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EFFECT OF SURFACE ACTIVE AGENTS ON RUBBER-FILLER INTERACTION IN SILICA-FILLED NATURAL RUBBER LATEX VULCANIZATES

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The influence of four surface active agents on rubber-filler interaction in natural rubber latex vulcanizates has been studied. The surface active agents studied are casein, polyvinyl alcohol, ammonium alginate and sodium carboxymethylcellulose. Silica-filled natural rubber latex vulcanizates were found to show better tensile properties in the presence of polyvinyl alcohol and casein. The enhancement in tensile properties is attributed to better rubber-filler interaction.

Key words–Surface active agent, Precipitated silica, Latex-filler interaction, Reinforcement, Crosslinks.

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INTRODUCTION

Fillers are added to natural rubber latex in order to modify its properties and to reduce cost (Noble, 1953). In dry rubber compounding, fillers generally act as reinforcing agents but in latex they weaken the rubber films rather than improve its strength (Blackley, 1960). Some studies have already been conducted in this line and the poor rubber-filler interaction in latex vulcanizates is attributed to many factors such as insufficient distribution of fillers, non-simultaneous deposition of filler and rubber particles and the presence of protective layer of stabilizers around the rubber and filler particles in latex which prevents direct contact between them. A study was earlier conducted in styrene butadiene rubber (SBR) latex using carbon black as filler (Dogadkin *et al*, 1958). It was reported that casein, which is a surface active agent could improve rubber-filler interaction in SBR latex. It was suggested that casein replaced the already existing protective layer around the rubber particles in latex and the filler particles and in the process, caused better rubber-filler interaction. The increase in viscosity of the latex compound owing to the addition of casein also caused simultaneous deposition of rubber and filler particles.

In the present work we have studied the effect of four surface active agents on vulcanization, network structure and technical properties of natural rubber latex vulcanizates which contain precipitated silica as filler. The surface active agents used were casein, polyvinyl alcohol, ammonium alginate and sodium carboxymethylcellulose.

EXPERIMENTAL

Centrifuged latex conforming to Bureau of Indian Standards (BIS) 5430-1981 was used for this study. Other compounding ingredients were of commercial grade. The vulcanizing agents and the filler (precipitated silica) were used as dispersions in water using an anionic type dispersing agent, sodium salt of a sulfonic acid (Dispersol F) manufactured by M/s Indian Explosives Ltd. The surface active agents were prepared as five per cent solution in water. A base latex compound was prepared as per the formulation given in Table 1 and used in the experiments.

Table 1. Formulation of the base latex compounds

Ingredients	Parts by weight (wet)
60% centrifuged latex	167.0
10% potassium hydroxide solution	1.0
50% sulphur dispersion	3.0
50% zinc diethyl dithiocarbamate dispersion	2.0
50% antioxidant SP emulsion	2.0
50% zinc oxide dispersion	1.0

(a) EFFECT OF CONCENTRATION OF SURFACE ACTIVE AGENTS

A part of the base latex compound was treated with the surface active agents at different dosage of 0, 0.5, 1.0, 1.5 and 2.0 parts per hundred rubber (phr). Latex films were prepared by casting the compounds in shallow glass dishes. The film thickness was controlled in the range of 1 to 1.25 mm and the films were dried at 30°C for 24 h. The films were then vulcanized at 120°C for 30 min in an air oven. The tensile properties of the vulcanized latex films were then determined as per ASTM D412 (83) using a Zwick Universal Testing Machine (Model 1474).

To another portion of the base latex compound 30 phr of precipitated silica was added as a 25 per cent dispersion in water. The latex-filler system was then treated with different dosages of surface active agents and vulcanized films were then prepared from the compounds as described earlier. The tensile properties of the films were also determined.

(b) EFFECT OF SURFACE ACTIVE AGENTS ON THE PROCESSING PROPERTIES, STRESS-STRAIN BEHAVIOUR AND POLYSULPHIDIC LINKAGES

Another part of the base latex compound was mixed with 30 phr of precipitated silica added as a 25 per cent dispersion and the resulting compound was treated with the optimum concentration of the surface active agents (1.0 phr). The viscosity of the control and the treated compounds were determined using a Brookfield viscometer. For determining the cure behaviour of latex compounds, cast latex films (1–1.5 mm thickness) were prepared and dried for 24 h at 30°C. The dried films were plied up to give a total thickness of approximately 2.5 mm and test specimens were cut from the plied sheet. The cure characteristics were determined using a Monsanto Rheometer (R-100) at 120°C according to ASTM D2084 (83). The stress-strain behaviour of the vulcanizates were determined using a Zwick (Model 1474) UTM. The effect of surface active agents on network structure was studied by estimating the polysulphidic linkages in the treated and untreated samples. For this purpose, the concentration of chemical crosslinks in the vulcanizates were determined from swelling measurements. Each sample weighing 0.2–0.3 g was allowed to swell in an excess of benzene containing 0.5 per cent N–phenyl–β–naphthylamine at 30°C for 48 h. The swollen sample was weighed, the solvent removed *in vacuo* and the sample weighed again. Values of V_r , the volume fraction of rubber in the swollen vulcanizate, which is a measure of the total number of crosslinks, was determined using the method suggested by Ellis and Welding (1964). For determining the concentration of polysulphidic crosslinks, the samples each weighing 0.2 to 0.3 g, were treated with a solution of propane –2–thiol (0.4 M) and piperidine (0.4 M) in n-heptane for 2 h at room temperature under nitrogen. The samples were then washed with petroleum ether (b.p. 40–60°C) and dried *in vacuo*. The proportion of polysulphidic crosslinks was obtained by the difference from the value of V_r before and after the thiol treatment (Saville and Watson, 1967).

(c) DETERMINATION OF RUBBER–FILLER INTERACTION

A portion of the base latex compound (gum) was mixed with 5, 10, 20 and 30 phr each of precipitated silica and was treated with the optimum concentration of 1.0 phr of surface active agent. Cast latex films of the treated and untreated compounds were prepared and vulcanized at 120°C for 30 min. The extent of rubber-filler interaction was then studied using the equation given by Cunneen and Russel (1970). According to this:

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

where V_{ro} and V_{rf} are the volume fractions of rubber in the gum and filled vulcanizate, respectively, swollen in benzene, z is the weight fraction of the filler in the vulcanizate and a and b, being constants. By plotting V_{ro} / 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 (Mukhopadhyay and De, 1979; Pranab *et al,* 1983).

(d) EFFECT OF AMMONIA–MODIFIED SWELLING

To assess the extent of rubber-filler attachment further, rubber-filler bonds were cleaved chemically by swelling the vulcanizate samples for 48 h in flat dishes containing benzene in ammonia atmosphere (Polmanteer and Lentz, 1975). After swelling in ammonia atmosphere the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature (30°C) and tested for V_r by swelling in benzene. The difference in chemical crosslink density (measured as V_r values) as obtained by swelling studies in benzene of the original vulcanizate and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond.

RESULTS AND DISCUSSION

The effect of different dosages of the surface active agents on the modulus and tensile strength of the vulcanizates are given in Figs. 1 and 2, respectively. From these figures, it is evident that the surface active agents have no effect on the technical properties of the latex vulcanizates in the gum stage (without filler). But in the latex compounds containing precipitated silica, the surface active agents have marked effect on the technical properties of the vulcanizates. It can be seen that the latex compounds containing polyvinyl alcohol offer the highest modulus. Modulus of a vulcanizate is solely governed by the total number of crosslinks including intermolecular chemical crosslinks and coupling bonds (rubber-filler attachment). In the present study the modulus enhancement is found to be more with polyvinyl alcohol compared with casein. There was practically no improvement in modulus with ammonium alginate and carboxymethylcellulose. In the case of tensile strength, casein offers comparatively better tensile strength than with polyvinyl alcohol (Fig.2). It may be mentioned that for a strain crystallising rubber like natural rubber, enhancement in tensile strength by reinforcing fillers is less predominant than that occurs in non-crystallising rubbers. The optimum dosage of the surface active agents is found to be around 1.0 phr.

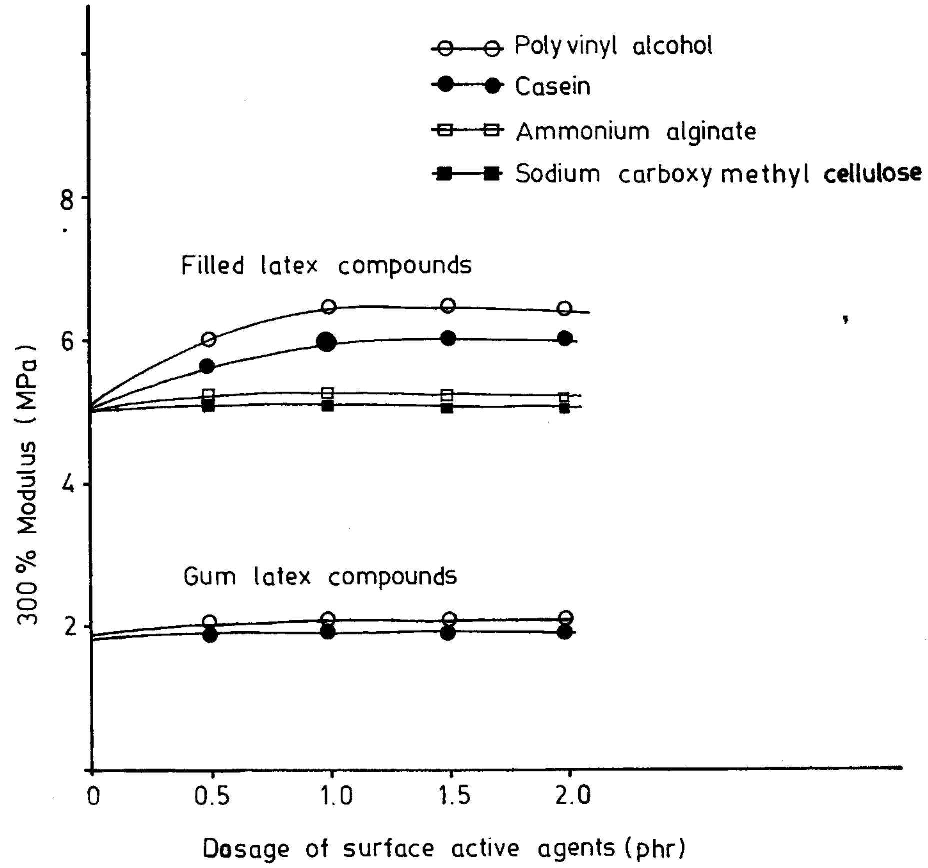

Fig. 1. Effect of surface active agents on modulus of latex vulcanizates.

The effect of adding 1.0 phr each of the surface active agents on the concentration of polysulphidic linkages of the latex vulcanizate are given in Table 2. It may be noted that the Brookfield viscosity is the maximum when sodium carboxymethylcellulose was incorporated and the least with casein. It can also be seen that cure rate of the compound was not affected by the incorporation of the surface active agents. It may also be noted from Table 2 that the polysulphidic content in the treated and untreated latex vulcanizates remains almost the same. The stress-strain behaviour of the treated and untreated latex vulcanizates, as given in Fig. 3, shows that strain induced crystallisation of natural rubber is unaffected by the presence of various surface active agents.

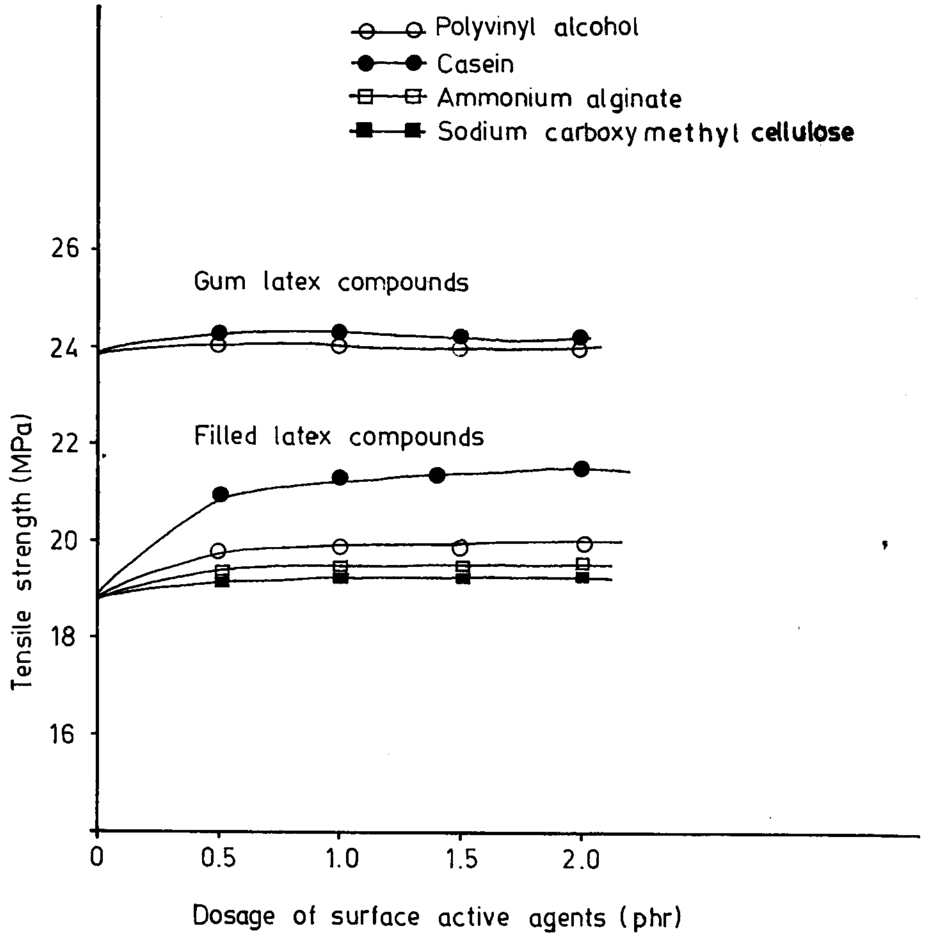

Fig. 2. Effect of surface active agents on tensile strength of latex vulcanizates.

Table 2. Effect of surface active agents on viscosity, cure rate index and network structure in the base latex compound containing 30 phr of silica.

Treatment	Brookfield viscosity (Cps)	Cure rate index	Polysulphidic crosslinks (%)
Nil	128	28.6	50
Casein, 1 phr	200	28.5	49
Polyvinyl alcohol, 1 phr	210	28.5	48
Ammonium alginate, 1 phr	500	28.5	50
Sodium carboxymethylcellulose, 1 phr	900	28.5	48

The plot of V_{ro} / V_{rf} against e^{-z} is given in Fig. 4. It may be seen that the latex compound containing polyvinyl alcohol and casein provide a higer slope than the mix containing no surface active agents. This gives an indication that better rubber-filler interaction is obtained by the incorporation of polyvinyl alcohol or casein. The same conclusion is also obtained from Fig. 5 and Table 3 which shows the results of ammonia modified swelling. The reduction in the V_r values is found to be more in the latex vulcanizate containing polyvinyl alcohol or casein. This indicates a higher level of rubber-filler attachment due to the addition of polyvinyl alcohol or casein.

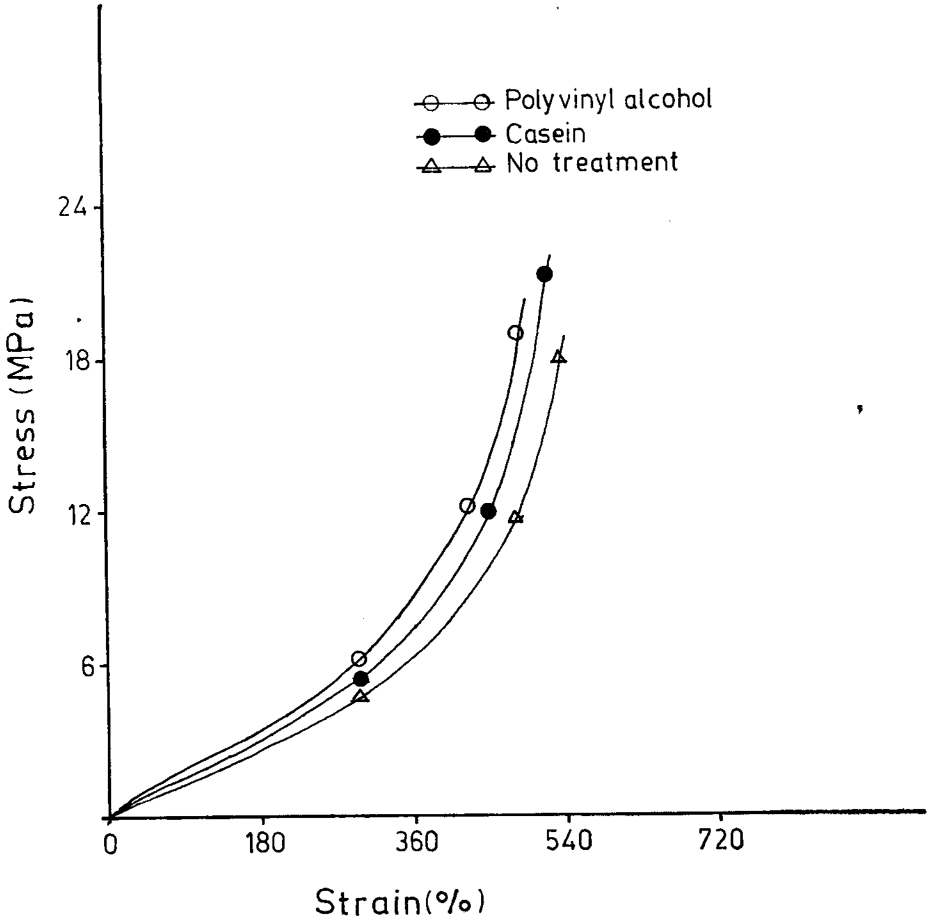

Fig. 3. Effect of surface active agents on stress-strain behaviour.

The enhancement in tensile properties on addition of polyvinyl alcohol or casein could not be attributed to improved homogeneity of dispersion of the filler in the film as the same effect was not obtained with sodium alginate or carboxymethylcellulose. In fact homogeneity of the filler could be better with the alginate and carboxymethylcellulose as they cause more pronounced thickening of the compound. Hence the improvement in tensile properties is attributed to better rubber-filler attachment.

Table 3. V_r values before and after ammonia modified swelling.

Silica loading, phr	Treatment	V_r original	V_r after ammonia modified
0	Nil	0.1705	—
5	,,	0.1640	0.1550
10	,,	0.1655	0.1533
20	,,	0.1715	0.1582
30	,,	0.1757	0.1592
5	Polyvinyl alcohol, 1 phr	0.1720	0.1500
10	,,	0.1755	0.1500
20	,,	0.1991	0.1588
30	,,	0.2153	0.1653
5	Casein, 1 phr	0.1722	0.1510
10	,,	0.1767	0.1497
20	,,	0.1015	0.1550
30	,,	0.2050	0.1587

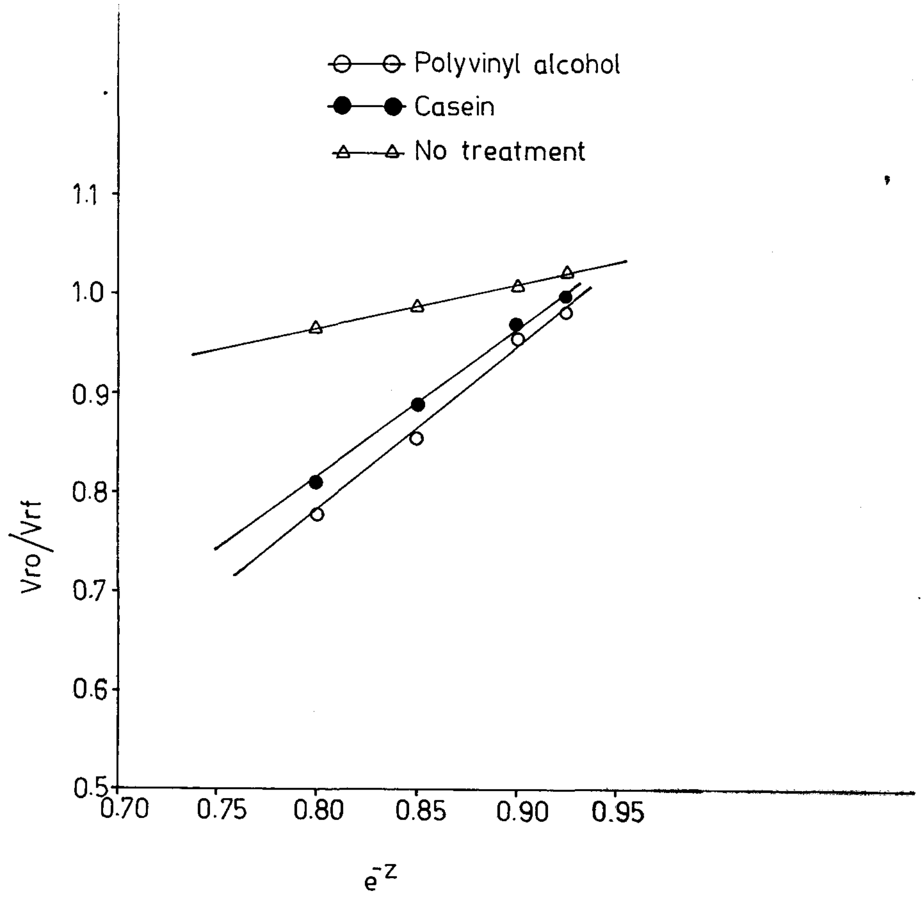

Fig. 4. Plot of $\frac{V_{ro}}{V_{rf}}$ against e^{-z}

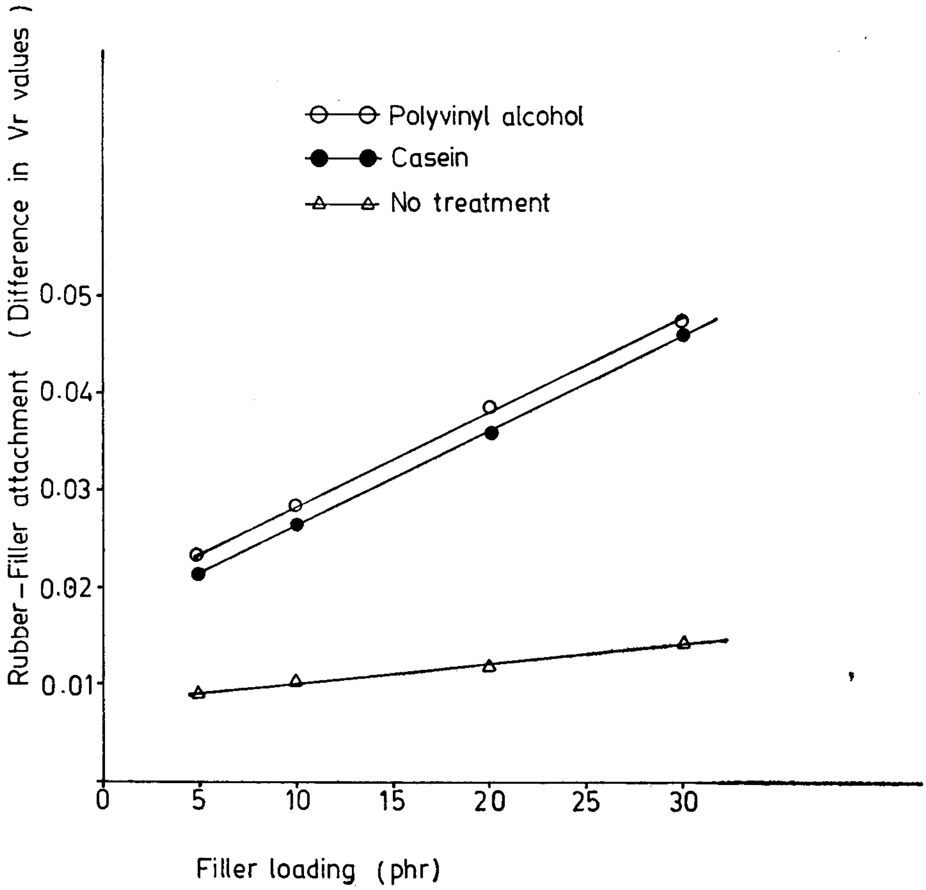

Fig. 5. Effect of ammonia modified swelling of the silica filled latex vulcanizates in the presence of surface active agents.

The rubber-filler attachment may be formed due to the interaction of polyvinyl alcohol or casein with the protective layer on the rubber and filler particles. During the interaction, partial desorption of protective layer on the rubber and filler particles may take place leading to direct contact between silica and rubber particles. Dogadkin *et al.* (1958) have proved through microscopic investigations that aggregation of rubber and carbon black are formed while adding casein to a mixture of SBR latex and carbon black. In the present study also a similar nature of aggregation of rubber and silica is expected to be formed leading to the formation of coupling bonds and improvement in tensile properties.

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