

Study of the Effect of Polyethylene Glycols and Glycerol in Filled Natural Rubber Latex Vulcanizates

LALIAMMA JOSE and RANI JOSEPH*

Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682022, India

(Received July 15, 1994)

The mechanical properties of filled natural rubber latex vulcanizates were found to be improved by the addition of polyethylene glycols of different molecular weight and glycerol. There is a slight reduction in the optimum cure times of the compounds containing PEG/Glycerol. The morphology study shows that the filler distribution is more uniform in the compounds containing PEG/Glycerol.

KEY WORDS NR Latex, polyethylene glycols, glycerol, silica, calcium carbonate, clay, mechanical properties, surface morphology.

INTRODUCTION

One of the major advantages of adding filler to rubber compound is the reduction in cost of the products. But fillers like calcium carbonate, clay, silica, carbon black etc. when added to latex yield vulcanizates of poor mechanical properties.¹ This may be attributed to the insufficiently fine distribution of the filler in the latex, the dispersed particles not being deposited simultaneously during formation of the deposit and due to the presence of protective surface coating on latex globules and fillers which prevents direct contact between rubber and filler after removal of the aqueous phase.² Earlier workers have studied the reinforcement of silica filler in NR, in the presence of silane coupling agent.³ More recently N. Radhakrishnan Nair *et al.* have studied the role of certain surface modifying agents like diethylene glycol, triethanolamine and bis[triethoxysilyl propyl]tetra sulphide (Si-69) in improving the mechanical properties of the rubber compound.⁴ It has been shown that peptising agents, plasticizing agents etc. can be incorporated in NR latex for the purpose of modifying its properties.^{5,6} The use of poly glycol H.S.35/40 in NR latex has also been studied.⁷ In the present study we have compared the effect of polyethylene glycols and glycerol in improving the mechanical properties of filled NR latex vulcanizates.

*To whom correspondence should be addressed.

TABLE I

Formulation of the base latex compounds

Ingredients	Parts by weight (wet)
60% Centrifuged latex	167.0
10% KOH	1.0
10% Potassium oleate	1.0
50% ZnO	0.75
50% ZDC	3.0
50% S	3.0

TABLE II

 V_r values before and after ammonia modified swelling

Filler (phr)	PEG (mol.wt.)	V_r Original	V_r after NH_3 modified swelling
Silica (10)	300	.1820	.1583
	600	.1743	.1582
	1000	.1847	.1721
	2000	.1775	.1689
	Glycerol	.1647	.1542
$CaCO_3$ (10)	300	.1769	.1719
	600	.1689	.1660
	1000	.1682	.1646
	2000	.1740	.1730
	Glycerol	.1666	.1641
Clay (10)	300	.1705	.1520
	600	.1582	.1507
	1000	.1812	.1749
	2000	.1708	.1660
	Glycerol	.1801	.1744

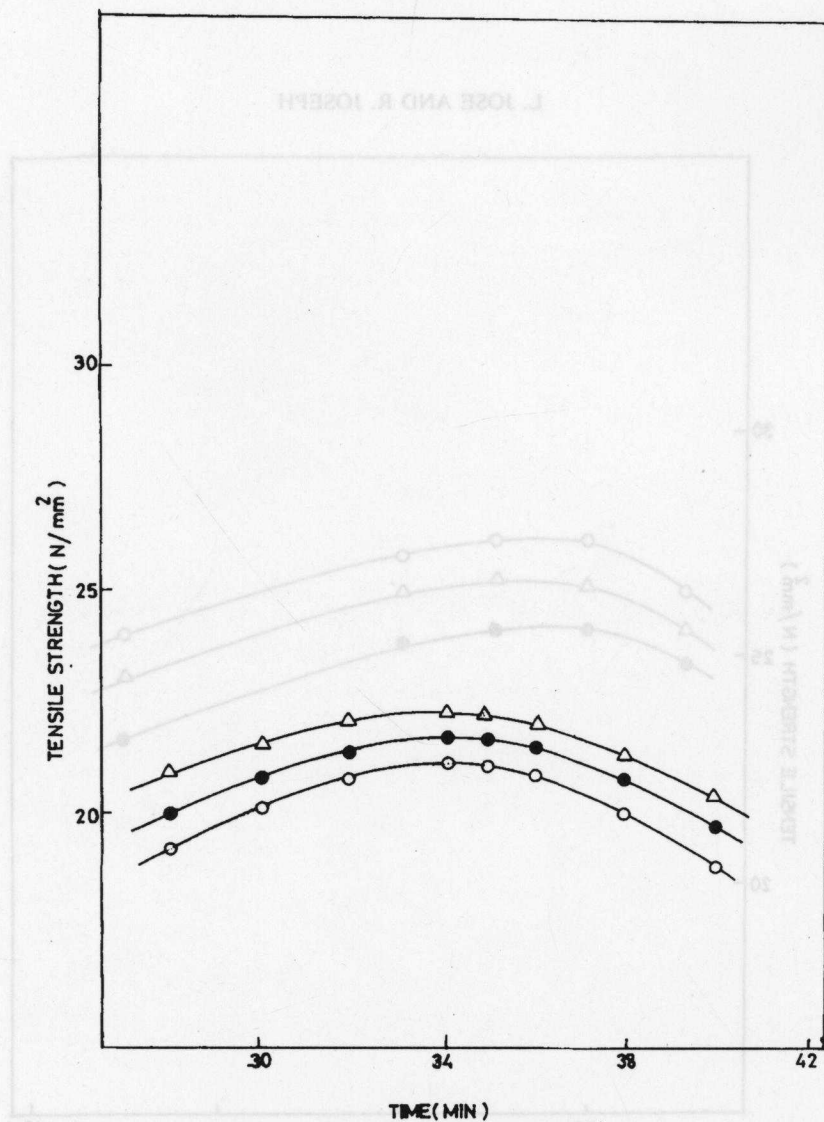


FIGURE 1 Variation of tensile strengths with cure time of the filled (10 phr) NR latex vulcanizate. Δ silica, \circ CaCO_3 , and \bullet clay.

EXPERIMENTAL

Centrifuged latex conforming to BIS 5430-1981 was used for the study. Other compounding ingredients used namely, ZnO, sulphur, KOH etc. were of commercial grade. ZDC used was supplied by ICI. Polyethylene glycols of mol. wt.

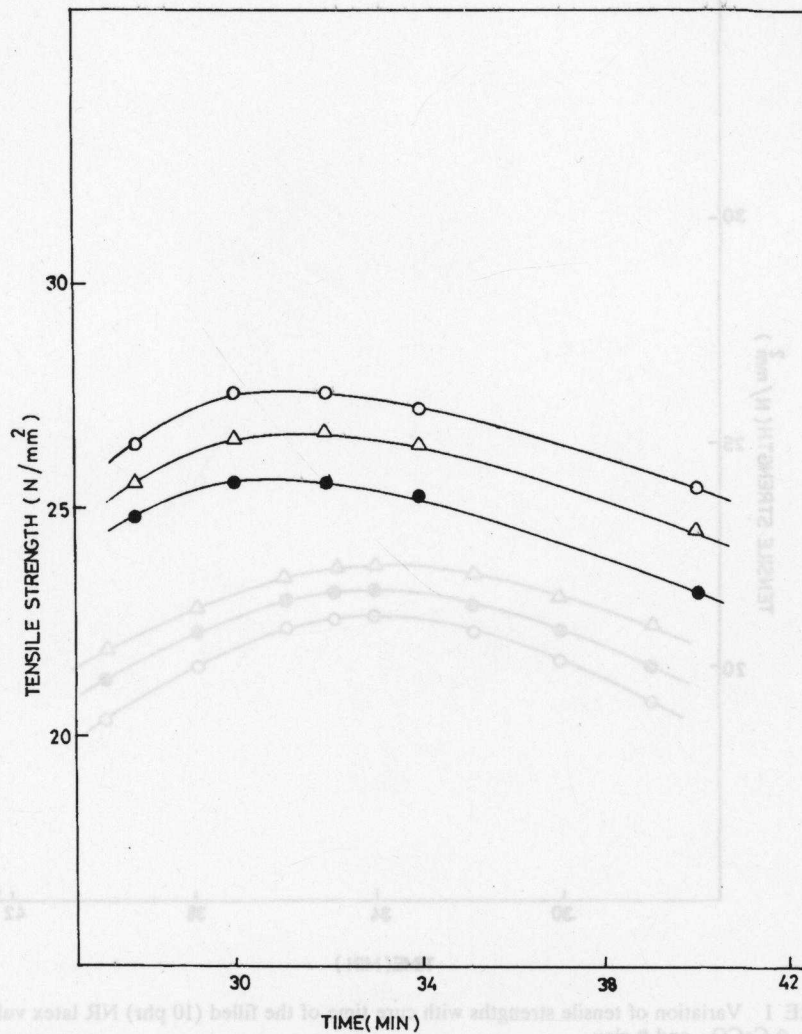


FIGURE 2 Variation of tensile strength with cure time of the filled (10 phr) NR latex vulcanizate containing PEG 300. Δ silica, \circ CaCO_3 , and \bullet clay.

300, 600, 1000 and 2000 referred to as PEG 300, PEG 600, PEG 1000, PEG 2000 and glycerol were supplied by MERCK.

COMPOUNDING AND PREPARATION OF SHEETS

Polyethylene glycols (mol. wt. 300, 600, 1000 and 2000) and glycerol were prepared as 50% solutions in water. The dispersions of the vulcanizing agents and the fillers (silica, CaCO_3 and clay) were prepared in water using the dispersing agent—Dispersol F.

A base latex compound was prepared as per the formulation given in Table II.

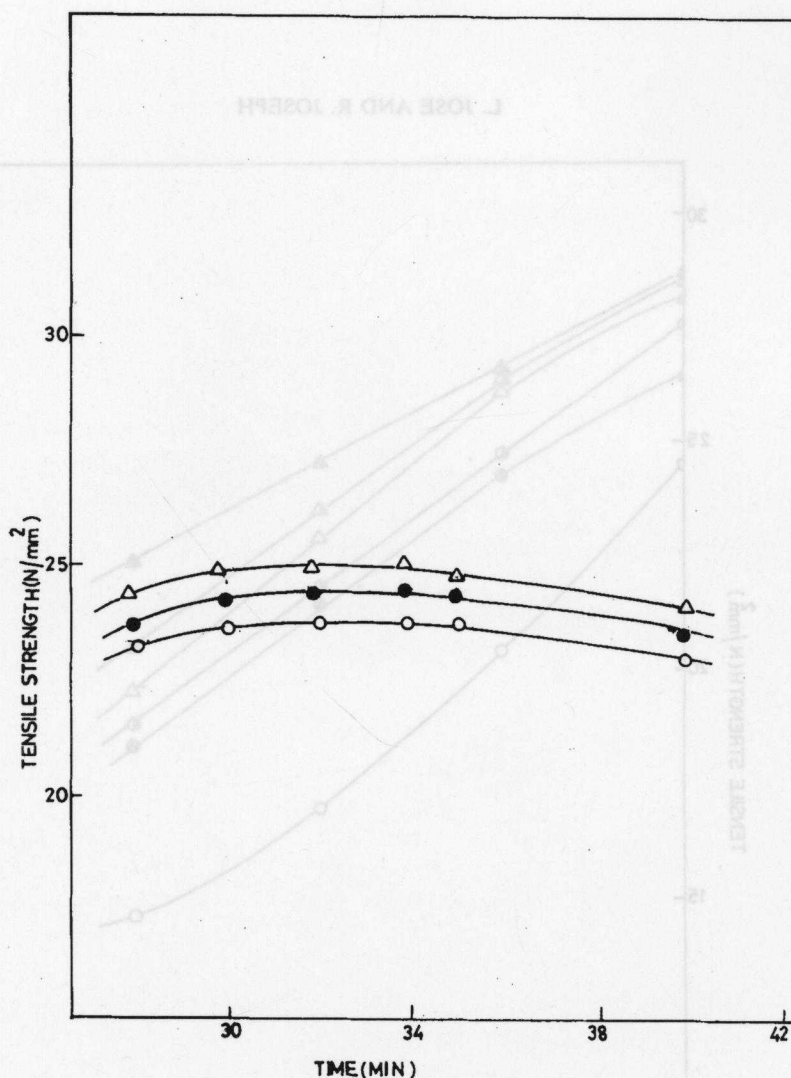


FIGURE 3 Variation of tensile strength with cure time of the filled (10 phr) NR latex vulcanizate containing glycerol. Δ silica, \circ CaCO_3 , and \bullet clay.

a) Optimum Cure Time of the Latex Sheets

In order to study the effect of PEG and glycerol on optimum cure time, the base latex compound was mixed with 10 phr of silica/ CaCO_3 /clay as a 40% dispersion in water and 1.0 phr (the optimum concentration) of PEG 300 as 50% solution in water.⁸ Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 hrs, they were vulcanised for times varying from 28–40 minutes at 120°C. Dumbbell shaped tensile test specimens were punched out of these casted sheets. The tensile properties were measured on a

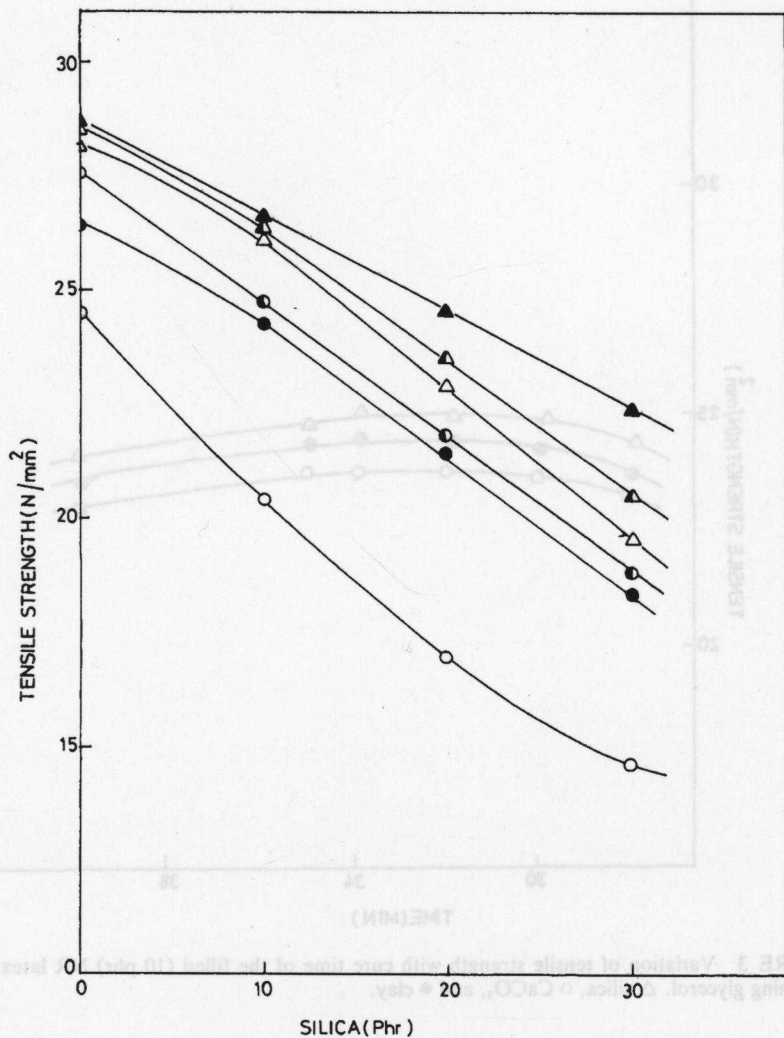


FIGURE 4 Variation of tensile strength with amount of silica before ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ● glycerol and ○ without PEG/glycerol.

Zwick Universal Testing Machine Model 1445 using a crosshead speed of 500 mm/min. as per ASTM D 412-80.

The same study was done with latex compounds containing 1 phr of glycerol instead of PEG and also with base latex compound containing 10 phr of silica/ CaCO_3 /clay.

b) Mechanical Properties of Filled Latex Vulcanizate

A portion of the base latex compound was mixed with 10, 20 and 30 phr each of silica and was mixed with 1 phr of PEG (mol. wt. 300, 600, 1000 and 2000) and glycerol. Cast latex films of the compounds containing PEG/glycerol were prepared

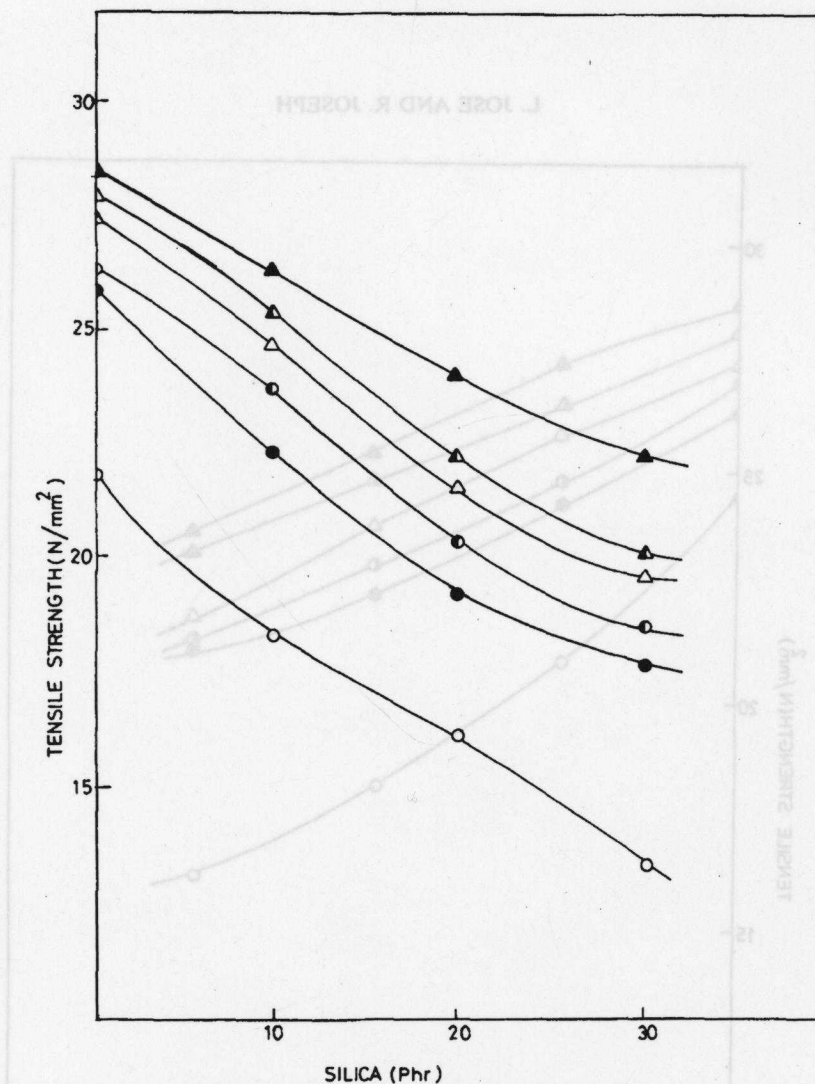


FIGURE 5 Variation of tensile strength with amount of silica after ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ● glycerol and ○ without PEG/glycerol.

and vulcanized at 120°C for optimum cure time. The compounds were also prepared without PEG/glycerol and cast latex films were cured up to the optimum cure time. The tensile properties of the films were determined.

The same experiment was repeated with dispersions of CaCO₃ and clay.

c) Ageing at 70°C for 48 hours

Test specimens from these sheets were aged at 70°C for 48 hrs and the retention in tensile properties were determined.

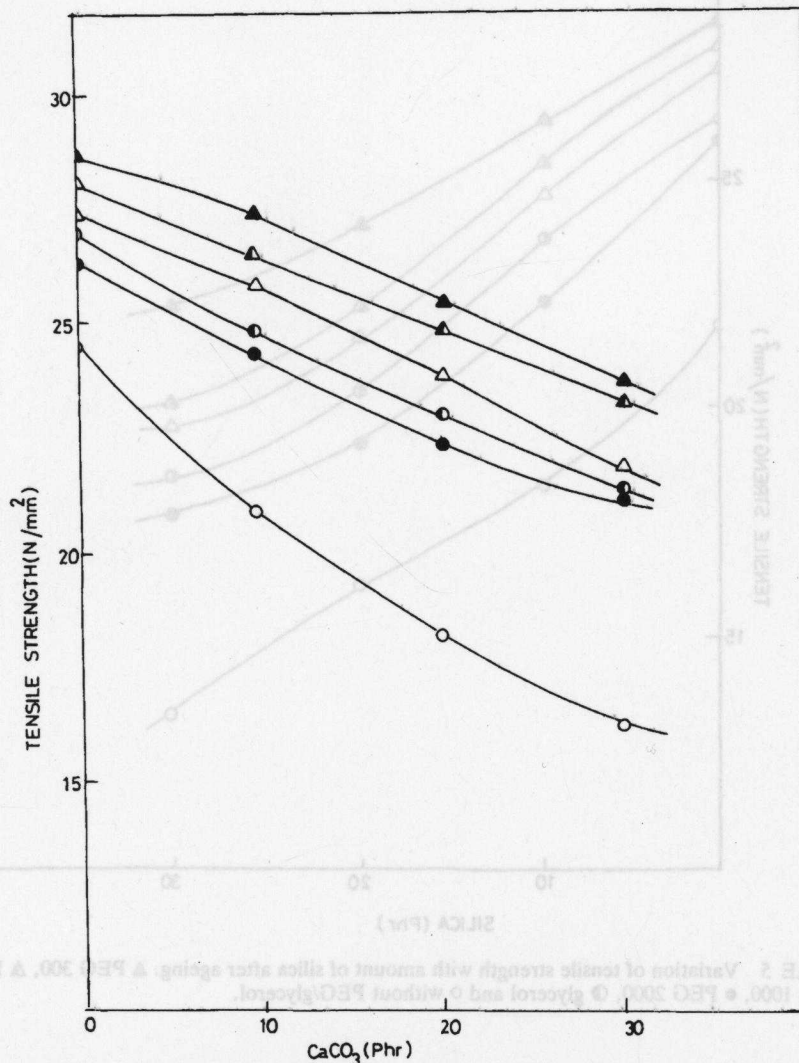


FIGURE 6 Variation of tensile strength with amount of CaCO_3 before ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ○ glycerol and ○ without PEG/glycerol.

d) Determination of Rubber-Filler Interaction

The vulcanized latex films were subjected to swelling for 48 hrs in toluene. The extent of rubber-filler interaction was studied using the equation given by Cunneen and Russel.⁹ According to this,

$$V_{ro}/V_{rf} = ae^{-z} + b$$

where V_{ro} and V_{rf} are the volume fractions of rubber in the gum and filled vulcanizate respectively. Z is the weight fraction of the filler in the vulcanizate and a

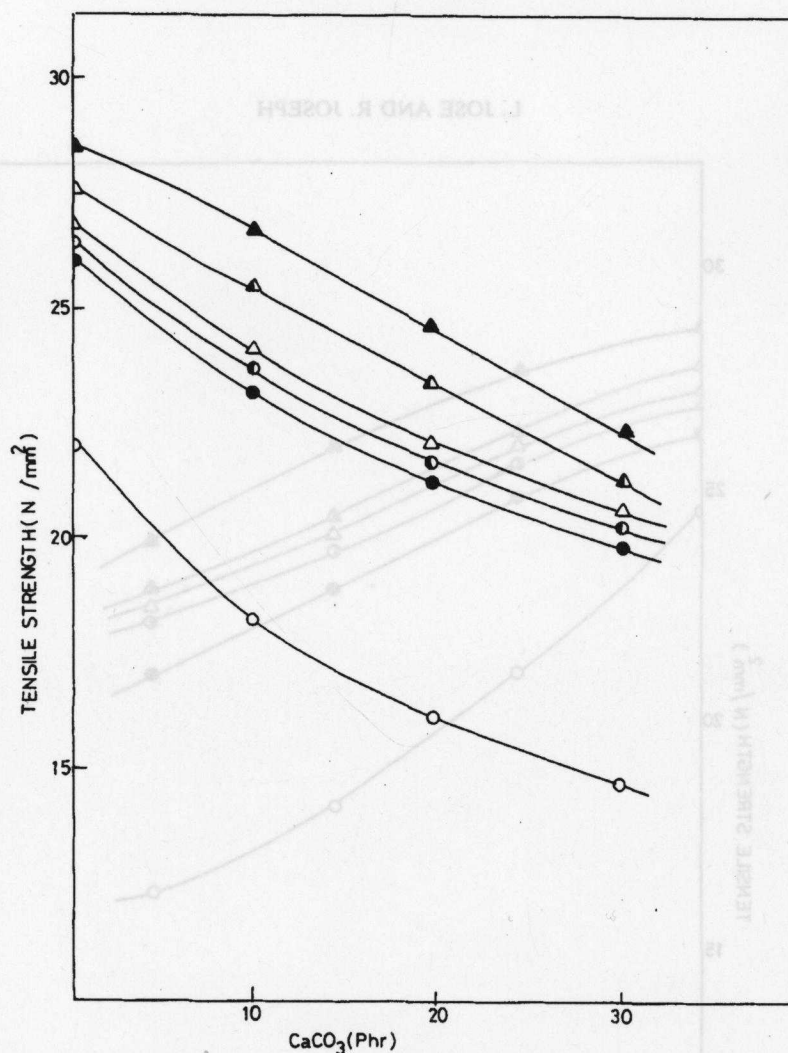


FIGURE 7 Variation of tensile strength with amount of CaCO_3 after ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ○ glycerol and ○ without PEG/glycerol.

and b are constants. By plotting V_{rd}/V_{rf} against e^{-z} , value of a (slope) and b (intercept) were determined. The higher the value of a , the higher the swelling restriction and the better the rubber filler interaction.¹⁰

e) Ammonia-modified Swelling

The extent of rubber-filler attachment was further studied by conducting the swelling of vulcanized samples for 48 hrs in toluene in ammonia atmosphere.¹¹

The difference in V_r values as obtained by swelling studies of the vulcanizate in toluene and the same after ammonia treatment gives a measure of rubber-filler attachment.

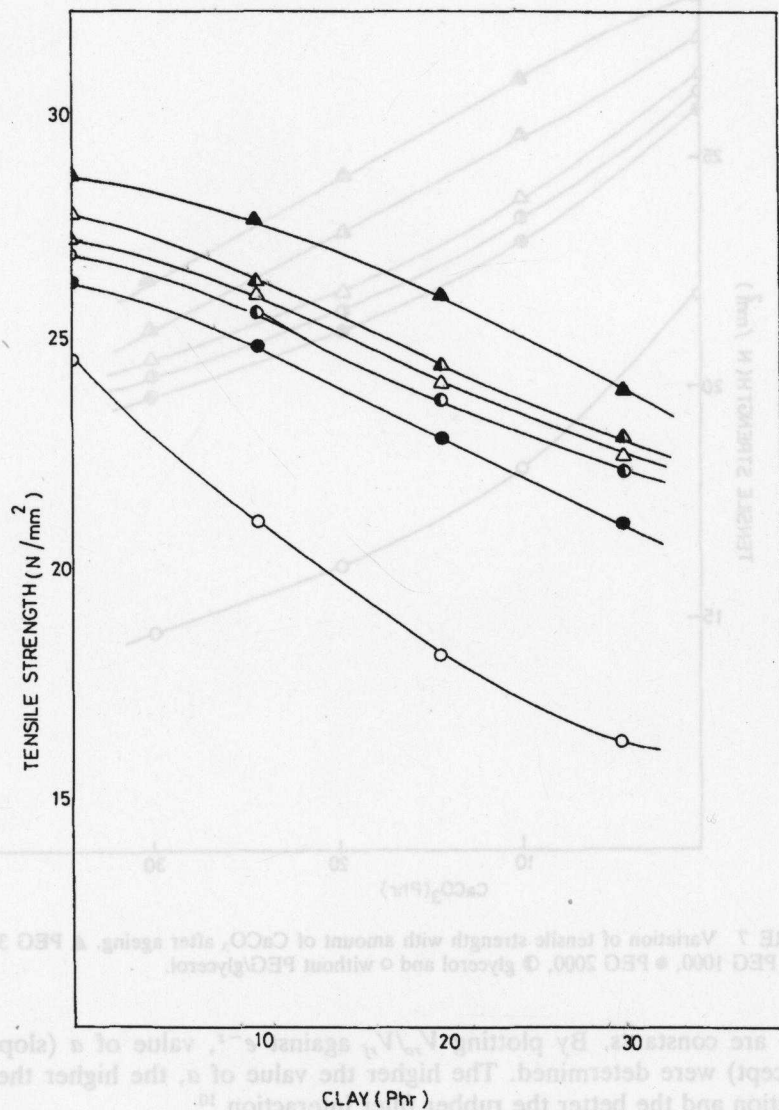


FIGURE 8 Variation of tensile strength with amount of clay before ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ● glycerol and ○ without PEG/glycerol.

f) Optical Studies

The morphology of the filled compounds with and without PEG/glycerol was studied. The compounds were matured for 24 hrs and were cast into thin films. It was then cut into a convenient size and mounted on a microscope slide. Photo micrographs were taken on Leica wild M_8 zoom stereo microscope and wild MPS 46/52 photoautomat using NOV a FP4 films.

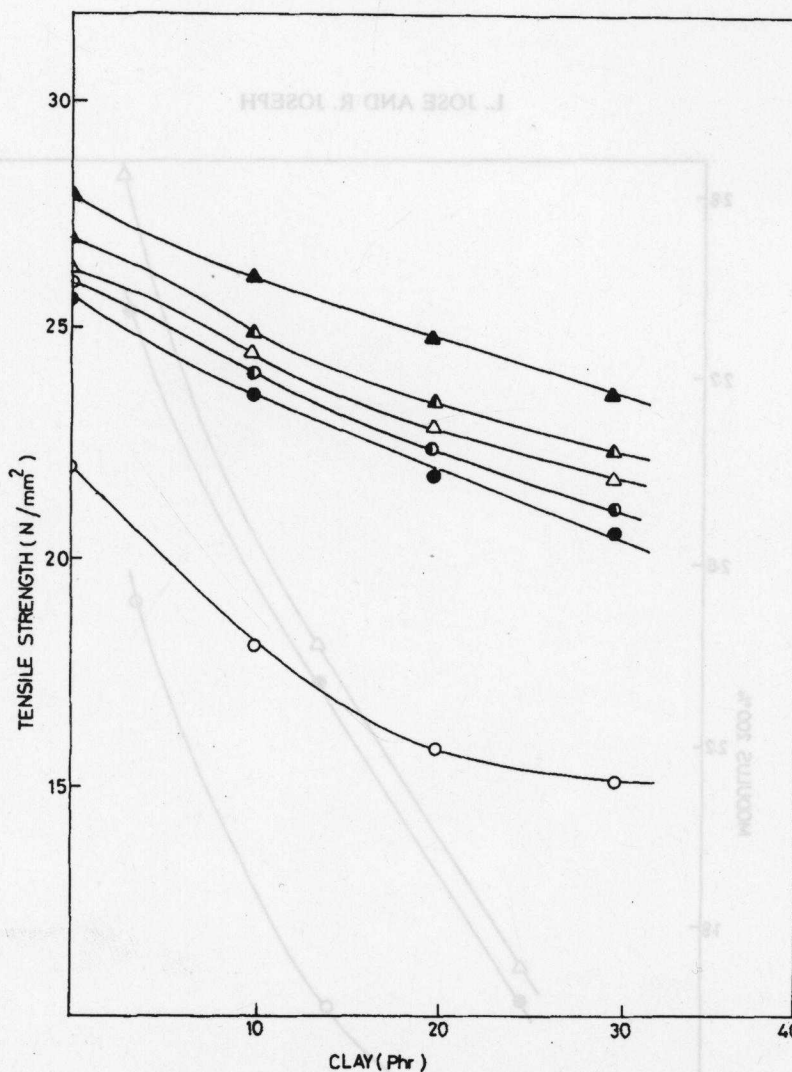


FIGURE 9 Variation of tensile strength with amount of clay after ageing. ▲ PEG 300, △ PEG 600, △ PEG 1000, ● PEG 2000, ● glycerol and ○ without PEG/glycerol.

RESULTS AND DISCUSSIONS

Figures 1, 2 and 3 show the variation of tensile strength with cure time. For compounds containing PEG, as the cure time is increased from 28 to 40 minutes, the tensile strength increases, reaches a maximum at 30 minutes and then decreases whereas the attainment of maximum tensile strength occurs at 32 minutes for the compounds containing glycerol and at 34 minutes for compounds without PEG/glycerol. It shows that the addition of PEG and glycerol can reduce the optimum cure time. This may be attributed to the reduced accelerator adsorption on the

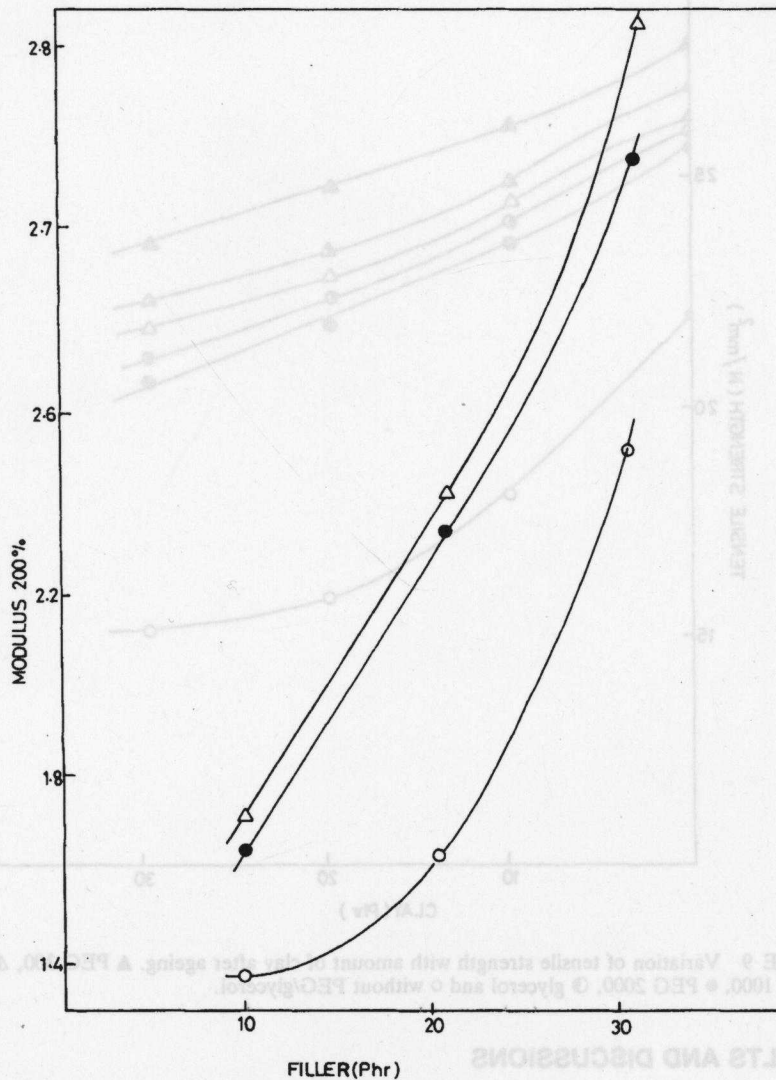


FIGURE 10 Variation of modulus with amount of filler in presence of PEG 600. Δ silica, \circ CaCO_3 , and \bullet clay.

filler surface in the presence of PEG and glycerol. All the three fillers studied follow the same trend.

Figures 4 and 5 show the variation of tensile strength of the silica filled natural rubber latex vulcanizate before and after ageing. The addition of optimum amount of PEG of different mol. wts. in the compounds improve the tensile properties before and after ageing. This may be attributed to the improved filler rubber interaction and the more homogeneous distribution of filler in the latex compounds in the presence of PEG or glycerol. Low molecular weight glycols are found to be more effective in improving the tensile properties. Figures 6 and 7 show the var-

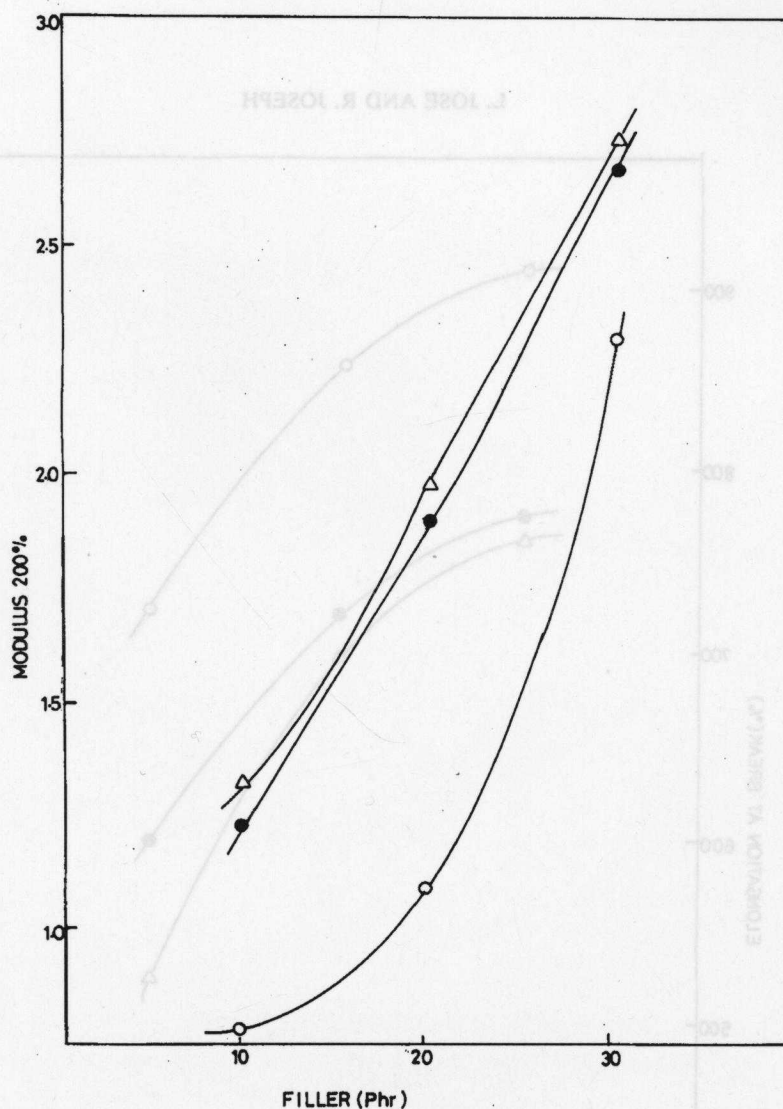


FIGURE 11 Variation of modulus with amount of filler in the absence of PEG 600. Δ silica, ○ CaCO₃, and ● clay.

iation of tensile strength of the calcium carbonate filled NR latex vulcanizates, with the amount of filler before and after ageing. The filled compounds containing PEG or glycerol are found to show improved tensile strength similar to the silica filled compounds. Figures 8 and 9 showing the variation of tensile strength of clay filled NR latex vulcanizates before and after ageing also follow a similar pattern. The improvement in tensile strength is found to be more in the case of CaCO₃ and clay compared to silica. The tensile strength improvement is dependent on the amount of filler, as the filler loading is increased from 10 to 30 phr, the maximum improvement in tensile strength is observed at 30 phr filler loading. Glycerol is found

(000) Figure 11 shows variation of modulus of filled NR latex vulcanizates with amount of filler in the absence of PEG. The modulus is found to be higher for compounds containing PEG. This shows that there is good filler rubber interaction in vulcanizates containing PEG. Figure 12 shows the variation of elongation at

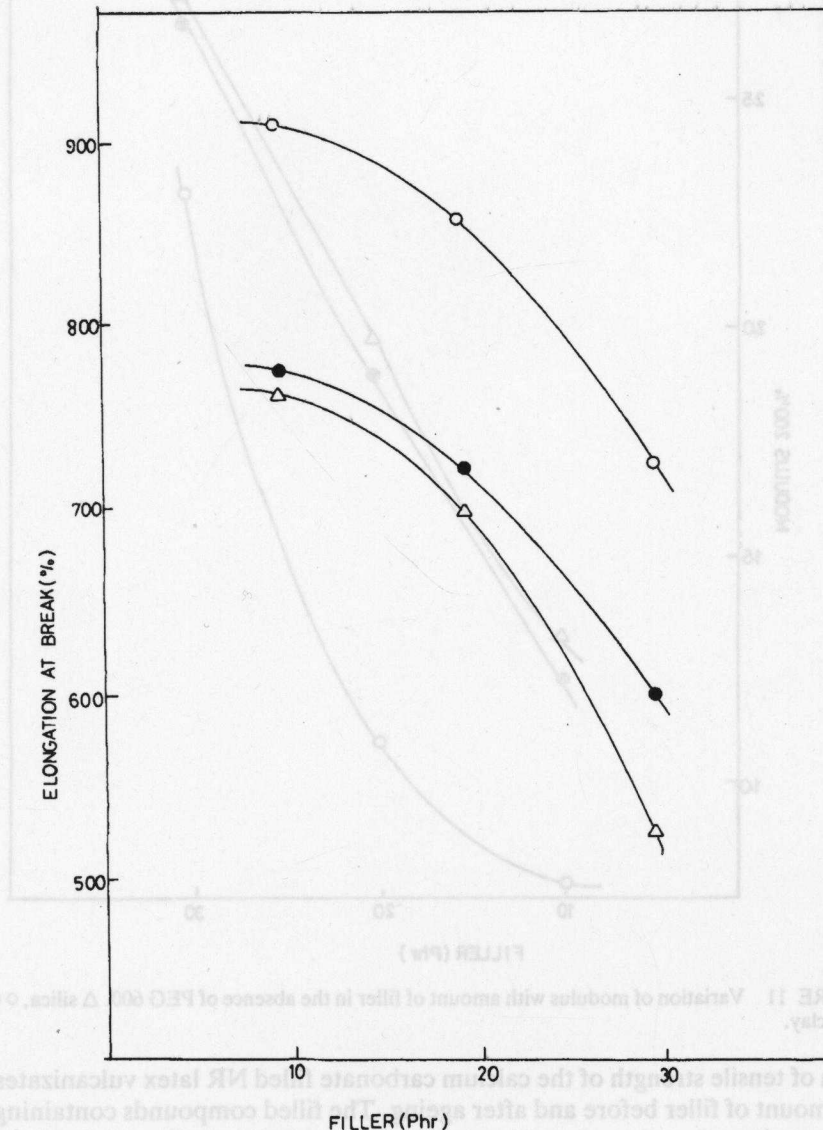


FIGURE 12 Variation of elongation at break with amount of filler in the presence of PEG (600). Δ silica, \circ CaCO_3 , and \bullet clay.

to be less effective compared to PEG of mol. wt. up to 1000 and more effective compared to PEG of mol. wt. up to 2000. This may be due to the higher density of glycerol compared to PEG of mol. wt. up to 1000. Figure 10 shows the variation of modulus of the filled NR latex vulcanizates with filler concentration in the presence of PEG (600). Figure 11 shows variation of modulus of filled NR latex vulcanizate with amount of filler in the absence of PEG. The modulus is found to be higher for compounds containing PEG. This shows that there is good filler rubber interaction in vulcanizates containing PEG. Figure 12 shows the variation of elongation at

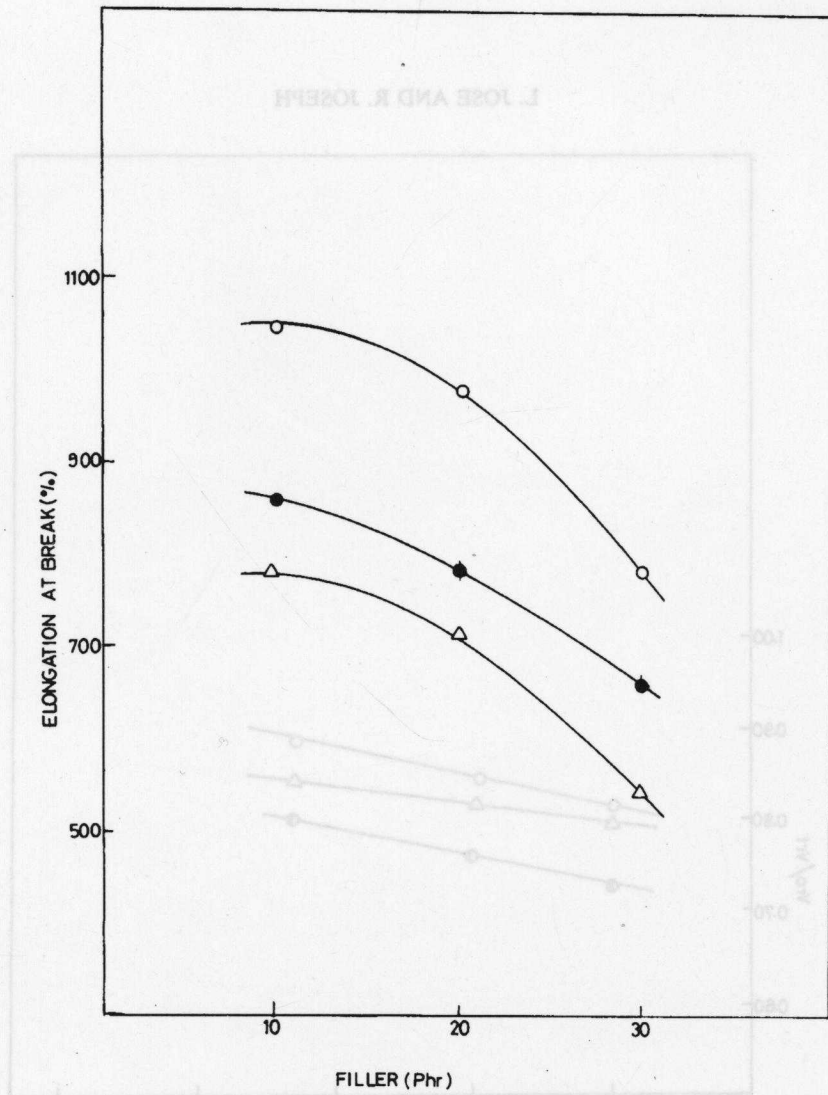


FIGURE 13 Variation of elongation at break with amount of filler in the absence of PEG. Δ silica, \circ CaCO_3 , and \bullet clay.

break of the filled vulcanizates in the presence of PEG (600). Figure 13 shows the variation of elongation at break of the filled NR latex vulcanizate with amount of filler in the absence of PEG. The elongation at break is found to be decreased for compounds containing PEG. This again shows that PEG can form some filler polymer physical linkages. Figure 14 shows the variation of V_{r0}/V_{rf} with e^{-z} . The latex compounds containing PEG or glycerol exhibit higher slope than the compounds without PEG/glycerol. This shows that addition of PEG/glycerol restrict swelling due to more polymer filler attachment. Table II shows the V_r values of compounds containing 10 phr silica, 10 phr CaCO_3 and 10 phr clay in the presence

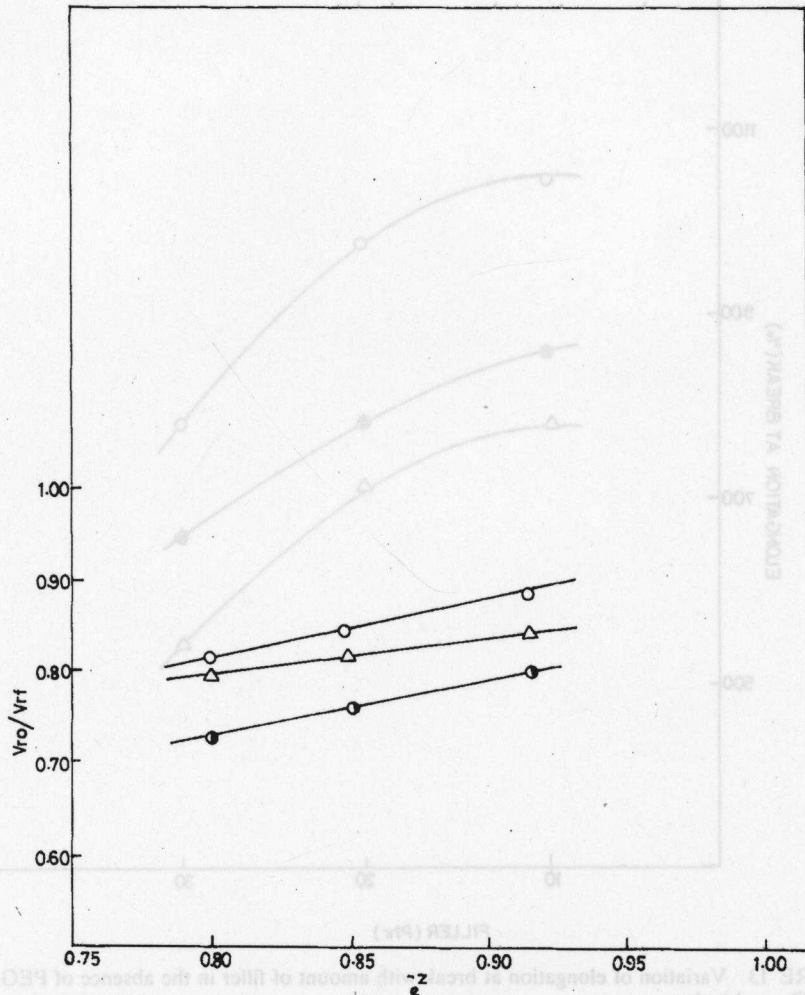
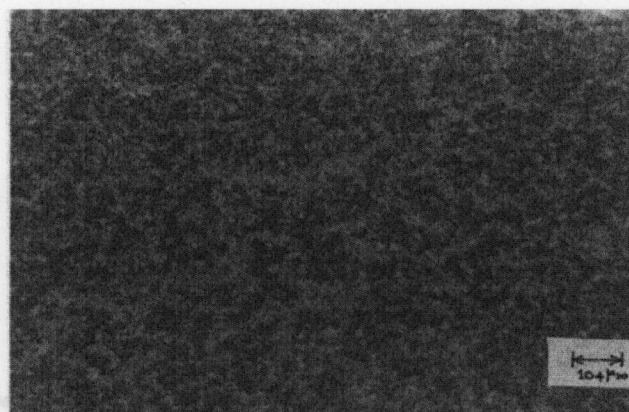


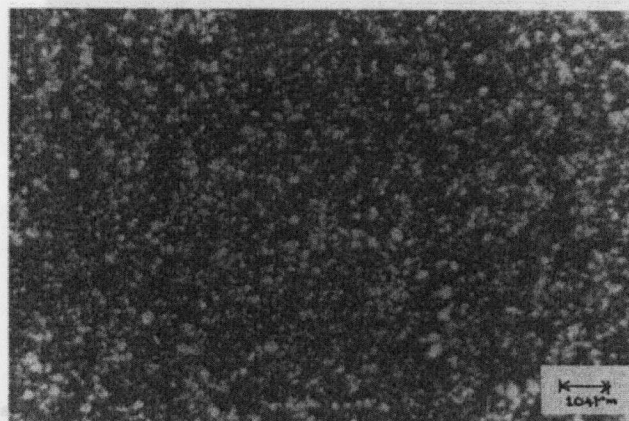
FIGURE 14 Variation of V_{ro}/V_{rf} with e^{-z} . Δ silica alone, \bullet silica with PEG 300, and \circ silica with glycerol.

of PEG/glycerol, before and after ammonia modified swelling. The values show that there is good interparticle bonding between the filler and rubber. The interaction is found to be more pronounced in the compounds containing clay and silica. This again confirms the increased modulus and decreased elongation at break in the presence of PEG as shown in Figures 10 and 12.

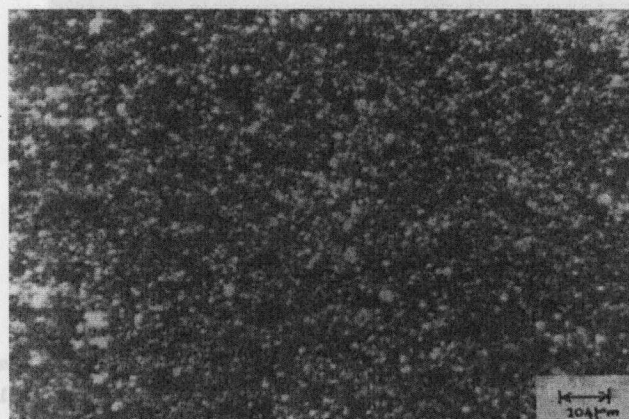
Figure 15 shows the photomicrographs of latex compounds containing 20 phr silica alone, silica with PEG (300) (1 phr) and silica with glycerol (1 phr). Figure 16 shows photomicrographs of latex compounds containing 20 phr CaCO_3 alone, CaCO_3 with PEG (300) (1 phr) and CaCO_3 with glycerol (1 phr). Figure 17 shows the photomicrographs of latex compounds with 20 phr clay alone, clay with PEG (300) (1 phr) and clay with glycerol (1 phr). These photographs show that there is more uniform distribution of the filler in the matrix when PEG or glycerol is present.



**Silica
alone**



**Silica with
PEG (300)**



**Silica with
glycerol**

FIGURE 15 Photographs of filled NR latex compounds.

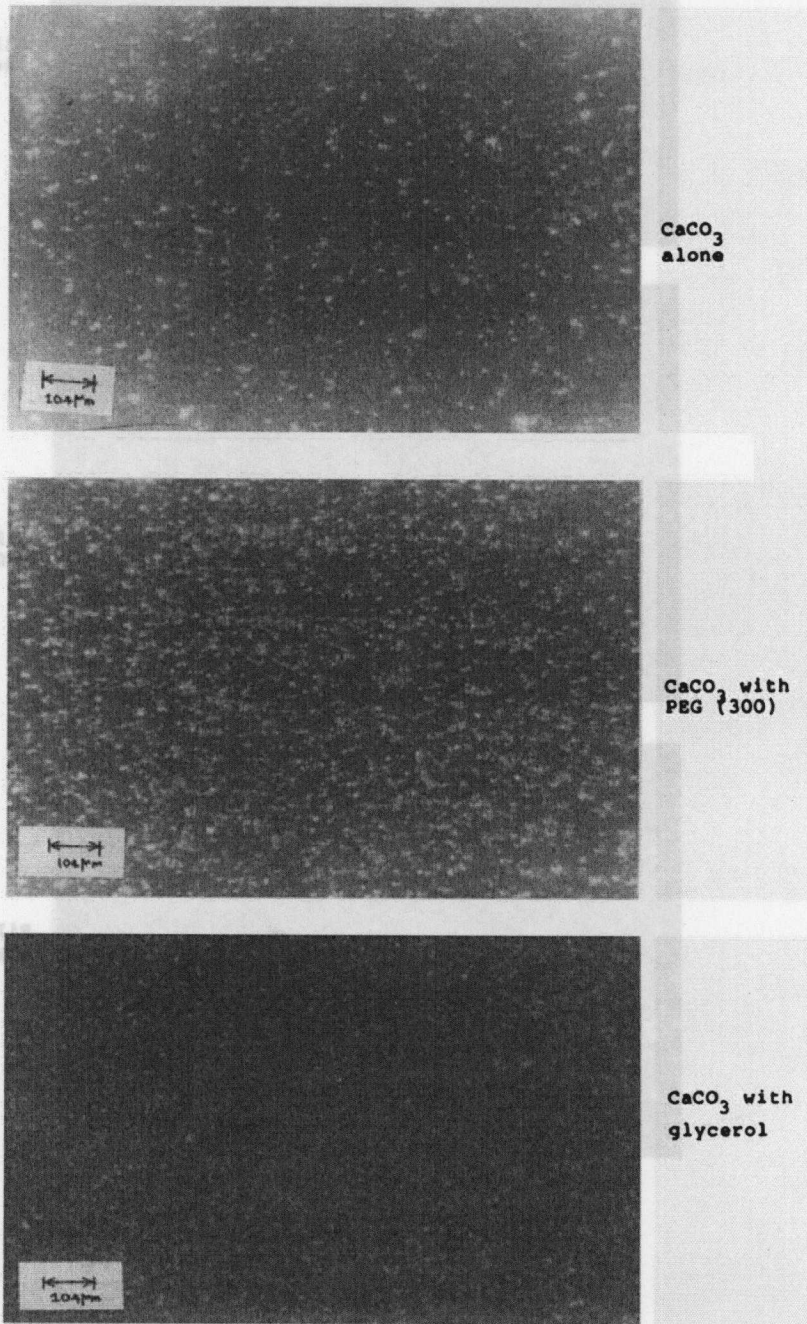
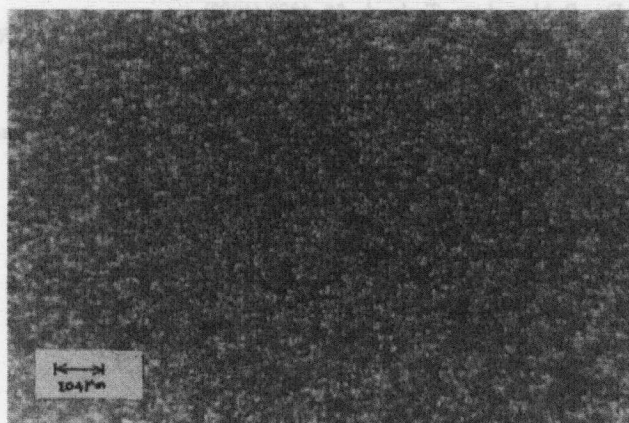


FIGURE 16 Photographs of filled NR latex compounds.



Clay alone



Clay with PEG (300)



Clay with glycerol

FIGURE 17 Photographs of filled NR latex compounds.

CONCLUSION

Polyethylene glycols/glycerol act as surface active agent in latex compounds and improve filler polymer interaction. It improves the filler dispersion in the rubber matrix.

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