Effect of Fillers on the Properties of Prevulcanized Natural Rubber Latex Film

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ABSTRACT: Precipitated silica, china clay and whiting were incorporated in NR latex compounds up to 20 phr and prevulcanized at 70°C for 2 h. Cast films were prepared and the effect of leaching in water on mechanical properties evaluated. Rubber-filler interaction, ageing resistance, stress relaxation and morphology of the leached films were also studied. Presence of precipitated silica, china clay and whiting decreased tensile strength and elongation at break but increased the modulus of the prevulcanized latex film. Leaching of the films improved the properties. The presence of precipitated silica and china clay improved the tear strength of the films. Ageing resistance was also increased by the presence, of up to 10 phr, of precipitated silica. The rate of stress relaxation was slightly higher for the film containing precipitated silica followed by those containing china clay and whiting. Morphology of the films revealed uniform distribution of fillers in the rubber matrix.

KEY WORDS: prevulcanized latex, precipitated silica, china clay, whiting.

INTRODUCTION

THE MAJOR OBJECTIVES of adding fillers to rubber are improvement in processability, enhancement of certain properties, and reduction in cost. Reinforcement of dry rubber is attained by certain inorganic fillers but no similar effects are observed when the same fillers are in-

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corporated in latex compounds [1]. The poor rubber-filler interaction in latex vulcanizates is attributed to many factors such as absence of chemical interaction between filler and rubber, difficulty in achieving simultaneous deposition of filler and rubber particles and the presence of a protective layer of stabilizers around the rubber and filler particles which prevents direct contact between the two [2]. Lamm and Lamm [3] claimed that some reinforcement of latex film by carbon black can be achieved by subjecting the latex compound to irradiation by ^{60}Co gamma rays. According to van Rossem and Plaizier [4] small additions of bentonite clay enhanced the tensile strength and modulus of the vulcanized deposits. It has been reported by Andersen [5,6] that ageing resistance of natural rubber vulcanizates may be improved by the incorporation of small amounts of fine particle silicas. Silica filled NR latex vulcanizates were found to show better tensile properties in the presence of polyvinyl alcohol and casein [7]. Gamma irradiation of silica filled NR latex has improved rubber-silica interaction considerably [8]. It is reported that polyethylene glycol can act as a surface active agent in latex compounding improving polymer-filler interaction [9]. The present study reports the effect of addition of fillers such as precipitated silica, china clay and whiting on properties of prevulcanized latex film. The effect of leaching on mechanical properties of the films was evaluated. The volume fraction of rubber, rubber-filler interaction, ageing resistance, stress relaxation characteristics and morphology of the leached films were also evaluated.

EXPERIMENTAL

Materials

Centrifuged latex (high ammonia) conforming to the specification of Bureau of Indian Standards, IS 5430-1981, was obtained from the Pilot Latex Processing Centre of Rubber Board. Sulphur, zinc oxide, zinc diethyldithiocarbamate, precipitated silica, china clay, and whiting were of commercial grade and were prepared as dispersions in water by ball milling. Other chemicals were of laboratory grade and were used as solutions in water.

Prevulcanization

Latex compounds were prepared as per the formulation given in Table 1. Precipitated silica (pptd silica), china clay, and whiting were

Table 1. Formulation of the base latex compound.

Ingredients	Parts by Weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Potassium laurate solution, 20%	1.3
Sulphur dispersion, 50%	3.0
Zinc diethyldithiocarbamate dispersion, 50%	2.0
Zinc oxide dispersion, 50%	0.4

added at 5, 10, and 20 phr. Precipitated silica was added as 25% dispersion while china clay and whiting were added as 50% dispersion. The total solids content of the latex was adjusted to 48%. Prevulcanization was carried out by heating the latex compounds in beakers immersed in a water bath set at 70°C. The compounds were subjected to continuous slow stirring and the beakers were kept covered to minimize loss of ammonia. After 2 h the latex compounds were cooled and kept at room temperature. On the next day, after straining the latex compounds, films were cast in glass cells to a thickness of approximately 0.75 mm. After drying, a set of films were kept without any after-treatment. All other films were leached in water for 4 h and dried at room temperature.

Volume Fraction of Rubber

Volume fraction of rubber in the swollen vulcanizate was determined from equilibrium swelling of the films in toluene at 30°C following the method suggested by Ellis and Welding [10].

Physical Testing

Tensile properties, tear resistance and stress relaxation measurements were performed on a Zwick Universal Testing Machine (model 1474). Tensile properties of the films before and after ageing were measured as per ASTM D 412-87 using dumbbell specimens, tear strength as per ASTM D 624-86 using 90° angle test specimens and stress relaxation according to Mackenzie and Scanlan [11] using dumbbell specimens.

Morphology

Photomicrographs of the films were taken on a Leica Wild M8 Zoom Stereo Microscope and Wild mps 46/52 Photoautomat using NOVA FP_4 film.

RESULTS AND DISCUSSION

Volume Fraction of Rubber and Rubber-Filler Interaction

Table 2 shows the effect of increasing filler content on volume fraction of rubber. It is seen that volume fraction of rubber slightly increased on increasing the filler content. This is mostly owing to the restricted swelling offered by the presence of fillers. The effect was comparatively more pronounced in the case of silica followed by clay and less in the case of whiting. The difference in V_r values (Table 2) as obtained from swelling measurements in toluene in the original vulcanizate and the same after ammonia treatment [12] gives a measure of rubber-filler interaction. This is comparatively higher for silica followed by clay and whiting. However, the level of interaction is observed to be much lower compared to that in the case of dry rubber mixes.

Tensile Properties

Figures 1, 2 and 3 show the effect of fillers on tensile strength, elongation at break and modulus at 100% elongation respectively of prevulcanized latex (PVL) films. Presence of fillers decreased the tensile strength and elongation at break, but increased modulus of the films marginally. As the filler content increased the effect became more pronounced. These observations are comparable to the earlier reports [9] on postvulcanized films. The films containing precipitated silica exhibited the highest increase in modulus followed by those containing

Table 2. Volume fraction of rubber.

Type of Filler	Concentration (phr)	V_r	V_r in Ammonia Atmosphere	Difference in V_r
Nil	0	0.1689	—	—
	5	0.1690	0.1548	0.0142
Ppld silica	10	0.1694	0.1547	0.0147
	20	0.1726	0.1451	0.0275
	5	0.1691	0.1552	0.0139
China clay	10	0.1696	0.1556	0.0140
	20	0.1710	0.1489	0.0221
	5	0.1656	0.1518	0.0138
Whiting	10	0.1659	0.1519	0.0140
	20	0.1664	0.1524	0.0140

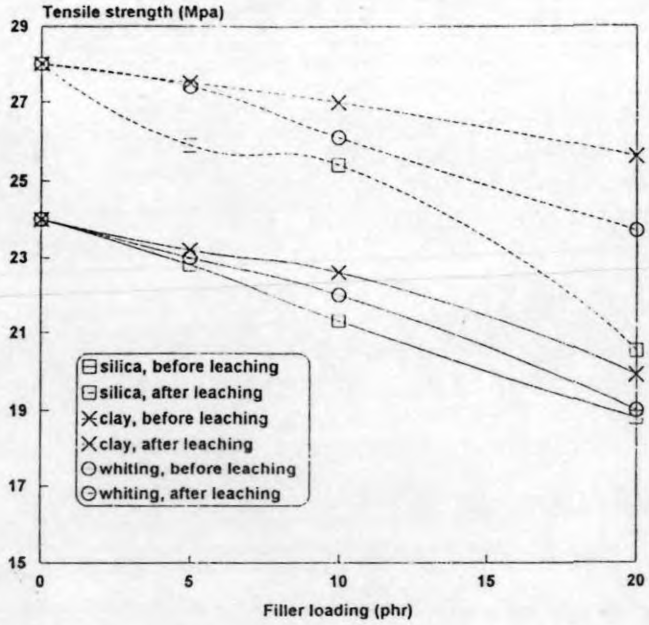
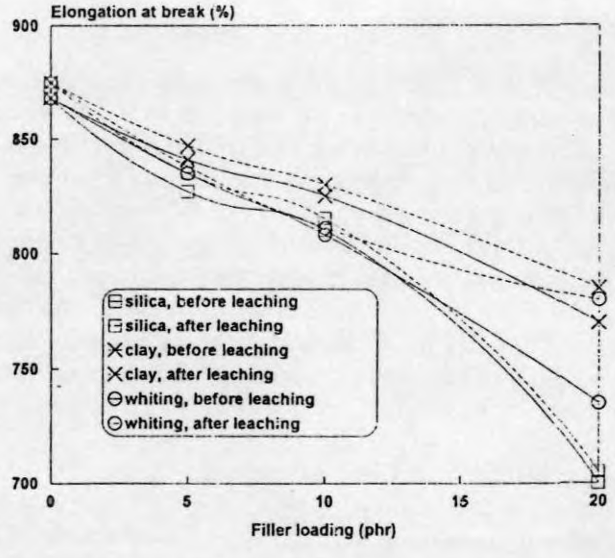


FIGURE 1. Effect of fillers on tensile strength of PVL films before and after leaching.



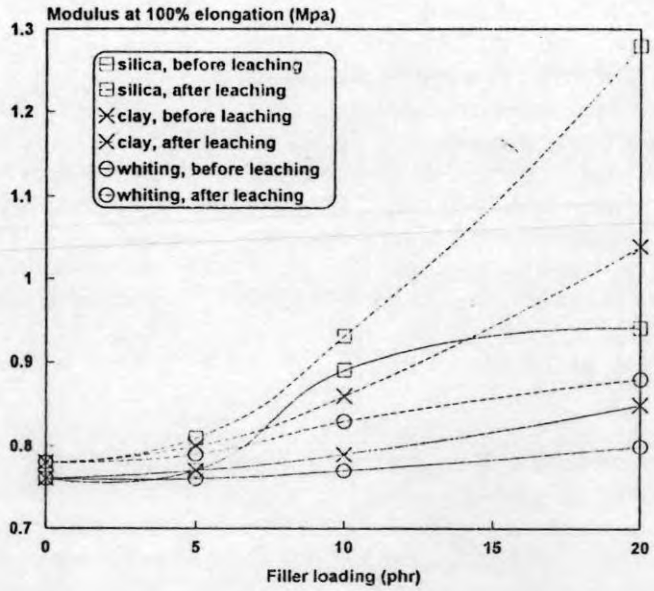


FIGURE 3. Effect of fillers on modulus at 100% elongation of PVL films before and after leaching.

china clay and whiting. The properties of postvulcanized films containing 10 phr of filler, as shown in Table 3, reveal that the effect of fillers on prevulcanized film is comparable to that of post-vulcanized film.

The filled rubber can be considered to be a two phase system of hard and soft segments. On application of stress, deformation takes place in the soft region and the filler particles do not deform. Thus, the applied load is distributed only among the polymer chains. However, there could be stress concentration on the polymer-filler interface resulting in low tensile strength and elongation at break.

Table 3. Effect of 10 phr of filler on tensile properties of postvulcanized films.

Type of Filler	Modulus, 100% (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Nil	0.73	27.7	1025
Pptd silica	1.00	21.8	880
China clay	0.84	27.5	987
Whiting	0.80	26.0	990

Effect of Leaching

The effect of leaching of PVL films, containing 0 to 20 phr of fillers, on tensile properties is also shown in Figures 1, 2 and 3. Leaching improved the properties of the films, but the trend on increasing the filler content on tensile properties remained the same as in the case of the unleached films. During leaching most of the soluble hydrophilic materials are removed, thus facilitating better cohesion of the rubber particles allowing greater degree of entanglement between molecules anchored in different particles leading to enhanced tensile properties.

Tear Strength

Figure 4 shows the effect of addition of fillers on tear strength of leached PVL films. It can be seen that addition of precipitated silica and china clay improved the tear strength of the films. The effect was more pronounced in the case of precipitated silica where a maximum was observed at around 7.5 phr. Tear strength was not significantly affected by the presence of whiting in the film. Improvement in tear

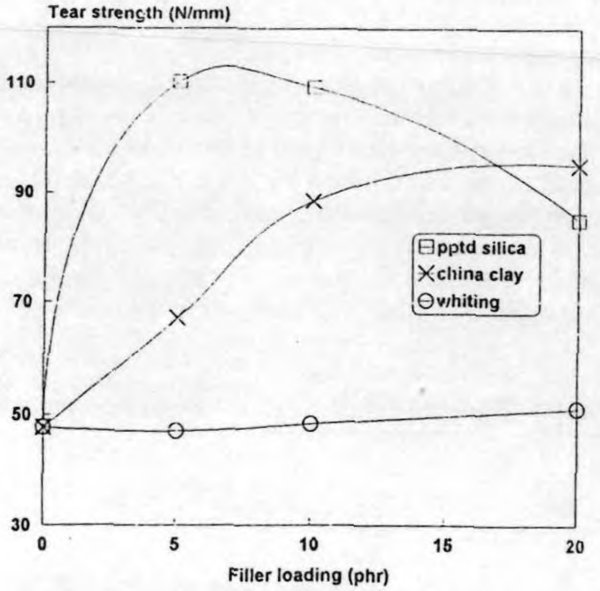


FIGURE 4. Effect of fillers on tear strength of leached PVL films.

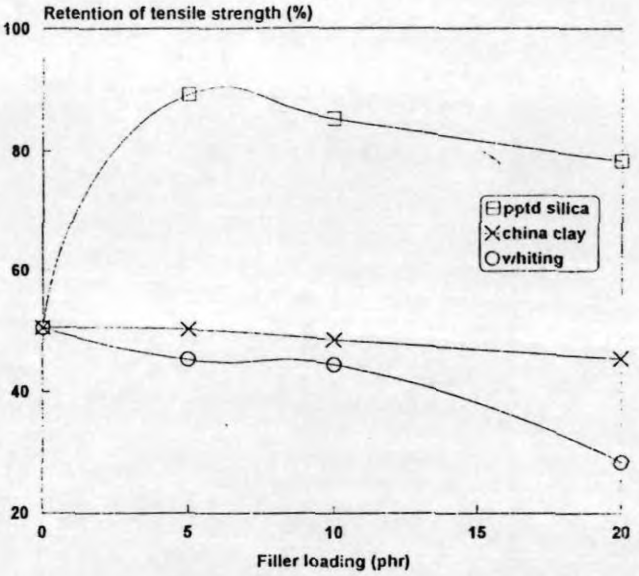


FIGURE 5. Effect of ageing on tensile strength of leached PVL films containing fillers.

strength can be attributed to the improvement in modulus of the films and to the slightly higher rubber-filler interaction as stated earlier.

Ageing Properties

The effect of ageing of the leached films at 70°C for 14 days on tensile properties is shown in Figures 5, 6 and 7. It is observed that ageing resistance of the films is increased by the addition of silica. It has been reported [5,6] that ageing resistance of NR sulphur vulcanizates may be improved by the incorporation of fine particle silicas. Percentage retention of tensile strength and elongation at break has been found to be decreasing with filler dosage. The minimum effect is shown by precipitated silica and the maximum by whiting. As clay and whiting are prepared directly from natural deposits, chances of contamination are more. Many of the contaminants including metal ions are known to be pro-oxidants for rubber.

Stress Relaxation Characteristics

Figure 8 shows the stress relaxation pattern of leached PVL film without filler and those containing 10 phr each of precipitated silica,

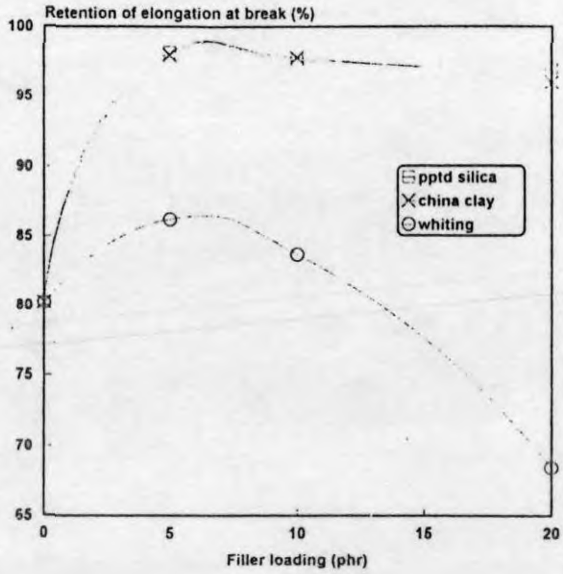


FIGURE 6. Effect of ageing on elongation at break of leached PVL films containing fillers.

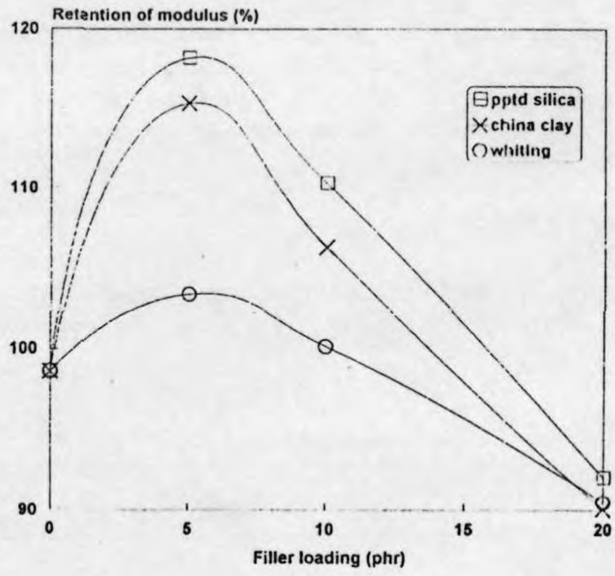


FIGURE 7. Effect of ageing on modulus at 100% elongation of leached PVL films containing fillers.

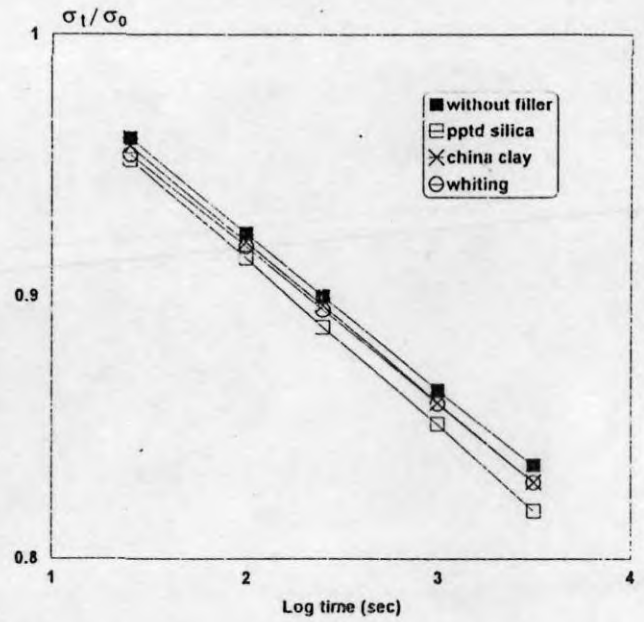


FIGURE 8. Semilog plots of stress decay as a function of time for leached PVL films containing fillers.

china clay and whiting. Table 4 shows the slope of these lines. The rate of stress relaxation was more for the film containing precipitated silica followed by that containing china clay and whiting.

The phenomenon of stress relaxation is the result of physical and chemical changes in the rubber, both of which can occur simultaneously. The physical changes are due to the viscoelastic nature of rubber and the chemical effects due to changes in the molecular structure by ageing, oxidation, etc. Physical effects are more important at normal temperatures. A low level of rubber-filler interaction is observed (Table 2) in the case of vulcanizate containing silica. The linkages formed due

Table 4. Effect of fillers on stress relaxation.

Type of Filler	Slope of the Lines
Nil	0.0545
Pptd silica	0.0658
China clay	0.0575
Whiting	0.0554

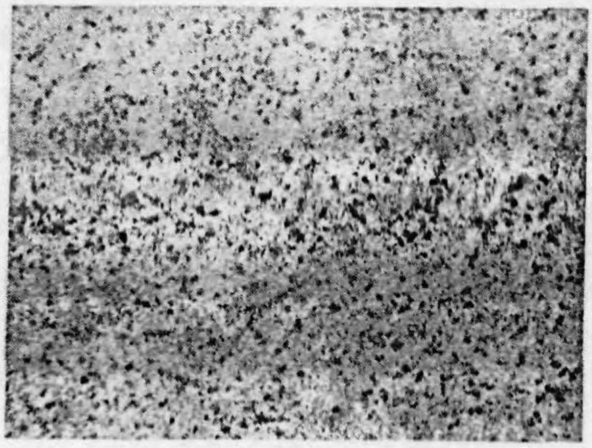


FIGURE 9. Optical micrograph of leached PVL film containing precipitated silica (×120).

FIGURE 10. Optical micrograph of leached PVL film containing china clay (×120).

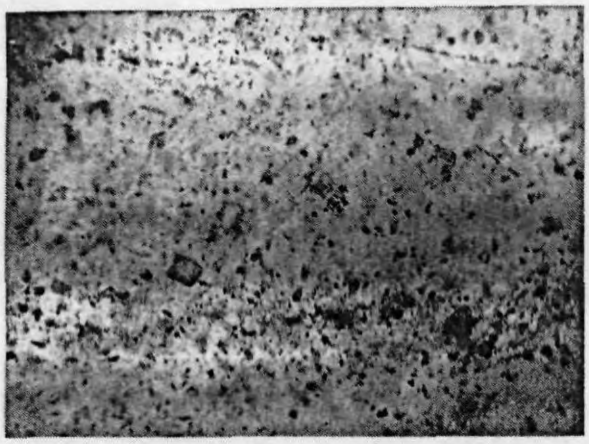


FIGURE 11. Optical micrograph of leached PVL film containing whiting (×120).

to the interaction are getting reduced on stretching which causes a higher stress relaxation rate.

Morphology

The photomicrographs of leached films containing 5 phr of filler are given in Figures 9, 10 and 11. These reveal that the fillers are more or less uniformly distributed in the rubber matrix, however the difference in properties appears to be due to difference in particle size of the fillers as shown in Table 5.

CONCLUSIONS

The presence of fillers such as precipitated silica, china clay and whiting decreased the tensile strength and elongation at break but in-

Table 5. Average particle size of fillers [13].

Type of Filler	Average Particle Size (nm)
Pptd silica	20
China clay	2×10^3
Whiting	12×10^3

creased modulus of the prevulcanized latex film. Leaching of the films improved them. The presence of precipitated silica and china clay improved the tear strength of the films, but the presence of whiting did not significantly affect it. The presence of up to 10 phr of silica improved the ageing resistance of the film but no significant effect was observed in the case of china clay or whiting. The rate of stress relaxation was slightly higher for the film containing precipitated silica followed by those containing china clay and whiting. Morphology of the films revealed uniform distribution of fillers in the rubber matrix.

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Coinjection Molded Pregenerated Microcomposites

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ABSTRACT: This work was concerned with the coinjection molding of poly(ethylene terephthalate) (PET) reinforced with pregenerated thermotropic liquid crystalline polymer (TLCP) fibrils, where the TLCP (DuPont, HX1000) had a higher melt processing temperature than PET. A novel dual extrusion process was used to spin strands of PET reinforced with HX1000 fibrils. The strands were compression molded into cartridges and then coinjection molded to form plaques. In comparison to conventionally injection molded pregenerated microcomposites, coinjection molded composites had higher flexural moduli. The coinjection molded composites also had smoother surfaces than glass fiber-filled PET. It was determined that the best mechanical properties were achieved using a core of glass fiber-filled PET.

KEY WORDS: coinjection molding, pregenerated microcomposites, thermotropic liquid crystalline polymer, composites.

INTRODUCTION

INJECTION MOLDING THERMOTROPIC liquid crystalline polymers (TLCPs) blended with commodity thermoplastics has attracted considerable interest in recent years because of the reinforcing ability of the TLCP phase [1–7]. Proper processing conditions can impart a fibrillar TLCP structure within the matrix, producing an increase in

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