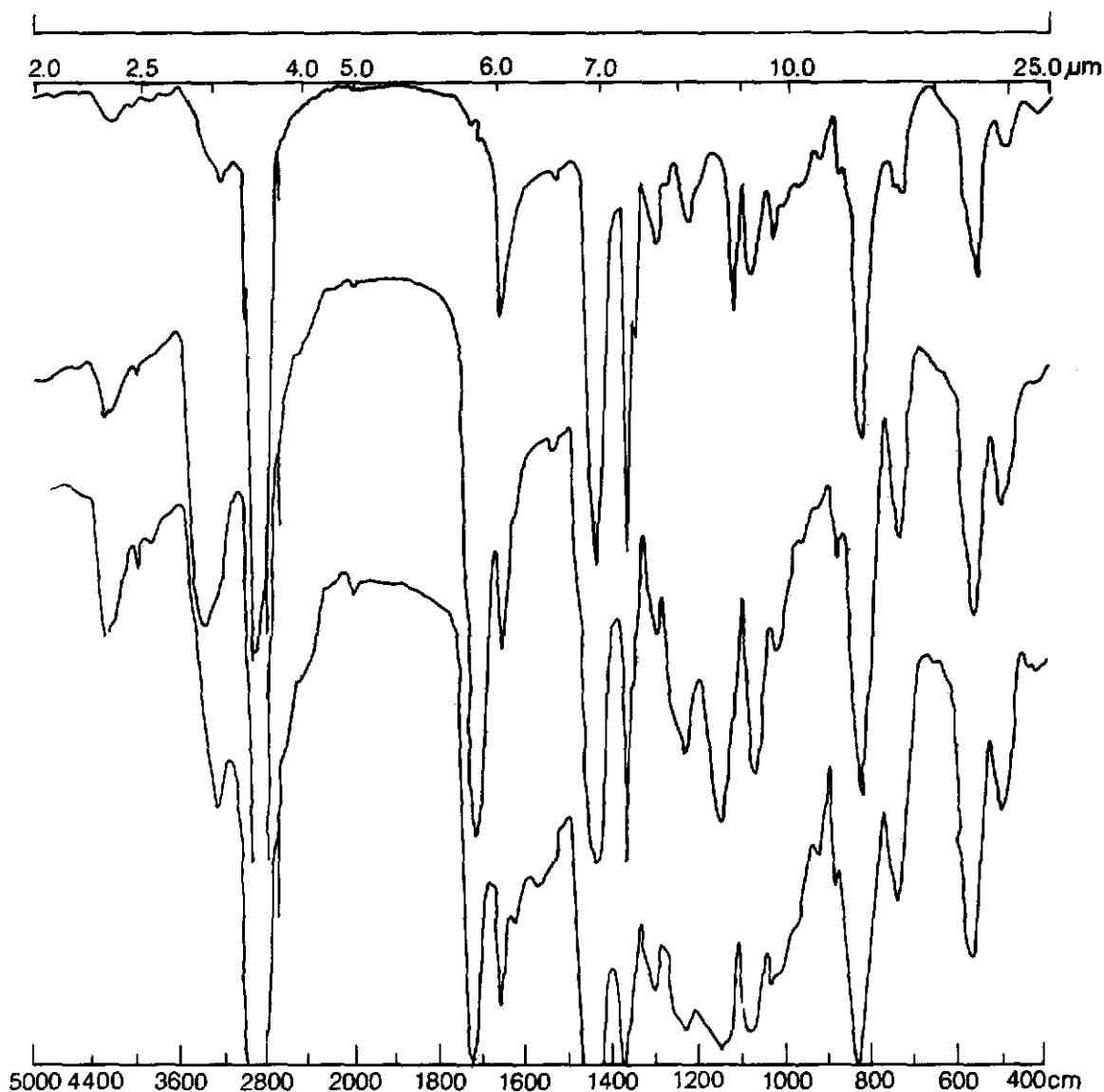


Figure 2. Infra-red spectra of NR, HEMA-NR and DE-NR dry films. The concentration of the monomer used for HEMA-NR and DE-NR copolymers was 15 p.h.r. and their latices were irradiated at 1 MR.

broad absorption band at  $3400\text{ cm}^{-1}$  was due to OH (the polymeric OH of HEMA). The strong absorption band at  $1720\text{ cm}^{-1}$  was attributed to the C=O stretching vibration. For the DE-NR spectrum, except for the absorption band at  $1720\text{ cm}^{-1}$  which was due to the C=O stretching vibration, there were no other useful bands to indicate the presence of amine or amide groups as a result of the polymerisation of DE in NR latex. Table 6 shows the water absorption behaviour of GMA-NR, HEMA-NR and DE-NR copolymers. Generally, the percentage water absorption decreased initially and then subsequently increased with increasing monomer concentration. The initial decrease was due to increase in the crosslink density of the rubber (by radiation induced crosslinking) while the subsequent increase was due to increase in the hydrophilic content in the copolymer.

The results shown in Figure 3 show the effect of dosage on the tensile strength property of the HEMA-NR copolymer. The results were rather scattered. Generally, the tensile strength increased with increasing dosage. The gel fraction also increased with dosage (Figure 4). Since the gel fraction values (for a particular dosage) of the copolymer were rather similar to the control and they were not very dependent on monomer concentration, the increase in tensile strength with dosage

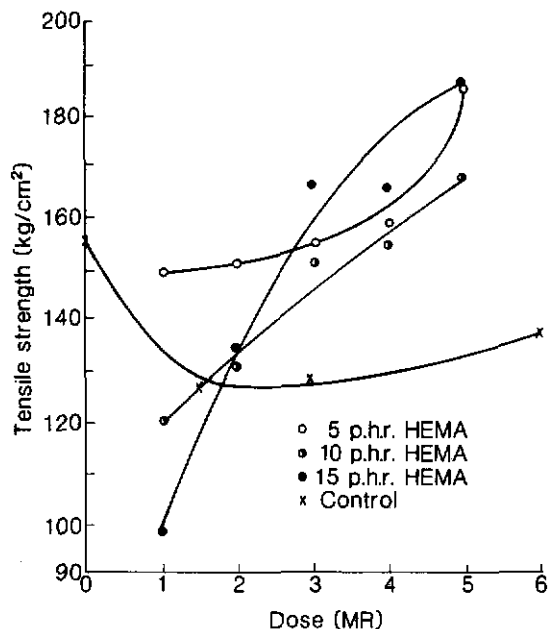


Figure 3. Effects of dosage on tensile strength of HEMA-NR copolymer.

was due to an increase in the crosslink density of the rubber (NR). Generally, there was an improvement in the tensile strength relative to the control sample. This observation indicates that the polymerised monomers positively contributed to certain mechanical properties of the copolymer.

The relation between the tensile strength and gel fraction with dosage for the DE-NR copolymer was rather similar to that of the HEMA-NR copolymer

TABLE 6. WATER ABSORPTION BEHAVIOUR OF COPOLYMERS

| Property                                   | Control | GMA-NR |      | HEMA-NR |                  |      | DE-NR |      |      |
|--------------------------------------------|---------|--------|------|---------|------------------|------|-------|------|------|
| Monomer level (p.h.r.)                     | 0       | 2      | 5    | 6.1     | 12.2             | 18.3 | 6.1   | 12.2 | 18.3 |
| Dose (MR)                                  | 1.25    | 1.25   | 1.25 | 1       | 1                | 1    | 1     | 1    | 1    |
| Water absorption <sup>a</sup><br>(% by wt) | 26.9    | 22.7   | 10.5 | 12.8    | 2.5 <sup>b</sup> | 16.5 | 8.5   | 8.3  | 9.9  |

<sup>a</sup>For 25 h.

<sup>b</sup>The very low figure obtained seemed to be in error although a repeat test showed a similar result.

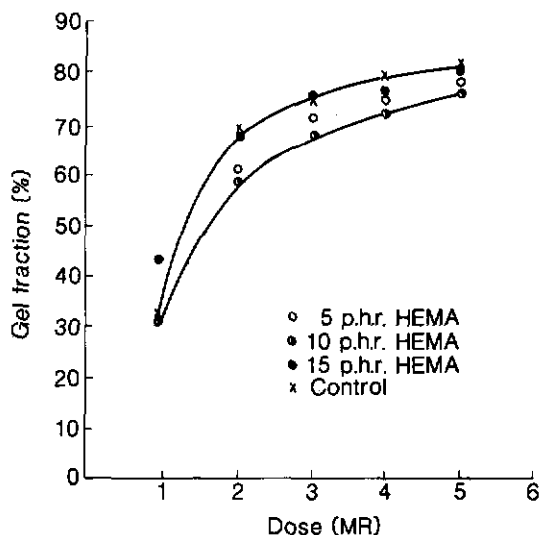


Figure 4. Gel fraction versus dosage of HEMA-NR copolymer.

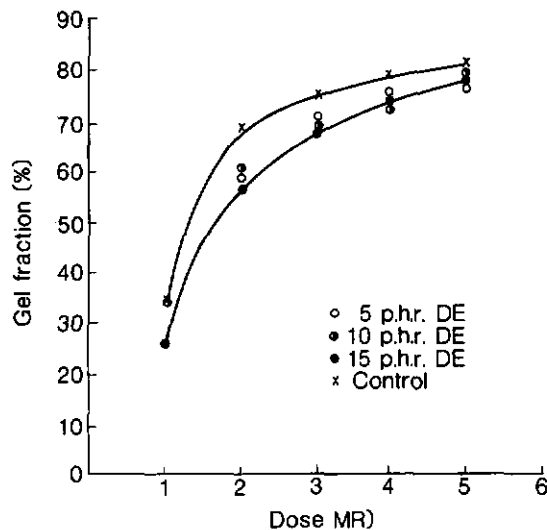


Figure 6. Gel fraction versus dosage of DE-NR copolymer.

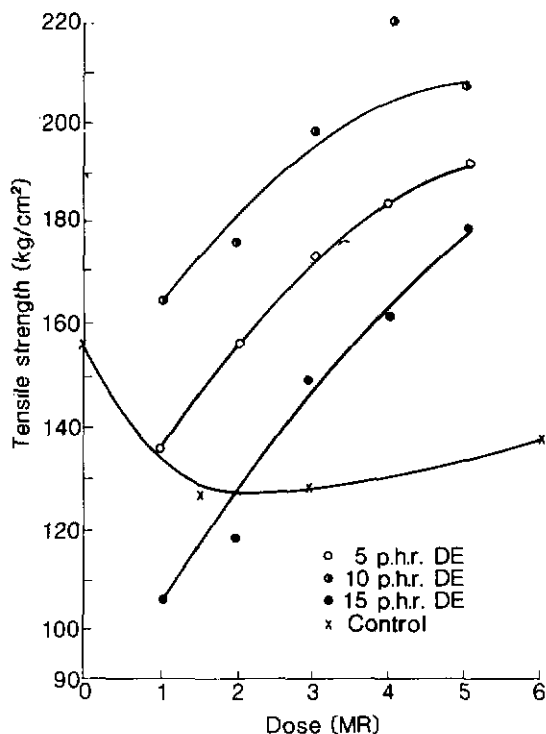


Figure 5. Effects of dosage on tensile strength of DE-NR copolymer.

(Figures 4, 5 and 6). However, there was an optimum DE monomer concentration (10 p.h.r.) to obtain the highest possible tensile strength. The decrease of tensile strength above 10 p.h.r. monomer concentration was due to an increase in incompatibility between the NR polymer, homopolymer, graft and homopolymer polyDE components.

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#### REFERENCES

1. ALLEN, P.W., BELL, C.L.M. AND COCKBAIN, E.G. (1959) Polymerisation of Vinyl Monomer in Rubber Latices. *Proc. Int. Rubb. Conf. Washington 1959*, 521.
2. ALLEN, P.W. (1963) Graft Copolymers from Natural Rubber. *The Chemistry and Physics of Rubber Like Substances*. (Bateman, L. ed), p. 97. London: Maclaren and Sons Ltd.

3. BURFIELD, D.R. AND NG, S.C. (1975) Graft Copolymerisation of Methacrylamide in Natural Rubber Latex. *Proc. Int. Rubb. Conf. Kuala Lumpur 1975*, 4, 235.
4. ANGIER, D.J. AND TURNER, D.T. (1958) Graft Interpolymers Formed by Gamma Irradiation of Methyl Methacrylate - Natural Rubber Mixtures. *J. Polym. Sci.*, 28, 265.
5. COCKBAIN, E.G., PENDLE, T.D. AND TURNER, D.T. (1959) Formation of Graft Polymers by Gamma Irradiation of Natural Rubber Latex and Methyl Methacrylate. *J. Polym. Sci.*, 39, 419.
6. COOPER, W., VAUGHAN, G., MILLER, S. AND FIELDEN, M. (1959) Graft Copolymers from Natural Rubber Latex Using Visible, Ultraviolet, and Gamma Ray Initiation. *J. Polym. Sci.*, 39, 651.
7. LUSKIN, L.S. (1974) Basic Monomers. *Functional Monomers (Yocom, R.H. and Nyquist, E.B. ed)*, Volume 2, p. 686. New York: Marcel Dekker, Incorporation.