CHAPTER 5

VULCANIZATION CHARACTERISTICS OF LOW PROTEIN LATEX
Extractable proteins (EP) in natural rubber latex products can cause allergic reactions in sensitized people\(^\text{(1-4)}\). A form of natural rubber latex which can result in very low EP in latex products, has been developed by a non-enzymic deproteinization process\(^\text{(5)}\). This low protein latex (LPL) contains low level of non-rubber materials, especially proteins. The sulphur vulcanization characteristics of natural latex are, to a certain extent, controlled by the level of non-rubber materials especially proteins\(^\text{(6-8)}\). Since LPL is low in total proteins also, its vulcanization behaviour is likely to be different from that of standard centrifuged latex (SCL).

LPL can find application in the production of medical and pharmaceutical products like catheters, examination gloves, teats, soothers, condoms etc, which make intimate contact with human body. Another area of application is medical tubing. Latex products made from LPL will be of advantage to persons sensitive to latex proteins. For achieving desirable properties for the vulcanizates, the vulcanization conditions have to be standardized. The basic objective of the development of a vulcanization system for an elastomer is to transform essentially linear polymer molecules into a three dimensional network by the insertion of crosslinks.

Crosslinking have the effect of preventing the polymer chains moving bodily past each other when an external force is applied to the matrix. Vulcanization of NR is generally brought about by heating with sulphur and accelerator(s). The amount of sulphur and accelerator determine the crosslink density and type of crosslink, which in turn control the physical properties. Vulcanization can be achieved by peroxides or high energy gamma radiation also. This chapter, dealing with vulcanization of LPL is divided into three parts:

A. Vulcanization of low protein latex in conventional sulphur cure system.

B. Vulcanization of low protein latex in EV (efficient vulcanization) cure system.

C. Radiation prevulcanization of low protein latex.
REFERENCES


CHAPTER 5A

VULCANIZATION OF LOW PROTEIN LATEX IN CONVENTIONAL SULPHUR CURE SYSTEM
Traditionally crosslinking reaction in natural rubber is brought about by using sulphur and organic accelerators. From an economic point of view, the most widely used cure system is the one employing low levels of accelerator (about 0.4–1.2phr) along with high levels of sulphur (about 2.0–3.5phr). This is known as conventional sulphur cure system.

The ratio of the amount of any given accelerator to sulphur largely determines the type of sulphur crosslinks formed and the amount of sulphur which combines with the rubber in non-crosslink structures such as cyclic sulphides\(^1\). Low ratios favour polysulphidic crosslinks with a relatively high level of cyclic sulphides.

For the sulphur vulcanization of products made from latex two alternate methods exist\(^2\). The first is that the chemicals required for vulcanization are mixed into the latex then the latex mixture (compound) is formed into the required shape and dried. The dried rubber matrix containing the chemicals is then heated to effect vulcanization. This is known as post-vulcanization since crosslinking occurs essentially after the product has been formed. The other alternative involves heating the latex with the vulcanization ingredients dispersed in it. This is called prevulcanization and the resulting prevulcanized latex can be formed into latex products in the normal way. Only drying is required to obtain the vulcanized rubber product.

Post-vulcanization of latex products is fundamentally the same as that of vulcanization of dry rubber compounds. The main difference between the two processes is that in latex products the ingredients are incorporated into latex as aqueous dispersion/emulsions, then removing water. In dry rubber the chemicals are added as powders using an open mill or internal mixer.

The mechanism of accelerated sulphur vulcanization has been extensively studied\(^3\-5\). The first step in the combination of accelerator with activator, forming an active accelerator, soluble in rubber. The active accelerator reacts with sulphur to produce an active sulphurating agent which reacts with the rubber
hydrocarbon to give a pendent group of chain of sulphur atoms terminated with the accelerator derivative. The pendent group can form a crosslink.

Sulphur prevulcanization of concentrated natural latex has been studied by several authors. Recent developments in the prevulcanization of natural latex have been described by Blackley\(^6\). Low\(^7\) has studied the prevulcanization rates of natural latices from different sources and age and also the effect of storage on the properties of prevulcanized latex/latex films after clarification of the prevulcanized latex. Teik and Poh\(^8\) and Wong and Loo\(^9\) have studied the room temperature prevulcanization of natural latex as a means of reducing cost of production. Various general purpose and special purpose formulations for prevulcanizing natural latex have been described by Gorton\(^{10}\). The kinetics and mechanism of sulphur prevulcanization has been described by Merrill\(^{11}\) and Loh\(^{12}\). Compounding formulations suitable for the production of special medical/food items such as teats and soothers are also described by Gorton\(^{13}\). The effect of temperature on prevulcanization of latex has been reported by Claramma and Mathew\(^{14}\). The effect of leaching on properties of prevulcanized latex films has been described by several authors\(^{6,8,10}\). Sulphur prevulcanization of double centrifuged natural latex also has been studied recently\(^{15}\).

It has been believed that the presence of various non-rubber constituents, especially proteins are essential for the occurrence of sulphur prevulcanization reaction\(^{16}\). Also there are reports that tensile properties of prevulcanized latex films are considerably affected by the level of proteins in the films. Hence it seemed worthwhile to study the post-vulcanization and prevulcanization characteristics of LPL using conventional sulphur system.

The extent of crosslink formation depends on temperature of vulcanization and duration of heating. This chapter reports the results of studies on the effect of duration of post-vulcanization on crosslink density of the film, its tensile properties, behaviour of the films on accelerated heat ageing and the synergistic effect of accelerator combinations. Prevulcanization studies include effect of temperature and duration of heating on crosslink density and tensile properties of latex films,
effect of leaching of films and accelerated ageing. The extractable protein content in these latex films also were determined.

**Materials and methods**
From a batch of SCL preserved in HA system, DCL and LPL were prepared by the method described in Chapter 4. Potassium hydroxide used as stabilizer in latex compounding was prepared as 10% aqueous solution. Vulcanizing chemicals, sulphur, ZDC and Zinc oxide each were prepared as 50% dispersion by ball milling.

The formulation of the latex compound for post-vulcanization and prevulcanization in conventional sulphur cure system is shown in Table 5A.1. The latex compound after preparation was matured for 24h. For post-cure studies, cast films were prepared on levelled glass plate and heated at 100°C for various intervals, and leached in water at room temperature.

To study the synergestic effect of accelerators in conventional system and also for improving the modulus of vulcanized films, a combination of ZDC and ZMBT (total quantity of accelerator was 1phr) was used as per the formulation in Table 5A.2. Cast films were vulcanized by heating at 100°C in air for predetermined periods and leached in water at room temperature.

For prevulcanization, the matured latex compound was heated on a water bath at a given temperature under constant slow stirring. Samples were withdrawn at constant intervals and cooled immediately to arrest further crosslinking. To study the effect of temperature on prevulcanization, the latex compound was heated at 50, 60 and 70°C. Attempt to prevulcanize LPL at 70°C was not successful, as the latex compound was getting destabilized, due to the heat sensitizing activity of PPG.

Cast films were prepared by pouring enough latex on levelled glass plates and dried in air. Leaching of the films was carried out in water at 30°C for 1h except in cases where duration of leaching was a variable. The leached films were dried in
air at room temperature. The state of cure of the films was assessed by solvent swelling method\(^{18}\) and crosslink density was evaluated by using Flory-Rhener equation\(^{19}\). Tensile properties were determined on a Hounsfield Universal Testing Machine following the Indian Standard procedure\(^{20}\). Ageing of latex films was done at 70°C for 7 days. Extractable protein contents in latex films were estimated by RRIM modified Lowry method\(^{21}\) using distilled water as the extractant and laboratory grade reagents were used for these estimations.

**RESULTS AND DISCUSSION**

**POST-VULCANIZATION**

**Effect of duration of post-vulcanization in conventional cure system on crosslink density and effect of accelerated heat ageing**

Variations in crosslink density of SCL, DCL and LPL films with time of post-vulcanization and the effect of heat ageing are shown in Figure 5A.1. For all the three types of latex films crosslink density increases with time of vulcanization, reach a maximum and then declines; however, the maximum crosslink density, and the duration of heating to achieve the state of cure differ. In general, at all durations of post-vulcanization, SCL films have higher crosslink density than DCL and LPL films. Thus DCL and LPL are slow curing than SCL and this difference in cure rate may be primarily due to difference in protein content. The three types of latex films post-vulcanized for short intervals, on ageing, show higher crosslink density due to further crosslink formation. Crosslink densities in DCL and LPL films are almost similar and are lower than that of SCL films. Higher crosslink density in aged SCL films, over DCL and LPL films, is due to the higher initial value for SCL films and antioxidant activity provided by accelerator residues\(^{1}\) and naturally occurring antioxidants\(^{22}\). Natural antioxidants are less in DCL and LPL compared to SCL films because of their removal during second centrifugal concentration. It is observed that crosslink densities in aged films of the three types of latices decrease with duration of post-vulcanization. In conventional cure system the crosslinks are mainly polysulphidic. The decline in crosslink density is believed to be due to main chain modifications occurring as a result of breakdown of polysulphidic crosslinks with the insertion of liberated sulphur in
cyclic sulphides\(^{(13)}\). Reduction in crosslink density is thus due to molecular rearrangement. It is observed that in vulcanized LPL films maximum crosslink density is achieved when duration of post-vulcanization is 1h. However, maximum crosslink density in aged film is observed when initial duration of post-vulcanization was about 45 minutes at 100°C, prepared as per the formulation given in Table 5A.1.

**Effect of duration of post vulcanization in conventional cure system on tensile properties of latex films and effect of accelerated heat ageing**

Figure 5A.2 shows the effect of variation of modulus of latex films against duration of post-vulcanization at 100°C, both before and after ageing. Modulus of all the latex films increase initially with duration of post-vulcanization. SCL films show maximum modulus at about 1.2h of vulcanization while DCL and LPL have maximum at 1.1h of vulcanization. Beyond this state of cure modulus decline. For a given period of post-vulcanization, SCL films have higher modulus than DCL or LPL films. Higher crosslink density of SCL films is the major factor contributing to the higher modulus. It is observed that LPL films have higher modulus than DCL films, even though crosslink densities are similar in these films. This is probably due to higher forces of attraction between latex particle of LPL films due to high Hydrogen bonding originating from adsorbed PPG molecules on particles surface. Ageing of latex films is accompanied by increase in modulus, when the period of post-vulcanization is below the period corresponding to maximum modulus. It is observed that the modulus of SCL and LPL films post-vulcanized for 1h remain more or less constant even after ageing. This is probably because the molecular rupture occurring during ageing is compensated by additional crosslink formation. Films vulcanized beyond this period are accompanied by reduction in modulus. Reduction in crosslink density of the aged films is mainly responsible for reduced modulus on ageing. However, both SCL and LPL latex films vulcanized to the optimum level show high retention of modulus, probably due to the antioxidant activity of dithiocarbamate accelerator residues\(^{(1)}\) and naturally occurring antioxidants\(^{(22)}\). However in the case of DCL films beyond a period of 1h of post-vulcanization accelerated ageing
is accompanied by fall in modulus. This is primarily a result of low crosslink density in the aged film.

As seen from Figure 5A.3 post-vulcanized SCL and LPL films show high tensile strength and the gradation is

\[ \text{SCL} > \text{LPL} > \text{DCL} \]

Before ageing, for the three types of films maximum tensile strength is achieved when post-vulcanized for about 1h at 100°C which is considered to be the optimum period of vulcanization. Slightly higher tensile strength is exhibited by SCL films over LPL. Higher tensile strength of SCL and LPL films is primarily due to high crosslink density. Attractive forces due to Hydrogen bonding between proteins and/or PPG adsorbed on the surface of coalesed latex particles in the film make a secondary contribution. However, in DCL films, crosslink density is least among the three latices. Contribution due to Hydrogen bonding is low due to reduced level of proteins and absence of PPG. On ageing, under-cured SCL, DCL and LPL films show a slight improvement in tensile strength followed by a fall. In the case of DCL and LPL films tensile strength after ageing reduce linearly with increase in vulcanization time. On heat ageing, there is net reduction in crosslink density for optimum and over-cured films. After ageing, retention of tensile strength is higher for SCL film, even though crosslink density in aged SCL and LPL films vulcanized for 1h are almost equal. Thus in addition to crosslink density, effectiveness of interparticle coalescence during film formation also contributes to higher tensile strength of SCL films after ageing. LPL films post-cured for 0.5h showed considerable improvement in tensile strength after ageing. Formation of additional crosslinks on ageing makes substantial contribution to this improvement. Other LPL films initially cured for longer duration show lower retention. Retention of tensile strength on ageing is lowest for DCL films. This may be due to the rupture of crosslinks on ageing and removal of naturally occurring antioxidants, during the second centrifugal concentration, involved in the production of DCL and LPL.
Elongation at break of the SCL, DCL and LPL films vulcanized in the conventional system are shown in Figure 5A.4. The data show that for both SCL and LPL films elongation at break decreases with increase in cure time, reaches minimum value and then increase. However DCL films show a constant decrease. Ultimate elongation os lowest for DCL films. This reduction is attributed to the increase in crosslink density and modulus of the films. However, over-cured films of SCL and LPL show slightly higher elongation. This is probably due to the reduction in crosslink density and modulus of the over-cured films. Also ageing of the films reduces ultimate elongation. The reduction in elongation is probably due to the thermal and oxidative degradations that have occurred to the polymeric chains and/or crosslinks in all films.

**Synergestic effect of accelerator combination on tensile properties**

**post-vulcanized latex films**

It is a common practice in the technology of natural latex to replace a portion of dithiocarbamate accelerator by thiazole for improving the modulus of latex films\(^{23-25}\). The results obtained by replacing different portions of zinc diethyldithiocarbamate (ZDC) by zinc salt of mercaptobenzothiazole (ZMBT) in post vulcnizaion of LPL films is given in Figure 5A.5 (to limit the volume of data, this study is confined to LPL films alone). It is seen that replacement of 20% ZDC by ZMBT improves the modulus for all samples studied except where the film is under-cured. However, ZMBT addition above 20% reduces the modulus in the case of films cured beyond the optimum period of vulcanization.

However, it is seen from Figure 5A.6 that partial replacement of ZDC by ZMBT is accompanied by a reduction in tensile strength for all the combinations and the extent of reduction increases with increasing content of ZMBT in the vulcanizate.

Figure 5A.7 shows the effect of accelerator combinations on elongation at break (EB) of LPL films. It is seen that for a given duration of vulcanization, up to about 25% content of ZMBT in the accelerator combination, EB reduces, is minimum at about 25-30% ZMBT and increases for higher ZMBT content. The initial reduction in EB is due to higher modulus and subsequent increase in ultimate
 elongation is probably because of the lower state of cure due to the slow curing nature of ZMBT.

The effect of heat ageing on modulus of LPL films post-vulcanized for 1h at 100°C using different combinations of ZDC/ZMBT is shown in Figure 5A.8. It is seen that for all combinations of ZDC and ZMBT under study, modulus of the films increases on ageing. The extent of increase is least for ZDC/ZMBT combination 1.0/0 and maximum for 0.5/0.5. As ZMBT is not a fast accelerator as ZDC, by 1h heating at 100°C the films have not cured to the optimum. Hence, further curing occurs during heat ageing, leading to increase in modulus. It is seen that for maximum modulus after ageing, replacement of 0.25 parts of ZDC by ZMBT is necessary.

Heat ageing of LPL films is accompanied by fall in tensile strength for all combinations of ZDC/ZMBT. The results obtained are shown in Figure 5A.9. Tensile strength decreases slightly with increase in the content of ZMBT. It is believed that the reduction in tensile strength is due to thermal degradation of the rubber molecules. However, the overall retention of tensile strength on ageing is good. Ageing of the vulcanized latex films, containing various levels of ZDC and ZMBT is accompanied by reduction in elongation at break, as seen from Figure 5A.10. As in the case of tensile strength the reduction in ultimate elongation is attributed to thermal degradation of molecular chains. It does not appear that a rational explanation in terms of the chemistry of accelerated sulphur vulcanization reaction has ever been proposed.

**Effect of duration of post-vulcanization on physical properties of latex films containing different levels of ZDC/ZMBT combinations**

Figure 5A.11 shows the variation in modulus of LPL films post-vulcanized for different durations and containing different levels of ZDC and ZMBT, the total content of accelerators being 1phr. It is seen that the time required to achieve a given modulus slightly reduces with increasing content of ZMBT. For all accelerator combinations, modulus increases from a low value, reaches a maximum and then declines. The fall in modulus on continued heating beyond
the optimum is possibly due to the thermal degradation occurring during continued heating.

The variation in tensile strength is shown in Figure 5A.12. The highest tensile strength is observed at about 1h of post-vulcanization for all ZDC/ZMBT combinations and maximum tensile strength is achieved when ZDC alone is used as accelerator. For each of the accelerator combinations investigated, tensile strength increases from a low initial value, reaches a maximum at about 1h and then declines.

The variation of elongation at break with duration of post-vulcanization is shown in Figure 5A.13. EB initially decreases and is minimum at about 1h of vulcanization and then increases. For a given duration of vulcanization the lowest EB is shown by ZDC/ZMBT combination of 0.6/0.4.

**PREVULCANIZATION**

**Swelling index and crosslink density of pre-vulcanized latex films**

Natural latex films absorb hydrocarbon solvents and swell. The extent of solvent absorption and swelling are inversely proportional to extent of cure\(^\text{25}\). Table 5A.4 shows the variation of weight swelling index for three types of latex films at 60°C and also at LPL films at 50°C which are prepared from latex prevulcanized for different intervals. The values obtained for DCL and LPL films are almost similar, indicating that their states of cure are almost comparable. Swelling Index for LPL at 50°C shows a progressive fall, while the data at 60°C for SCL, DCL and LPL films initially decreases with prevulcanization time, passes through a minimum value and then increase. But the minimum value for SCL films at 60°C is appreciably lower than that of DCL and LPL films. This indicates that the state of cure of SCL is much higher than that of DCL and LPL films. According to Gorton and Pendle\(^\text{17}\) weight swelling index values between 15–7 corresponds to lightly vulcanized film, 7–5 for moderately vulcanized and less than 5 for fully vulcanized film. Thus it is seen that DCL and LPL are slow in vulcanizing compared to SCL and do not achieve a fully cured state.
Figure 5A.14 gives the variation of crosslink density with time of prevulcanization. In the case of LPL at 50°C, crosslink density steadily increases during 5h of heating and does not show a maximum. Generally prevulcanization times are of the order of 2–3h and the crosslink density achieved during this period is about 2.5–3.0×10¹⁹ per gram of rubber hydrocarbon. However, crosslink density in rubber particles of LPL at 50°C in 2–3h is too low. Thus for practical application, prevulcanization temperature of 50°C is of no use for LPL. The three types of latices when prevulcanized at 60°C, crosslink density increases initially with time, reaches a maximum and then slowly declines on continued heating. For SCL, maximum crosslink density is observed at about 3.5h while DCL and LPL show maximum at 3h heating. The maximum value exhibited by DCL and LPL are much lower than that of SCL. Moderate levels of crosslinks are formed in LPL at 60°C, while SCL under similar conditions are crosslinked to a higher state. Since the crosslink density achieved at 60°C in LPL was low, prevulcanization at 70°C was tried. However, attempts to prevulcanize LPL at 70°C failed, as the latex was destabilized after 1h of heating due to the presence of polypropylene glycol in latex, which can function as a heat sensitizing chemical.

It is observed that sulphur can transfer from sulphur particles originally present in the aqueous phase of latex to the rubber particles remarkably rapidly, while zinc dialkyl dithiocarbamate accelerator by itself does not transfer from its particles to any significant extent. However, in presence of sulphur, the accelerator can transfer more rapidly, although more slowly than does sulphur on its own. The first major step in vulcanization of latex particles is the formation of a sulphur-accelerator species in the aqueous phase of the latex. During prevulcanization of latices, sulphur and sulphur-accelerator species can independently dissolve in the serum, with the assistance of some serum constituents and form a loose complex having some surface activity and get adsorbed at the rubber-serum interface. However, after adsorption, the hydrophilic component of the adsorbed species is somehow lost, thus becoming hydrophobic. The hydrophobic species dissolves in rubber and migrates to the interior of the latex rubber particle where they react with rubber molecules thus leading to the formation of crosslinks. The hydrophilic
component of the sulphur-accelerator complex returns to the aqueous phase facilitating further complex formation and adsorption at the rubber-serum interface. Some non-rubber components in latex assist in the dissolution and adsorption of sulphur/accelerators\(^{(27)}\). In DCL and LPL the non-rubber materials are less and hence the amount of sulphur and accelerator entering rubber particles are believed to be less. Thus the degree of vulcanization is low in DCL and LPL. In LPL at 50°C, initially crosslink insertion is very slow; after 3–3.5h, there is a rapid increase as shown in Figure 5A.14. This in turn, may be probably due to the slow transfer of vulcanizing ingredients into the rubber phase. This slow entry of curatives to LPL particles at 50°C may be due to some hindrance made by polar hydroxyl groups of adsorbed polypropylene glycol molecules at the rubber particle surface. At 60°C, crosslink insertion is more rapid in three types of latices, probably due to higher rate of activity of sulphurating species. However, this individual rate is highest for SCL. The decrease in crosslink density on continued heating at 60°C in the case of SCL, DCL and LPL is probably due to the breakdown of effective crosslinks, which are mostly polysulphide in conventional cure system\(^{(28,29)}\). Crosslinks and pendent groups undergo a variety of further reactions; these are considered ‘side reactions’ in sulphur vulcanization. These take place at the same time as crosslinking, during over-cure and in the service life of the vulcanizate. Consequently their relative rates determine the efficiency of vulcanization. Desulphuration and decomposition are the two most important types of reactions occurring after crosslinking. These side reactions predominate beyond optimum cure\(^{30}\), leading to an overall reduction in crosslink density, on continued heating.

**Tensile Properties of prevulcanized latex films**

Figure 5A.15 shows the variation of modulus (at 500% elongation) of cast films against time of prevulcanization of latex. At 50°C for LPL, there is a gradual increase in modulus initially; but modulus increases more rapidly beyond 3h of prevulcanization. The observed variation in modulus is in agreement with the formation of crosslinks at 50°C as shown in Figure 5A.14.
When prevulcanization is carried out at 60°C, SCL, DCL and LPL films exhibit increasing modulus with increase in duration of prevulcanization. In the whole interval of prevulcanization modulus of SCL film is higher than that of DCL and LPL films and exhibit the order

**SCL > LPL > DCL**

ie, LPL gives softer vulcanizates. The lower modulus of LPL films compared to SCL films is mainly due to the lower crosslink density. Even though crosslink density in DCL and LPL films are more or less similar, modulus is higher for LPL films. This observation suggests that in addition to crosslink density some secondary factors are also involved in the overall modulus. At about 3h of prevulcanization, the observed modulus of 1.45 to 1.50MPa in the case of LPL films is sufficient enough to meet the modulus requirement for examination and surgical gloves. Also, low modulus of vulcanized LPL films is a desirable characteristic in the manufacture of products like examination gloves, as the wearer will not feel uneasy, on prolonged usage.

For a given duration of prevulcanization, the difference in modulus between LPL and SCL films remains somewhat constant initially and the difference increases marginally as prevulcanization proceeds. However, this observed difference is not in line with the difference in crosslink density between LPL and SCL films. The wide difference in crosslink density observed in Figure 5A.14 as prevulcanization proceeds is not reflected in modulus. This may probably be due to better inter-particle integration in LPL films via increased van der Waals attraction and Hydrogen bonding caused by adsorbed surface-active molecules. Eventhough crosslink density in DCL and LPL films are more or less equal, for a given duration of prevulcanization lower modulus of DCL films is attributed to reduced inter particle attractive forces.

Figure 5A.16 shows the variation of tensile strength of latex films with respect to prevulcanization period at different temperatures. The tensile strength observed for LPL films even after 4h of prevulcanization at 50°C is less than that achieved in 0.5h at 60°C. This is in line with the extent of crosslink formation at 50°C.
However, after 4.5h of prevulcanization at 50°C, the crosslink density of LPL films exceeds that of the LPL film prepared from latex prevulcanized at 60°C for 0.5h. However, the tensile strength of the latter film is higher. This is probably because a portion of crosslinks may be intermolecular, and do not contribute to tensile strength. This is in agreement with the results reported earlier in the case of dry rubber products. It is also observed that DCL films exhibit lower tensile strength than LPL films even though crosslink densities are almost similar in both types of latex films. This is also in agreement with observation that crosslink density is not the only factor controlling tensile strength of latex film. In addition to crosslink formation, tensile strength is controlled to some extent by the effectiveness in the fusion of individual latex particles during film formation. At 60°C, the highest tensile strength is exhibited in about 2.5 to 3h of prevulcanization for the three types of latex films. This time interval does not coincide with the maximum of crosslink density Vs prevulcanization time curve (Figure 5A.14). Prevulcanization beyond a period of 3h is accompanied by a fall in tensile strength in the case of films made from three types of latices. The fall in tensile strength may be partly due to modification of crosslinks on continued heating and also due to less effective fusion when they become more crosslinked. From the data presented in Figures 5A.15 and 5A.16 it can be seen that at moderate temperatures for a given crosslink density, the higher the temperature of prevulcanization, the higher the tensile strength of cast films. It is believed that at moderate temperatures, the crosslinks are more of an intermolecular nature, rather than main chain modifications.

Figure 5A.17 shows the variation of elongation at break of latex films against time of prevulcanization. LPL films at 50°C show lower elongation than that at 60°C. This is due to lower crosslink density and modulus of the former film. Further, LPL films show higher elongation compared to SCL and DCL films, even though LPL film has lower crosslink density. This observation suggests that effective inter particle fusion during film formation is a more important factor in deciding the tensile properties of latex films, than degree of crosslinking itself.
Effect of heat ageing on crosslink densities of prevulcanized latex films

Since latex films prepared from LPL prevulcanized at 50°C was low in crosslink density and tensile properties, ageing studies were not conducted on these films. The variation in crosslink densities of latex films on heat ageing at 70°C for 7 days is presented in Figure 5A.18. In the case of SCL films there was initially an increase in crosslink density on ageing, followed by a net fall as prevulcanization advanced. The maximum in the aged crosslink density occurred at about 2h of prevulcanization. DCL films prepared from latex prevulcanized for 0.5h melted, while 1h film showed a small increase in crosslink density on heat ageing and with other films, there was a net decline. In the case of DCL films, crosslink density after ageing was highest in the film prepared from latex prevulcanized for 2h. With LPL films, a trend similar to DCL was observed. In LPL films the highest crosslink density after ageing was observed in films which were prevulcanized for 2-2.5h among the three types of films the reduction in crosslink density due to ageing was highest in SCL films as prevulcanization time increased. In undercured SCL and LPL films, there was a net increase in crosslink density due to the formation of additional crosslinks, by utilising the residual curatives. In conventionally cured latex films, the crosslinks are polysulphidic and the fall in crosslink density on heat ageing is attributed to breakdown of polysulphidic crosslinks with the inscrption of liberated sulphur in cyclic sulphides.

Effect of heat ageing on tensile properties of prevulcanized latex films

The effect of heat ageing on modulus of prevulcanized latex films is given in Figure 5A.19. Cast films prepared from DCL and LPL, prevulcanized for half an hour, on ageing at 70°C for 7 days melted due to severe degradation. The modulus of three types of films decreases on ageing. This decrease in modulus roughly corresponds to fall in crosslink density of latex films. The major difference between the unaged and heat aged latex films is that for all the three types of latex films modulus of unaged films steadily increase throughout the course of prevulcanization, while a peak is observed in the aged modulus of films of the three types of latices. The aged modulus of DCL, and LPL films increased up to a prevulcanization period of 2-2.5h, and thereafter gradually decreased, while the
maximum in the aged SCL curve was at about 3h of prevulcanization. The observed modulus values after heat ageing is the net result of two processes:

- further crosslink formation due to residual curatives available in the films
- thermal and oxidative degradation of the polymer network.

It is believed that some naturally occurring antioxidants in latex, residual ZDC or its fragments available in the film function as antioxidants, thus protecting the film to some extent in the ageing process. However, the net fall in modulus indicates that contribution of degradative process is more in determining the modulus of the films on ageing.

Variation in tensile strength of the three types of latex films, before and after ageing against duration of prevulcanization are given in figure 5A.20. Films of LPL exhibit reasonably good retention of tensile strength on heat aging at 70°C for 7 days. Upto a period of 3h of prevulcanization, the aged tensile strength of LPL films were better than those of SCL, even though the tensile strength before ageing was higher for SCL. After ageing DCL films had lowest tensile strength among the three types. At prevulcanization times beyond 3h aged SCL films were slightly better in tensile strength than LPL films. However, this observation is not much significant, as optimum prevulcanization time for SCL was 3h at 60°C.

One of the major factors contributing to tensile strength of latex films is crosslink density. After ageing crosslink densities of SCL films were higher than those of LPL films. But LPL films after ageing had higher tensile strength up to prevulcanization period of about 3h. It is therefore suggested that the forces of attraction due to Hydrogen bonding, originating from adsorbed PPG contributes to the tensile strength.

The results of elongation at break after ageing are given in Figure 5A.21. The under-cured LPL films show a slight increase in elongation at break, whereas those cured beyond optimum, show reduced elongation. The longer the duration of prevulcanization, the lower the ultimate elongation. Reduction in crosslink
density is the main factor contributing to this behaviour. SCL and DCL films prevulcanized for various durations show decrease in elongation.

In general the tensile properties of prevulcanized LPL films after ageing are reasonably good. Forces of attraction via Hydrogen bonding plays an important role. The residual dithiocarbamate accelerator or its fragments functioning as antioxidants also have contributed to the good retention of tensile properties on heat ageing.

**Effect of leaching on properties of sulphur prevulcanized latex films**

Leaching of dipped latex products, either as wet gel or as dry film is beneficial for several reasons\(^ {32,33} \). The most important is improvement in physical properties. In medical products, accelerator residues causing skin irritation and dermatitis (type IV allergy) and naturally occurring proteins causing contact eczema and anaphylactic shock (type I allergy) are reduced by leaching. In products like electrician's gloves, the ionic components are removed by leaching, thereby improving electrical resistance. Also the appearance of latex products are improved by leaching.

The improvement in physical properties of latex films can be due to either increase in crosslink density or better fusion of latex particles during film formation\(^ {30} \) or both. To assess the separate contributions of each of the above factors, crosslink densities of LPL films prepared from conventionally sulphur prevulcanized LPL were leached for different intervals and the physical properties of the leached films were evaluated. To limit the volume of data, the effect of leaching is limited to LPL films alone. The data obtained on crosslink density are given in Figure 5A.22. It is observed that leaching of LPL films imoroves crosslink density. Water at room temperature followed by room temperature drying has no effect on crosslink density. This is in line with earlier reports\(^ {29} \).

The variation in the modulus of unleached and leached latex films are given in Figure 5A.23. It is observed that for a given state of vulcanization (as determined by the time of prevulcanization), modulus of unleached films is the least and it
progressively increases with time of leaching. However, as indicated by the position of curves in Figure 5A.23 it is further observed that rate of increase in modulus decreases with increase in leaching period and beyond a period of 2h, there is practically no increase in modulus of dry LPL film. It is also observed that for a given duration of leaching, effect of leaching on modulus is high, when films are prepared from LPL prevulcanized for short periods, and the improvement is decreasing with duration of prevulcanization. It is believed that during leaching, some of the adsorbed non-rubber materials on the surface of the rubber particles are removed, thus permitting better inter-particle fusion.

The tensile strength of sulphur prevulcanized LPL films are affected by leaching. The data obtained are presented in Figure 5A.24. As in the case of modulus, the tensile strength of leached films increase with increase in the duration of leaching. Again this increase in tensile strength by leaching of the film is believed to be due to better inter-particle integration. However, a decrease in tensile strength is observed for long leaching periods (eg. 2h leaching). It is believed that in addition to increased inter-particle fusion, the contribution from Hydrogen bonding and van der Waals forces of attraction due to adsorbed polypropylene glycol and remaining proteins would have contributed to tensile strength. Prolonged leaching in water remove a portion of these adsorbed materials, causing reduction in Hydrogen bonding and van der Waals attractive forces between the adjacent particles, net result being a reduction in tensile strength.

Effect of leaching on the ultimate elongation of sulphur prevulcanized LPL films prevulcanized for different intervals is given in Figure 5A.25. Elongation figures for the unleached film also are given for comparison. The variation in elongation at break decreases with leaching time. This is almost in line with the inverse relation between modulus and ultimate elongation of latex films.

Effect of leaching on tensile properties of sulphur prevulcanized LPL films after accelerated ageing
The tensile properties of LPL films after heat ageing are appreciably affected by their leaching history. The data on the effect of duration of leaching in water on
aged modulus of LPL films are presented in Figure 5A.26. A comparison of Figure 5A.26 with Figure 5A.23 shows that in the case of unleached films, modulus of films increases slightly on ageing up to about 2.5h of prevulcanization, which is the optimum period of prevulcanization and then decreases. However, the observed maximum modulus of unleached LPL films is slightly lower than those of the leached films prevulcanized for the same period. It is further observed that the best retention of aged modulus is observed for those films, which previously were leached for half an hour and longer leaching reduces the aged modulus.

The aged modulus of latex films are the net result of several factors:

- Crosslink density of the films before and after ageing
- The extent of inter-particle integration during film formation and its modification by leaching
- Role of ZDC and its fragments functioning as antioxidants
- Role of naturally occurring antioxidants\(^{34,35}\).

Major naturally occurring antioxidants in natural latex are tocotrienols\(^{36}\), tocopherols\(^{37}\), betaines, amino and phenolic compounds\(^{38}\).

Ageing of prevulcanized latex films is accompanied by a reduction in crosslink density (except those which were highly under-cured). However, leaching or its duration have practically no effect on crosslink density\(^{33}\). Longer leaching effectively removes the non-rubber materials facilitating better inter-particle integration\(^{8}\). However, residual ZDC/its fragments and the naturally occurring antioxidants are removed by long leaching. Thus it is observed that for maximum retention of modulus of LPL films after ageing, duration of leaching has to be restricted to less than half an hour. However, even the 2h leached film, after ageing shows higher modulus than the unleached one, which still retains all the naturally occurring or added antioxidants. This observation suggests that effective inter-particle fasion makes lower contribution to the modulus of aged films.
Maximum tensile strength for leached films is observed when films are leached for 1h (Figure 5A.24). However, long leaching reduces aged tensile strength as seen from Figure 5A.27. It is observed that for achieving maximum tensile strength for aged films, optimum leaching period is half an hour. As in the case of aged modulus, the reduction in aged tensile strength of leached films is attributed to removal of added (dithiocarbamate residues) and naturally occurring antioxidants, thus promoting degradation. Tensile strength of aged films, which were initially leached for short intervals were higher than that of unleached film, while the 2h leached film is only marginally higher than that of unleached film. This suggests that tensile strength of aged latex film depend on the presence of antioxidants more than that in the case of modulus.

From Figure 5A.28 it is observed that short leaching improves elongation at break; lowest elongation at break after ageing is observed when latex was prevulcanized for about 2.5h and films previously leached for 2h. However, for films prepared from latex cured beyond optimum, unleached films had the lowest elongation at break.

**Extractable protein content in prevulcanized latex films**

Extractable protein content of SCL, DCL and LPL films of different states of vulcanization, both before and after leaching for 5min in static water, at film to water ratio of 1:400 are given in Figure 5A.29. Even though a definite trend cannot be observed for the EP content, the following general conclusion can be made.

- EP content in unleached latex films in the order
  
  **SCL > DCL > LPL**

- EP content in the three types of unleached latex films increase with the duration of prevulcanization.

- The same order is seen in the above films after leaching for 5min.

- Leaching for a short period of 5min is accompanied by a drastic fall in EP content.
Processing of DCL and LPL from SCL is accompanied by dilution of latex, followed by centrifugal concentration. Generation of second stage of skim latex in the process, facilitates removal of proteins. Thus DCL and LPL are lower in EP. Use of PPG in LPL processing facilitates protein displacement from rubber-serum interface, so that LPL had least EP content. For prevulcanization, latices are heated at 60°C for various intervals. During this heating process some of the strongly observed proteins are degraded and made water soluble, so that unleached films show increased – EP and EP content increases with duration of prevulcanization\(^{39}\).

EP content increases with increase in duration of prevulcanization. It is believed that, during prolonged heating, some of the strongly adsorbed proteins are degraded and made water extractable. During the short period of leaching (as in online leaching) they are removed. Thus all the three types of leached films show low EP contents in comparison with their unleached counterparts. The residual EP contents in LPL films leached for even 5 minutes are generally very low, in the range of 30–60mg/kg. This is lower than the EP content reported for LOPROL. Thus Figure 5A.29 clearly indicates the superiority of LPL, over SCL and DCL with respect to residual extractable protein content in leached film.

The effect of duration of leaching on residual EP content in LPL films is shown in Figure 5A.30. As seen from Figure 5A.29, even very short leaching is enough to reduce EP in LPL films to low levels. From Figure 5A.30 it is seen that prolonged leaching reduces residual EP still further. It is believed that during the prolonged leaching the degraded proteins in the interior layers of the films migrate to the surface and are removed. However, the reduction brought in by further leaching is only marginal. This is because the degradation that has occurred to proteins in LPL film is sufficiently high so that they are easily removed even by a short leaching period, so that very little is retained.
CONCLUSIONS

Following conclusions are derived from the above study:

- LPL, like SCL can be compounded and post-vulcanized in the conventional sulphur cure system. The physical properties of LPL films are slightly lower than that of SCL films; however, they are sufficiently high to meet the specifications of common dipped latex articles. The ageing behaviour of post-vulcanized LPL films are good.

- In post-cured LPL films, this modulus of LPL films can be improved by replacing a portion of dithiocarbamate accelerator by thiazole and the physical properties are optimum when ZDC/ZMBT ratio is 75:25. Physical properties of films after ageing are satisfactory.

- LPL can be sulphur prevulcanized to a reasonably high degree of crosslinking by using conventional cure system. However, rate and state of prevulcanization are less compared to SCL. The highest crosslink density is achieved in 3h of prevulcanization at 60°C. Reasonably good tensile properties are exhibited by prevulcanized LPL films, even though little lower than that of SCL. The highest tensile strength is achieved after 2.5h of prevulcanization. However, modulus continuously increases with time of prevulcanization. Ageing behaviour of LPL films are reasonably good and comparable to those of SCL films.

- The physical properties of LPL films are influenced by leaching. For maximum physical properties, leaching for a minimum period of 1h is essential. However, for achieving best combination of physical properties after ageing leaching has to be limited to less than half an hour.

- During the course of prevulcanization, more of proteins are becoming soluble and can be removed by leaching. LPL films leached for even 5min show EP content in the range of 30–60mg/kg only. Prolonged leaching still reduces residual EP, but the decrease is only marginal.
REFERENCES


### TABLE 5A.1
Formulation of latex compound for post- and prevulcanization in conventional cure system

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
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<tbody>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>60% Natural latex</td>
<td>100</td>
</tr>
<tr>
<td>10% Potassium hydroxide</td>
<td>0.1</td>
</tr>
<tr>
<td>50% Sulphur</td>
<td>1.75</td>
</tr>
<tr>
<td>50% Zinc diethyldithiocarbamate</td>
<td>1.0</td>
</tr>
<tr>
<td>50% Zinc oxide</td>
<td>0.25</td>
</tr>
</tbody>
</table>

### TABLE 5A.2
Formulation of latex compound for post-vulcanization in conventional cure system using accelerator combinations

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>60% Natural latex</td>
<td>100</td>
</tr>
<tr>
<td>10% Potassium hydroxide</td>
<td>0.1</td>
</tr>
<tr>
<td>50% Sulphur</td>
<td>1.75</td>
</tr>
<tr>
<td>50% Accelerators (ZDC + ZMBT)</td>
<td>1.0</td>
</tr>
<tr>
<td>50% Zinc oxide</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Fig 5A.1. Effect of duration of post-cure in conventional system at 100°C on crosslink density of latex films and the effect of heat ageing
Fig 5A.2. Effect of duration of post-cure in conventional system at 100°C on modulus of latex films and the effect of heat ageing.
Fig 5A.3. Effect of duration of post-cure in conventional system at 100°C on tensile strength of latex films and the effect of heat ageing.
Fig 5A.4. Effect of duration of post-cure in conventional system at 100°C on elongation at break of latex films and the effect of heat ageing
Fig 5A.5. Effect of accelerator combination on modulus of LPL films vulcanized for various intervals
Fig 5A.6. Effect of accelerator combination on tensile strength of LPL films vulcanized for various intervals
Fig 5A.7. Effect of accelerator combination on elongation at break of LPL films vulcanized for various intervals.
Fig 5A.8. Effect of accelerator combination on aged modulus of vulcanized LPL films
Fig 5A.9. Effect of accelerator combination on aged tensile strength of vulcanized LPL films
Fig 5A.10. Effect of accelerator combination on elongation at break of vulcanized LPL films after ageing
Fig 5A.11. Effect of duration of post-cure on modulus of LPL films using different accelerator combinations.
Fig 5A.12. Effect of duration of post-cure on tensile strength of LPL films using different accelerator combinations.
Fig 5A.13. Effect of duration of post-cure on elongation at break of LPL films using different accelerator combinations.
Fig 5A.14. Effect of duration of prevulcanization on crosslink formation in latex films.
Fig 5A.15. Effect of duration of prevulcanization on modulus of latex films.
Fig 5A.16. Effect of duration of prevulcanization on tensile strength of latex films.
Fig 5A.17. Effect of duration of prevulcanization on elongation at break of latex films.
Fig 5A.18. Effect of heat ageing on crosslink density of prevulcanized latex films.
Fig 5A.19. Effect of heat ageing on modulus of prevulcanized latex films.
Fig 5A.20. Effect of heat ageing on tensile strength of prevulcanized latex films.
Fig 5A.21. Effect of heat aging on elongation at break of prevulcanized latex films.
Fig 5A.22. Effect of leaching on crosslink density in LPL films.
Fig 5A.23. Effect of leaching on modulus of LPL films.
**Fig 5A.24.** Effect of leaching on tensile strength of LPL films.
Fig 5A.25. Effect of leaching on elongation at break of LPL films.
Fig S5A.26. Effect of leaching on modulus of LPL films after ageing.
Fig 5A.27. Effect of leaching on tensile strength of LPL films after ageing.
Fig 5A.28. Effect of leaching on elongation at break of LPL films after ageing.
Fig 5A.29. Effect of heating time and leaching on EP content in prevulcanized latex films.
Fig 5A.30. Effect of leaching on residual EP content in LPL films.
CHAPTER 5B

VULCANIZATION OF LOW PROTEIN LATEX IN EV CURE SYSTEM
Natural rubber being an olefinic polymer is generally susceptible to rapid ageing and oxidation. The situation becomes all the more acute if the rubber articles have to function at relatively higher temperature or have to undergo any type of repeated heat treatment at elevated temperatures. The situation is further aggravated, if the article has high surface area to volume ratio. For example, surgical gloves, a natural rubber product has to undergo repeated sterilization at about 120°C. To retain high mechanical properties after each heat treatment the inherently poor oxidation resistance of natural rubber has to be improved.

Chemical antidegradants are widely used to confer ageing and oxidation resistance to rubber products. A second approach involves modifying the cure system. It is generally accepted that EV (efficient vulcanization) cure system, employing a higher proportion of accelerator and low level of sulphur is useful in such situations. The ratio of any given accelerator to sulphur largely determines the type of sulphur crosslinks formed and also the amount of sulphur which combines with the rubber in non-crosslink structures such as cyclic sulphides. In EV system the crosslinks are mainly monosulphidic along with some disulphidic ones which have higher thermal stability than polysulphidic crosslinks and main chain modifications, common to conventionally sulphur cured vulcanizates. Monosulphidic crosslinks are more stable to heat than polysulphidic crosslinks, because the energy to rupture the C-S bond is higher than that of the S-S bond. In EV cured vulcanizates high concentration of accelerator residues are available which function as antioxidants probably by deactivating the hydroperoxides and behave synergistically with added antioxidants of the phenolic or amine type. Since LPL can find application in products like surgical gloves, which requires high heat resistance, curing of LPL in EV system seems worth studying. However, curing of NR latex in EV system has not been much extensively studied. Peethambaran and George have studied the prevulcanization of NR latex in EV system and the application of this prevulcanized latex in elastic thread production. This chapter reports the results of studies on pre- and post-vulcanization of LPL in...
EV system, properties of the films obtained from it and their behaviour on accelerated ageing. The results are compared with SCL and DCL.

**EXPERIMENTAL**

LPL was processed out of centrifuged latex by following the method described in Chapter 4. For post – and prevulcanization in EV system, latex compounding was carried out as per the formulation given in Table 5B.1. For post-vulcanization studies in EV system, the compounded latices were matured for 24h, cast films were prepared on leveled glass plates and vulcanized at 100°C for predetermined duration. Dried films were leached in water for 60 minutes at room temperature and dried in air.

For prevulcanization studies also compounded latices were matured for 24h. For effecting prevulcanization, latex compounds were heated on water bath at 60°C for predetermined intervals. For determining the effect of extent of cure on physical properties, samples were withdrawn at definite intervals and cooled immediately to arrest any further crosslinking. Films were prepared by casting and dried in air. The air dried films were leached in water for 1h and dried at room temperature.

The state of cure of the latex films was assessed by determining crosslink density by solvent swelling method using Flory-Rhener equation. Physical properties of the films were determined by as per Indian Standard procedures. Ageing of latex films was carried out by heating at 70°C for 7 days.

**RESULTS AND DISCUSSIONS**

**Effect of duration of post-vulcanization in EV system and accelerated heat ageing on crosslink density of latex films**

Figure 5B.1 shows the variation of crosslink density of SCL, DCL and LPL films with duration of post-vulcanization in EV system. The data indicate that for the three types of latex films crosslink density increases with duration of post-vulcanization. DCL and LPL films are slow curing than SCL films, as seen from
Figure 5B.1. It has been postulated that sulphur\textsuperscript{(11)} and sulphur accelerator complex\textsuperscript{(12)} are able to dissolve in the aqueous phase of latex with the assistance of some of the non-rubber substances present in latex, forming some loose complex having some surface activity and get adsorbed at the rubber-serum interface. After adsorption, the hydrophilic component is somehow lost and the hydrophobic species containing sulphur-accelerator complex migrates into rubber and form crosslinks on heating. In DCL and LPL, due to the second stage of centrifugal concentration and also by displacement by PPG to some extent in the case of LPL, the level of active non-rubber substances are low, ultimately leading to a net reduction in crosslink density.

Figure 5B.1 also shows the variation in crosslink density after ageing of the films at 70°C for 7 days. On ageing there is an overall increase in crosslink density. This is partly due to absence of poly sulphide crosslinks, which on rupture give main modifications and the additional crosslink formation during ageing, utilizing the residual curatives in the film. Due to the high thermal stability of the predominantly mono- and disulphidic crosslinks in the films cured by EV system, crosslink rupture is minimum. The high concentration of accelerator residues also function as antioxidants. Films that were initially under-cured showed the highest crosslink density after ageing. This shows that crosslink formation is a predominant reaction during the accelerated ageing process. However, the films which were initially Vulcanized beyond the optimum, on ageing, show a reduction in crosslink density. However, the crosslink density of all the aged films were higher than those of the unaged ones. This is again due to high thermal stability of mono and disulphidic crosslinks, which resists rupture.

**Effect of duration of post-vulcanization in EV system and accelerated heat ageing on tensile properties of latex films**

The variation of modulus of latex films with duration of post-vulcanization in EV system is given in Figure 5B.2. It is observed that modulus of all the latex films increases with duration of post-vulcanization and DCL and LPL films show lower modulus than SCL films for a given period of vulcanization. This is probably due
to the lower rate of cure in DCL and LPL film, as observed from crosslink density data. Even though crosslink density data are almost similar for DCL and LPL, modulus of LPL film is slightly higher than DCL films. This is attributed to the attractive forces originating from PPG molecules on the surface of rubber particles.

The data on the variation of modulus of aged films also is given in Figure 5B.2. It is observed that ageing of the three types of under-cured films result in increase of modulus and the aged modulus decrease as the duration of post-vulcanization increases. The fall in aged modulus along with duration of post-vulcanization is partly in agreement with crosslink density of the aged films. Even though crosslink density value is highest on ageing in LPL film post-vulcanized for 1h, a maximum is not observed in the modulus curve. This observation suggests that factors other than crosslink density are involved in determining the modulus of LPL film. It is suggested that as the latex particles become more crosslinked they became harder and the inter particle fusion became less effective.

Figure 5B.3 shows the variation of tensile strength with duration of post-vulcanization in EV system. Tensile strength increases with increase in duration of vulcanization, reaches a maximum and then decreases. Both SCL and LPL films show almost the same maximum tensile strength. However, the time required to achieve the maximum tensile strength is slightly more for LPL films. This is due to the lower rate of cure of LPL films. Tensile strength of DCL film is the lowest for any duration of post-vulcanization. This is mainly due to the lower crosslink density in DCL films. The maximum tensile strengths of the three types of films in EV system are lower than those of films cured in conventional system (when compared with Figure 5A.3). This observed reduction in tensile strength in EV system is attributed to the lower crosslink density in the EV cured films and reduced flexibility of mono- or disulphidic crosslinks when compared to polysulphidic crosslinks.

The variation of tensile strength of aged films also is presented in Figure 5B.3. The three types of films, initially under-cured, show high increase in tensile
strength after ageing. This is primarily due to increase in crosslink density on heating. However, DCL and LPL films vulcanized beyond optimum are accompanied by reduction in tensile strength on accelerated ageing. This may be due to the thermal degradation occurring in the molecular networks. However, with SCL films tensile strength increases after ageing. A probable factor contributing to higher tensile strength is increased crosslink density.

The effect of post-vulcanization time on elongation at break of latex films cured in EV system both before and after ageing is shown in Figure 5B.4. It is seen that elongation at break of the three types of films is maximum at the optimum cure time and then decrease with increase in cure time. This reduction in ultimate elongation is due to increase in crosslink density and modulus of the film. On accelerated ageing, all the three types of films show decrease in ultimate elongation for increase in cure time.

**Effect of duration of prevulcanization in EV system on crosslink density of latex films.**

The variation of crosslink density in SCL, DCL and LPL films with respect to duration of prevulcanization at 60°C in EV system is shown in Figure 5B.5. Crosslink density of rubber particles in three types of latices prevulcanized in EV system increased from a low initial value along with duration of prevulcanization. For a given duration of prevulcanization, SCL films showed higher rate of cure than DCL and LPL. From the slope of the cure curve for SCL it is seen that rate of vulcanization is high initially and reduces with duration of prevulcanization. However, the slopes of the cure curves for DCL and LPL increase continuously with duration of prevulcanization and achieve a high state of cure on continued heating. Thus there is marked difference in the prevulcanization characteristics of SCL, DCL and LPL in EV system.

The basic mechanism of sulphur prevulcanization of NR latex suggests that sulphur and accelerator can independently dissolve in the aqueous phase of latex with the assistance of some hydrophilic serum constituents, leading to the formation of some loose complex, having some surface activity. They get
adsorbed at the rubber serum interface\textsuperscript{(11,12)}. However, after adsorption, the hydrophilic component of the adsorbed species is somehow lost and it becomes hydrophobic. The hydrophobic species migrates to the interior of rubber hydrocarbon particles and form crosslinks. The hydrophilic component returned to the aqueous phase form new complexes and facilitates further transfer of curatives into rubber particles in latex. However, in latex serum the solubility of accelerator is much less, compared to that of sulphur and thus the rate of transfer of accelerator is much lower compared to that of sulphur\textsuperscript{(11)}. In EV cure systems the proportion of accelerator in the aqueous phase is very high compared to sulphur. However, the availability of curatives within the latex particles is limited, leading to the formation of mono and disulphidic crosslinks in the film with the assistance of available accelerator and sulphur.

It is also observed that for any given duration of prevulcanization state of cure in SCL film is much higher than in DCL and LPL films. The rate of entry of curatives into latex particles is determined by the concentration of the non-rubber substances which form surface-active loose complexes with sulphur and accelerator. In processing of DCL and LPL from SCL, portion of the dissolved non-rubber serum constituents and surface active substances, including proteins at the rubber-serum interface are removed. In SCL, the components that facilitate the entry of curatives into the latex particles are higher, while in DCL and LPL, their availability is much reduced. This accounts for the lower crosslink density in DCL and LPL films, compared to SCL films when prevulcanized in EV system. The crosslink density in LPL films are slightly higher that DCL. It is believed that proteins have some influences on the transfer of curatives in aqueous phase to rubber particles in latex. In LPL, even though protein content is slightly lower, crosslink density is higher than in latex particles of DCL. This observation suggests that adsorbed PPG assists the curatives in entering the latex particles in LPL.
Effect of duration of prevulcanization in EV system on tensile properties of latex films

Figure 5B.6. shows the variation of modulus of latex films against duration of heating for prevulcanization in EV system. For a given period of heating, modulus of films are in the order

\[ \text{SCL} > \text{LPL} > \text{DCL} \]

This is an agreement with the crosslink density data. It can be noted that in EV system, modulus of three types latex films increase with cure time. But the rate of increase in modulus reduces with cure time. However, the observed rate of crosslink formation in DCL and LPL particles and rate of increase in modulus of these films are not in agreement. Further, LPL films have slightly higher modulus than DCL films even though their crosslink densities are more or less comparable. Thus it can be seen that variation in crosslink density alone cannot fully explain the variation in modulus of latex films. In about 5h of heating, the three types of films do not show any signs of reversion. This is attributed to the high thermal stability of monosulphidic workslinks formed during EV cure. During film formation, modulus of the films are determined both by crosslink density and the extent of inter-particle integration\(^{(13)}\). In the case of leached SCL film, the inter-particle attractive forces are stronger due to the availability of more residual proteins on particle surface. It has been reported that proteins and aminoacids like 3-aminopropionic acid, generated from degraded proteins accelerate crosslink formation\(^{(14)}\). These factors contribute to the higher modulus of SCL films. Higher modulus of LPL films compared to DCL films may be partly due to slightly higher crosslink density and partly due to forces of attraction via Hydrogen bonding generated from adsorbed PPG molecules on the surface of LPL particles.

The variation of tensile strength with respect to duration of heating is given in Figure 5B.7. SCL, DCL and LPL films vulcanized in EV system show increase in tensile strength with duration of heating; however, the rate of increase in tensile strength decreases with increase in duration of vulcanization. The three types of
film attain maximum tensile strength in about 5h at 60°C. Tensile strength follow
the order

\[ \text{SCL > LPL > DCL} \]

as in the case of modulus. The increasing tensile strength with time of heating of
the three latex films in EV system is almost in line with their crosslink density. The
tensile strength of EV cured latex films is generally low. This is probably due to
the low flexibility of the mono- and disulphidic crosslinks in the EV system. Even
though crosslink densities of DCL and LPL films are more or less similar, the
tensile strength of LPL films are slightly higher than those of DCL films. As in the
case of modulus, this is attributed to higher forces of attraction between latex
particles in LPL film via Hydrogen bonding due to PPG molecules adsorbed on
rubber particles.

Data on elongation at break of vulcanized latex films can be seen from Figure
5B.8. The elongation at break of the three types of latex films is in the order

\[ \text{SCL > LPL > DCL} \]

Further, ultimate elongation decreases with increase in duration of
prevulcanization.

**Effect of accelerated heat ageing on crosslink density of prevulcanized
latex films in EV system**

The effect of accelerated heat ageing at 70°C for 7 days on crosslink density of
latex films prevulcanized in EV system for different duration is given in Figure
5B.9. For comparison, crosslink density data of the films before ageing are also
provided in the figure. In the case of SCL films, as stated earlier crosslink
formation before ageing initially increase rapidly with duration of heating.
Beyond 3h rate of crosslink formation is somewhat low and reaches about
2.5x10^{19} per gram in 5h. However, after ageing the highest crosslink density is
exhibited by films prevulcanized for half an hour. The lower the initial state of
cure the higher the crosslink density in the aged film. The crosslink density of the
film, prevulcanized for 3h remained almost constant. Beyond 3h of
prevulcanization, the crosslink density of films after ageing was lower than that
before ageing and the difference increased as duration of prevulcanization increased.

Accelerated ageing of DCL films prevulcanized for various duration are accompanied by increase in crosslink density. The crosslink density of LPL films before ageing increases with time of heating. However, the crosslink densities of these films after ageing remain more or less constant at about $2.05 \times 10^{19}$ per gram. This observation suggests that even in the under-cured films, curatives were available in sufficient quantity to generate additional crosslink during the accelerated ageing process, irrespective of the initial duration of prevulcanization. However, even the lowest crosslink density in SCL films after ageing is higher than the maximum of heat aged LPL films. The observed increase in crosslink density of various latex films after accelerated ageing clearly indicates that more crosslinks are formed during the ageing process utilizing residual curatives and not due to crosslink modification as the crosslinks in EV system are of high thermal stability. High thermal stability is attributed to the high proportions of mono- and disulphidic crosslinks and low proportion of polysulphidic ones in the EV films, as against high proportion of polysulphidic crosslinks in the conventional cure system.

The above data on crosslink density clearly indicates that films prepared from latex heated for only half an hour give the highest state of cure after ageing. This shows that sufficient quantity of curatives have entered the latex particles during maturation period. The rate of entry of accelerator particles into latex particles is slower than that of sulphur\textsuperscript{(11)}. Thus during prevulcanization more and more crosslinks are formed with the available accelerator as prevulcanization progresses. The data on crosslink density indicates that the reduction in protein content in DCL and LPL reduce the quantity of curatives that enter the latex particles. Thus DCL and LPL has lower crosslink density than SCL, both before and after ageing and at all durations of prevulcanization. The reduction in crosslink density in aged SCL films prepared from latices prevulcanized for longer durations indicates some breakage of existing crosslinks. Considering the high
thermal stability of mono- and disulphidic crosslinks, the crosslinks that break may probably be some physically effective crosslinks formed due to the poor fusion of highly crosslinked latex particles.

Aged LPL film has somewhat higher crosslink density than DCL films. This is attributed to the entry of more curatives to latex particles in LPL during maturation of latex compound and during its heating period.

**Effect of accelerated heat ageing on tensile properties of latex films prevulcanized in EV system**

Heat ageing has profound influence on modulus, tensile strength and ultimate elongation of latex films cured by EV system. The effect of accelerated heat ageing on modulus of SCL, DCL and LPL films is provided in Figure 5B.10. Modulus of aged films of the three latex types increases after ageing. The aged modulus increases with duration of prevulcanization, show a maximum at about 3h of prevulcanization and gradually decreases for all the three types. Also at all durations of prevulcanization, SCL films have higher modulus compared to DCL and LPL films, both before and after ageing. The higher modulus of SCL film is attributed to the higher state of cure and better interparticle attraction through Hydrogen bonding and van der Waals forces due to the presence of higher levels of proteins on their surface than in DCL and LPL films.

Films prepared from DCL and LPL prevulcanized for short intervals, after ageing show considerable increase in modulus and a maximum is observed for films prepared from latex prevulcanized for about 2.5h. Increase in crosslink density on heat ageing makes substantial contribution to increase in aged modulus. Since crosslink density after ageing is more or less constant for LPL films prevulcanized for different durations, the increase in aged modulus from 0.5–2.5h of prevulcanization is attributed to better interparticle integration and molecular chain entanglements. However, the decrease in aged modulus of three latex types beyond 2.5h of prevulcanization is probably due to less effective fusion of particles which were initially crosslinked to a high state of cure\textsuperscript{13}. The aged modulus of DCL and LPL films is lower than those of SCL films. Low crosslink
density in aged LPL films is a major contributing factor. Even though crosslink densities of DCL and LPL films, both before and after accelerated ageing are more or less similar, slightly higher modulus exhibited by LPL films after ageing. This is attributed to force of attraction due to Hydrogen bonding in LPL films due to PPG molecules.

Data on variation of tensile strength of prevulcanized latex film before and after ageing with respect to duration of prevulcanization is provided in Figure 5B.11. Irrespective of the time of prevulcanization, tensile strength of aged LPL films remains more or less constant at a high value of approximately 36MPa. Increase in crosslink density in the aged films and the thermal stability of predominantly mono- and disulphidic crosslinks in latex particles prevulcanized by EV system primarily contribute to high tensile strength after ageing of LPL films. Further because of the low level of non-rubber solids content, fusion between the particles during film formation would be better. This also contributes to increase in tensile strength. Tensile strength of SCL and DCL films also increases on ageing and the maximum value is reached for those films which were initially prevulcanized for a minimum of 2.5h. However, this maximum tensile strength of SCL film is lower than that of aged LPL films. This is probably due to the less effective fusion of crosslinked latex particles due to the presence of non-rubber substances adsorbed on latex particles. DCL films, which had lower tensile strength on accelerated ageing showed tensile strength similar to SCL films, even though crosslink density in aged DCL films were lower than those in SCL. This also in attributed to better particle fusion, due to lower non-rubber substances with DCL films.

At all duration of prevulcanization elongation at break decreases after ageing for the three types of latex films as shown in Figure 5B.12. Elongation at break after ageing is lower in SCL films than in LPL films and DCL film show the lowest values. This behaviour of SCL film is partly due to higher modulus of aged SCL films. Higher crosslink density and increased modulus of LPL films on ageing contribute to higher ultimate elongation. High elongation indicates that the molecular chains have become more flexible on ageing. van der Waals forces of
attraction between adsorbed PPG and residual proteins on rubber particle surface also contribute to the high ultimate elongation in the LPL films.

**CONCLUSIONS**

Following conclusions are derived from the above study:

- LPL films can be post-vulcanized in EV system. It is slightly slow curing than SCL, but more or less comparable to DCL films. Accelerated ageing of LPL films is accompanied by increase in crosslink density.

- Physical properties of post-vulcanised LPL films are slightly lower than SCL films, however, it is sufficiently high to meet the specifications for common latex products. Post-cured LPL films in EV System show good retention of physical properties.

- LPL can be prevulcanized using sulphur and accelerator in EV system for a given duration of prevulcanization the state of cure is slightly lower than that of SCL films, but slightly above DCL films. The rate of cure is almost comparable for SCL and LPL films. Accelerated heat ageing of LPL films is accompanied by increase in crosslink density. Physical properties of prevulcanized LPL in EV system are good, even though slightly lower than SCL film. LPL films show good retention of physical properties on accelerated ageing.
REFERENCES


10. IS 3400 (part 4) 1987: Methods of Test for vulcanized rubbers- Accelerated ageing (second revision).


TABLE 5B. 1
Formation of Latex compound for post and prevulcanization in EV system

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>60% Natural latex</td>
<td>100</td>
<td>167</td>
</tr>
<tr>
<td>10% Potassium hydroxide</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>10% Potassium laurate</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>50% Sulphur</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>33% TMTD</td>
<td>3.0</td>
<td>9.0</td>
</tr>
<tr>
<td>10% Thiourea</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>50% Zinc oxide</td>
<td>0.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Fig 5B.1. Effect of duration of post-cure in EV system at 100°C on crosslink density of latex films and effect of heat ageing
Fig 5B.2. Effect of duration of post-cure in EV system at 100°C on modulus of latex films and effect of heat ageing.
Fig 5B.3. Effect of duration of post-cure in EV system at 100°C on tensile strength of latex films and effect of heat ageing.
Fig 5B.4. Effect of duration of post-cure in EV system at 100°C on elongation at break of latex films and effect of heat ageing.
Fig 5B.5. Effect of heating time on crosslink density of prevulcanized latex films in EV system.
Fig 5B.6. Effect of heating time on modulus of prevulcanized latex films in EV system.
Fig 5B.7. Effect of heating time on tensile strength of prevulcanized latex films in EV system.
Fig 5B.8. Effect of heating time on elongation at break of prevulcanized latex films in EV system.
Fig 5B.9. Effect of accelerated heat ageing on crosslink density of latex films in EV system
Fig 5B.10. Effect of accelerated heat ageing on modulus of latex films in EV system.
Fig 5B.11. Effect of accelerated heat ageing on tensile strength of latex films in EV system.
Fig 5B.12. Effect of accelerated heat ageing on elongation at break of latex films in EV system.
CHAPTER 5C

RADIATION PREVULCANIZATION OF LOW PROTEIN LATEX
Natural rubber in dry form or as latex is usually vulcanized by sulphur and accelerators. Crosslinking can be brought about by organic peroxides or high energy radiations also. Radiation vulcanization is the process of crosslinking rubbery molecules in latex using high energy radiation\(^1\), either gamma rays or electron beams. However, the dose requirement is high, about 250–300kGy\(^2\). Hence the process is carried out in the presence of a sensitizer to reduce the dose required to impart adequate level of prevulcanization. n-Butylacrylate (nBA) is commonly used as sensitizer and the dose requirement is only about 15kGy\(^3\). Radiation vulcanization process does not involve the use of organic accelerators that can liberate carcinogenic nitrosamines and nitrosatable amines, whereas in conventional sulphur vulcanization organic accelerators are used. During irradiation of latex, proteins are partly degraded and can be removed by leaching\(^4,5\). Thus radiation vulcanization provides clean products, free from type IV allergic reactions\(^6\) originating from added chemicals. Varghese et al.\(^7\) have reported that addition of water soluble polymers like polyvinylalcohol and polyethylene oxide to radiation vulcanized latex, makes protein removal from latex films more fast by leaching.

It has been proved that extractable proteins in latex products can cause immediate type I allergies in sensitized people\(^8-10\). Low protein latex (LPL) is a form of natural rubber latex which shows very low levels of extractable proteins in leached films\(^11\). Irradiation of a latex, inherently low in extractable proteins is likely to provide latex products still lower in extractable proteins. Hence it is believed that radiation crosslinking of LPL will provide vulcanized films free from type IV allergic reactions arising from rubber chemicals, carcinogenic nitrosamines and nitrosatable originating from residues of dithiocarbamate and thiuram based accelerators and very low in extractable proteins.

However, it is observed that radiation vulcanized natural rubber latex films generally are low in modulus. Even though low modulus is an advantage in products like examination gloves, it is a disadvantage in the case of articles like latex tubing, catheters, feeding bottle nipples, soothers etc. where increased
modulus is desirable. In such situations radiation vulcanized latex films require reinforcement. Further the extent of crosslinking brought about in rubber molecules depends on how effectively high energy radiations are utilized. To some extent this is influenced by the rubber content in the latex being irradiation and the dose rate if irradiation. This chapter reports the effect of dose and dose rate of gamma radiation, rubber content in irradiated latex, the effect of leaching and post-drying of leached films on crosslink density, physical properties, extractable protein content of the films and reinforcement of radiation vulcanized LPL films using silica.

**EXPERIMENTAL**

Low protein latex was produced by the method described in chapter-4\(^{[11]}\). Gamma irradiation was carried out using Gamma Chamber 5000, developed by the Board of Radiation and Isotope Technology (BRIT), (Department of Atomic Energy, Government of India), Mumbai, which is loaded with Cobalt-60. Latex compound used for irradiation is prepared according to the formulation given in Table 5C.1 and allowed to mature for 6h before irradiation. Irradiation at different doses is achieved by varying the duration of exposure and dose rate is varied by the use of attenuators. Cast films were prepared on levelled glass plates\(^{[12]}\) and dried in air at room temperature until the films became transparent. Dry films were leached in distilled water for predetermined periods. Crosslink density of vulcanized films were measured using solvent swelling method\(^{[13]}\) following Flory-Rhener equation\(^{[14]}\). Tensile properties were evaluated on a Hounsfield Universal Testing machine using ASTM test methods. Extractable proteins in latex films were estimated by the RRIM modified Lowry method\(^{[15]}\).

Silica, used for improving the modulus, was prepared as 25% dispersion by ball milling. Silica dispersion was blended with radiation vulcanized LPL in various proportions and cast films were prepared for testing.
RESULTS AND DISCUSSION

Effect of dose of irradiation on crosslink density in vulcanized latex films

Radiation can interact with rubber in latex to form free radicals either by hydrogen abstraction or by chain scission\(^{(16)}\). Two such radicals can undergo addition reaction to form a crosslinked structure. Free radicals can also undergo transfer reaction and the newly formed radicals also can form crosslinked structure. The dose requirement for achieving adequate level of crosslinking reaction in the absence of sensitizers is about 300kGy\(^{(2)}\). By the use of acrylic monomers\(^{(3,17)}\) the dose requirement has been reduced to about 15kGy. By gamma ray irradiation acrylic monomers undergo hydrogen abstraction leading to the formation of \(^{1}\text{CH}=\text{CH—COOR}\) free radicals\(^{(18,19)}\). As this acrylic free radical is more mobile than the rubber chain, it attacks a double bond in an adjacent chain, forming a rubber free radical. The newly formed free radicals form crosslinked structures.

When an aqueous emulsion of nBA is irradiated, radicals like \(^{\cdot}\text{OH},\text{ H}\) and hydrated electrons \(\text{e}^{-}_{\text{hv}}\) are generated by the radiolysis of water\(^{(20)}\). The radiation polymerization of nBA in an aqueous matrix involves only hydrated electrons, \(\text{e}^{-}_{\text{hv}}\)\(^{(21)}\) and the reactions can be represented as

\[
\text{nBA} + \text{e}^{-}_{\text{hv}} \rightarrow \text{nBA}^{-}\cdot \\
\text{nBA}^{-}\cdot + \text{nBA} \rightarrow (\text{nBA})_{2}^{-}\cdot
\]

The mechanism of sensitization by nBA is via the transient produced by the reaction of \(\text{e}^{-}_{\text{hv}}\) with nBA, capable of propagating the radical reaction with the monomer at high rates leading to polymerization/ vulcanization. The solubility of nBA in natural rubber is high\(^{(17)}\) and nBA\(^{-}\cdot\) radicals formed in the rubber phase alone contribute to crosslinking reaction\(^{(21)}\).

Figure 5C.1 shows the effect dose of irradiation on the number of crosslinks formed per gm of dry film of LPL. The behaviour of the single centrifuged latex
(SCL) from which LPL was prepared also is given for reference. Data is also presented in respect of the double centrifuged latex (DCL) processed out of this SCL, since LPL processing involves a second stage of latex concentration by centrifuging. Data presented in Figure 5C.1 indicate that for the three types of latices, crosslink density increases with dose. However, the rate of increase in crosslink density decreases with increase in dose. As the dose of irradiation increases, the concentration of $e_{\gamma}^*$ within the rubber particles increase thus more nBA** radicals are formed resulting in the formation of more number of crosslinks. The decrease in the rate of formation of crosslinks at higher doses may probably be due to the decreasing concentration of free nBA available within the latex particles. Further, it is likely that simultaneous to crosslink formation, some extent of crosslink rupture also may occur, contributing to the reduction in the overall rate of crosslink formation.

It is also observed from Figure 5C.1 that at low doses of irradiation crosslink density in LPL films is intermediate between DCL and SCL films. However, at higher doses of irradiation, LPL films exhibit crosslink densities comparable to SCL films. The low crosslink density in DCL may probably be due to the lower availability of nBA within latex particles. Availability of adsorbed proteins at the rubber-serum interface is more in SCL compared to DCL or LPL. Proteins are likely to form weak hydrogen bonds with the oxygen atoms of nBA, thus facilitating the entry of nBA into rubber particles and then move into the rubber phase, because of its solubility in rubber phase. Among the three types of lattices, protein content in highest in SCL, permitting the entry of more nBA in DCL, content of proteins is less, thus restricting the entry of nBA. In the case of LPL, the reduction of proteins is compensated by the presence of surface active polypropylene glycol (PPG), which also can form hydrogen bonds with nBA molecules. This explains the comparable crosslink density in SCL and LPL films.

**Effect of dose of irradiation on tensile properties of latex films**

Figure 5C.2 shows the variation of modulus of latex films at 500% elongation with dose of irradiation. It is seen that modulus of SCL and LPL are almost
similar at all doses of irradiation, while DCL film is lower in modulus. For the three latex films, modulus increases with dose. However, the rate of increase in modulus decreases with increasing dose.

The modulus of prevulcanized latex films is contributed mainly by two factors: degree of crosslinking within individual latex particles and the degree of interparticle coalescence of latex particles during drying and film formation\textsuperscript{(22)}. From Figures 5C.1 and 5C.2 it is seen that the pattern of variation in crosslinks and modulus with dose of irradiation is more or less similar. This suggests that the nature of interparticle coalescence during film formation is more or less similar with the three types of latices, which in turn, is attributed to the removal of non-rubber materials during leaching. Thus the major reason for variation of modulus with dose of irradiation between the three latices is the variation in crosslink density.

From Figure 5C.3 it can be seen that for the three types of films, tensile strength initially increases with dose, reaches a maximum and then decreases. The initial increase in tensile strength with dose of irradiation is attributed to progressive increase in crosslink formation. In the case of natural latex highest tensile strength is centred around dose of 15kGy\textsuperscript{(3)}. For DCL and LPL films also maximum tensile strength is observed at about 15kGy. Further increase in dose is accompanied by fall in tensile strength. It is believed that high modulus of highly crosslinked latex particles prevent their effective fusion to form a strong and coherent film\textsuperscript{(22)} during drying.

Tensile strength of latex films prepared from latices irradiated to 15kGy the optimum dose of irradiation, is in the order

\textbf{SCL > LPL > DCL}.

At 15kGy, eventhough SCL and LPL films have almost the same crosslink density, tensile strength is slightly higher for SCL film. This is attributed to the higher forces of attraction between latex particles in the film via Hydrogen bonding originating from absorbed proteins, which is highest in SCL film. DCL
films exhibits the least tensile strength. This is due to low crosslink density and low attractive forces via Hydrogen bonding, due to low protein content.

The variation of elongation at break with dose of irradiation is presented in Figure 5C.4. For the three types of films, ultimate elongation reduces with increase in dose of irradiation. For various doses of irradiation elongation at break is slightly lower for LPL films than SCL films and DCL films the lowest. As the dose irradiation increase, the crosslink density in crease. Crosslinking restricts the movement of molecular chains when a streaching force is applied. Further, the effectiveness of fusion of latex particles are reduced, when they become more hard due to increased crosslink density.

**Effect of dose of irradiation on extractable protein content in latex films**

Out of the total proteins present in a vulcanized natural latex film only a small portion of it is extractable. Figure 5C.5 shows the variation of residual extractable proteins (EP) in radiation vulcanized SCL, DCL and LPL films, both before and after leaching. It is seen that in the case of the three types of unleached films, EP content is in the order

\[
\text{SCL > DCL > LPL}
\]

This observation is in agreement with the initial EP content of the three latex types, before irradiation. Further EP content increases with radiation dose. Similar observations were made by other workers also. However, after leaching residual protein content in latex film is substantially reduced. It is believed that proteins in natural latex are decomposed by gamma irradiation, resulting in substantial reduction in molecular weight, making them water soluble. A comparison between EP content in SCL and LPL films before leaching indicates that during LPL processing, easily degradable and/or extractable proteins were effectively displaced. At low doses of irradiation, leached LPL films contain practically no EP and films prepared from LPL irradiated at higher doses contain very low levels of EP. Even radiation crosslinked SCL films after leaching have EP content in the range 30–60mg/kg. It is reported that EP content below
100mg/kg does not generally cause allergic reactions\(^\text{24}\). However, there is no line of demarcation between allergic and non-allergic levels of EP. Even very minute levels of EP may be sufficient enough to cause allergic reactions in highly sensitized persons. Thus vulcanized LPL films containing almost nil EP can be safely used by even highly sensitized people.

**Effect of dose rate of irradiation on crosslink density in latex films**

Results on the effect of dose rate on crosslink density of latex films are presented in Figure 5C.6. For the three types of latices, there is only very small increase in crosslink density when a given dose (here 15kGy) is delivered at higher dose rates. Practically, the dose delivered, and not the rate at which it is delivered determines the number of crosslinks formed. The number of hydrated electrons \(e^-_{hy}\) generated within latex particles during irradiation determine the number of crosslinks formed\(^\text{21}\) and it is believed that their number is controlled by the total energy supplied, and not by the rate at which it is delivered. In addition to crosslinking reactions, \(e^-_{hy}\) can undergo certain side reactions with some impurities\(^\text{21}\). At low dose rate of generation of \(e^-_{hy}\) is also low and hence the ratio of the concentration of impurity to \(e^-_{hy}\) is high. This ratio is low when high concentrations of \(e^-_{hy}\) are generated at higher dose rates, leading to lower proportion of side reactions ie, more crosslinks are formed. This explains the slightly higher crosslink formation at higher dose rates.

The slope of the DCL and LPL curves are almost similar, while the SCL curve is little more steep, suggesting that some other factors are also involved in crosslink formation. It is suggested that some non-rubber components in the aqueous phase of SCL, which are removed during the second centrifugal concentration for processing DCL and LPL have contributed to increased crosslink formation with increase in dose rate of irradiation.

**Effect of dose rate on tensile properties of latex films**

The variations of modulus, tensile strength and elongation at break of dry latex film with dose rate are given in Figures 5C.7, 5C.8 and 5C.9 respectively. Figure 5C.7 shows that for the three types of latices, modulus increases to some extent
with dose rate. This increase in modulus closely parallels the slight increase in crosslink density at higher dose rates. The tensile strength decrease by irradiation at higher dose rates, even though crosslink density has increased slightly. This fall in tensile strength is believed to be due to the less effective fusion of well crosslinked latex particles. From Figure 5C.9, it seems that increase in dose rate is accompanied by a reduction in ultimate elongation. This is partly due to increased crosslinking restricting the relative movement of molecular chains and partly due to increase in modulus. In short, on increasing the dose rate of irradiation, the modulus is slightly increased and elongation at break is reduced by increasing dose rate, while tensile strength shows appreciable fall.

**Effect of dose rate on residual extractable protein content in latex films**

The data on the effect of dose rate during irradiation of latex on residual extractable protein content in latex films are presented in Figure 5C.10. Only slight variations are observed in the total EP in the unleached films. Thus dose rate has practically no effect on EP content in vulcanized films. This is probably because the protein degradation is mainly controlled by the total dose and not by dose rate. The films were leached for 5 min. and it is found that residual EP in leached films remains more or less constant at very low values. This observation suggests that irrespective of the dose rate, the proteins are so highly degraded that they are easily leached off over short leaching periods.

**Effect of rubber content in irradiated latex on crosslink density of latex films**

It has been reported that it natural rubber latex irradiated in the absence of a sensitizer, the vulcanization rate increases with decreasing concentration of rubber in latex. However, Makkuchi has reported that in presence of an irradiation sensitizer the effect is not remarkable. The extent of crosslink formation, when latex particles are irradiated at 15kGy at varying dry rubber contents of latices is shown in Figure 5C.11. For the three types of latices crosslink density in the films increases gradually with increasing DRC of irradiated latex, reaches a maximum
at 50% and then decreases. This is in agreement with previous reports. SCL films exhibit highest crosslink densities. However, the crosslink densities observed in LPL films at various DRCs are almost comparable to SCL. While DCL films show lower values. However, the fall in crosslink density beyond the optimum DRC of 50% is slightly higher for LPL films. As stated earlier the nBA* radicals formed within the latex particles by the action of nBA and e^−_{hv} contribute to crosslinking reactions. In a latex of low DRC, the ratio of water within the rubber phase to those in the aqueous phase of latex is very low and hence the e^−_{hv} generated within latex particles are comparatively less and thus the extent of crosslink formation is less within the latex particles. In higher DRC latex the concentration of nBA in the aqueous phase is high, thus allowing more nBA to diffuse into the rubber particles. Also the relative proportion of water within the rubber particles is higher leading generation of larger of e^−_{hv}. This inter facilities the formation of more nBA* free radicals and hence increased number of crosslinks are formed. However, above 50% DRC, crosslink density is observed to be decreasing. In latex of any rubber content, compounded with nBA, the available free space with in latex particles, initially occupied by water are now partially occupied by nBA and its content increases with increase in DRC of latex, and the availability of water in latex particles decreases. This leads to decreasing concentration of e^−_{hv} formed by the radiolysis water in rubber particles. Thus DRC of latex above 50%, crosslink densities in their latex particles are lower. Thus the relative availability of nBA and water with in latex particles determine the crosslink densities, when exposed to given dose.

**Effect of rubber content in irradiated latex on tensile properties of latex films**

The tensile properties of radiation vulcanized latices are affected by the rubber content in the latex irradiated. The variations in modulus at 500% elongation, tensile strength and elongation at break against the rubber content of the latex being irradiated are given in Figures 5C.12, 5C.13 and 5C.14 respectively. From Figure 5C.12 it is seen that modulus of the films initially increases with increase in DRC of latex, maximum modulus is observed at 50% DRC and then decreases.
As stated earlier, modulus of latex films is depending on the degree of crosslinking within latex particles and their effective coalescence during film formation. A comparison with Figure 5C.11 and 5C.12 shows that below the optimum DRC of 50%, the rate of increase in modulus is higher than the rate of increase in crosslink density. For any given DRC, the general trend in variation of modulus is

\[ \text{SCL} > \text{LPL} > \text{DCL} \]

Even though crosslink densities of DCL and LPL films are almost comparable. Further, modulus of LPL films are not much below SCL films, even though crosslink densities are higher for the latter film. Thus it is evident that below 50% DRC, inter-particle integration during film formation has a more important role in determining the modulus, than that above 50% DRC.

Figure 5C.13 shows that the effect of tensile strength of films on DRC of irradiated latex. Even though tensile strength depends on DRC of irradiated latex, it is more dependent on DRC in the case of SCL. Maximum tensile strength is exhibited at 50% DRC for three types of laticies. In the case of LPL its irradiation below about 42% DRC shows tensile strength above that of SCL, but in all other situations tensile strengths of films prepared from irradiated lattices are again in the order

\[ \text{SCL} > \text{LPL} > \text{DCL} \]

The maximum tensile strength for 50% DRC of SCL films is slightly higher than that of LPL. This is partly contributed by increased crosslink density of SCL films and partly because of the contribution of proteins to tensile strength via van der Waals forces\(^{(1)}\) of attraction and H–bonding.

Data on elongation at break presented in Figure 5C.14 shows that decrease with increase in DRC of irradiated latex upto 50% DRC. For SCL and LPL films EB passes through a minimum, at 50% DRC while DCL films do not show a minimum. Elongation at break is slightly low for LPL films than SCL films. This is also attributed to the effect of proteins where the individual particles are held together by strong van der Waals forces and H–bonding.
Effect of leaching on tensile properties of radiation vulcanized latex films

Leaching is an important processing step in the production of dipped latex articles for improving physical properties. Figures 5C.15, 5C.16 and 5C.17 show respectively the variation of modulus, tensile strength and elongation at break of radiation vulcanized latex films, against duration of leaching in water at room temperature. It is observed that for the three types of latex films modulus tensile strength and elongation at break increase along with an increase in duration of leaching. The modulus of SCL and LPL films are comparable at all periods of leaching, even though the former has a slightly higher modulus and DCL films shows lower values. Tensile strength is higher for SCL films at all periods of leaching, again DCL films showing lower values. Values of elongation at break are not much different for SCL and LPL films. These improvements in physical properties on prolonged leaching are attributed to the removal of non-rubber materials from the films, thus facilitating better inter-particle integration. From Figure 5C.15 it can be seen that the improvement in modulus diminishes with increase in duration of leaching. This is because by initial leaching substantial portion of non-rubber materials are removed from the thin latex films and the quantity left behind for subsequent removal decreases and thus the rate of removal of non-rubber materials diminishes with longer leaching period. Thus it can be seen that even though there is improvement in modulus with increase in duration of leaching, the rate of improvement decreases. A similar behaviour is observed from Figure 5C.16 for tensile strength also. It can further be seen from Figure 5C.16 that the improvement in tensile strength of films on leaching initially is higher for SCL than LPL and least for DCL films. However, after long leaching as the difference in tensile strength between the SCL and LPL films decreases. It is believed that during irradiation of latices various non-rubber substances including proteins undergo degradation and the degraded products are removed by leaching. This degradation of non-rubber substances is believed to be highest in SCL, which contains the highest level of non-rubber materials. After removal of these components, the differences between the characteristics of SCL and LPL films became more narrow, leading to a lower difference in tensile strength.
between the two. For the three types of latex films, elongation at break slightly increases with duration of leaching. Increase in elongation is associated with increase in interparticle integration and homogeneity in the film\textsuperscript{(30)}. However, the increase in elongation is slightly lower for SCL films than LPL films.

**Effect of leaching on residual EP content in radiation vulcanized latex films**

Figure 5C.18 shows the effect of leaching on residual extractable protein content in radiation vulcanized SCL, DCL and LPL films leached for various intervals. The latices were vulcanized by irradiating to a dose of 15kGy at the rate of 1.333kGy/h. SCL film shows high EP content due to degradation of the proteins and residual EP is progressively reduced by continued leaching. A similar phenomenon is observed in DCL and LPL also. But the total EP content even in the unleached LPL film is very low compared to SCL film and in radiation vulcanized LPL films leached for one hour and above residual EP content is practically nil. This indicates that treatment of latex with PPG replaces easily displaceable and degradable proteins and during the second centrifugal concentration they are carried away into the skim portion.

It is observed that in general longer leaching period is associated with reduction in EP content in the films. However, even after 2h of leaching SCL and DCL film still show some EP. This is believed to be due to migration degraded proteins from the inner layers of the latex films to the surface.

**Effect of post-cure heating of radiation vulcanized latex films on crosslink density**

Post-cure heating is an important after treatment adopted for latex films for improvement in physical properties\textsuperscript{(29)}. Figure 5C.19 shows the effect of post-cure heating at 80°C of radiation vulcanized latex films irradiated to a dose of 15kGy. It is seen that crosslink density of three types of latex films increase on heating at 80°C for short periods. In the case of SCL and LPL films, maximum in the crosslink density curve is attained in about 1h heating, while for DCL films it is
2h. The improvement in crosslink density is higher for LPL and DCL films than SCL films. However, on continued heating crosslink density decreases for the three types of films. Heating of sulphur prevulcanized latex films can result in the formation of higher number of crosslinks by continued vulcanization by utilizing the residual curatives in the films\textsuperscript{(a1)}. However, such a situation is not present in radiation vulcanized latex films as no curatives are used. The increase in crosslink density, even though small, may be probably due to rearrangement/modification of already formed crosslinks via bound nBA molecules. Continued heating causes more crosslink rupture, leading to net reduction in crosslink density. Hence for achieving maximum crosslink density, for radiation vulcanized latex films, the optimum period of heating is found to be 1h for LPL films. Crosslink density is some what higher in post-heated SCL films and the order is

\textbf{SCL > LPL > DCL}

films. However, improvement in crosslink density by post-heating is the highest in LPL films, compared to SCL and DCL films.

\textbf{Effect of post-cure heating on tensile properties of radiation vulcanized latex films}

Post-cure heating of sulpher vulcanized latex films is generally accompanied by improvement in physical properties. Post-cure heating of radiation vulcanized SCL, DCL and LPL films are also accompanied by improvement in physical properties. Variation of modulus, tensile strength and elongation at break with respect to duration of post-heating are shown in Figures 5C.20, 5C.21 and 5C.22 respectively. Modulus of SCL films increases upto a heating period of 2h while for DCL and LPL films, maximum modulus is observed at 3h of post-heating. Continued heating decreases modulus. Change in crosslink density has some influence on change in modulus. However, change in crosslink density cannot fully explain this observed variation in modulus on post-heating. Crosslink density increases on heating for 1h; however, modulus increases upto 2h heating for SCL and 3h heating for DCL and LPL films. This increase in modulus is believed to be due to better fusion of latex particles in the film.
Similarly tensile strength increases up to 2.5h of heating in the case of SCL films and 3h of heating for DCL and LPL films. Thus the maximum of tensile strength curves do not coincide with the maximum of crosslink density curve. This shows that inter-particle integration, resulting from a homogenous structure is also responsible for the improvement in tensile strength on post-cure heating. The elongation at break of the three types of latex films decrease on post-cure heating.

Thus it is seen that tensile properties of radiation vulcanized LPL films are improved by heating and the duration of heating is about 3h at 80°C for achieving maximum modulus and tensile strength.

**Effect of addition of silica to radiation vulcanized latex on tensile properties**

Reinforcing fillers such as carbon blacks and silicas are generally added to dry rubber vulcanizates for improving tensile properties. However, these fillers do not behave as truly reinforcing fillers in latex compounds. This abnormal behaviour of reinforcing fillers in latex vulcanizates is due to poor rubber-filler interaction. However, modulus of the latex film is improved.

Figure 5C.23 shows the effect of addition of silica to radiation vulcanized latex on modulus of dry films, both before and after ageing. It is seen that for a given content of silica in the vulcanizate, modulus of LPL films is slightly lower than that of SCL films. DCL films have lowest modulus. It is further observed that by addition of silica to radiation vulcanized SCL and LPL there is a linear increase in modulus with respect to the content of silica and both the curves are almost parallel; the extent of increase in modulus for a given filler content is almost the same in both the latices. However, with DCL films the modulus curve is not linear. The magnitude of increase in modulus decreases on increasing silica content. This observation suggests that silica-rubber interaction is better in SCL and LPL films than in DCL film. This is probably due to increased availability of polar materials in SCL and LPL films (proteins alone in SCL films and proteins and PPG in LPL films). On ageing, modulus of DCL and LPL films decrease and the reduction in modulus is more when silica content is higher. This reduction is
attributed mainly to polymer degradation. However, in the case of SCL films, modulus increases slightly on ageing for small additions of silica upto about 5phr and then decreases below that of the unaged films. This improvement in modulus at low silica levels is believed to be due to better rubber filler interaction on heating. However, this interaction becomes less effective at high silica levels.

The variation of tensile strength with silica content is shown in Figure 5C.24. In the case of SCL and LPL films there is almost a linear reduction in tensile strength on incorporation of silica while with DCL films reduction is higher at higher levels of filler additions. This also is believed to be due to poor rubber-filler interaction. This poor rubber-filler interaction in latex rubber vulcanizates is partly due to the absence of mechanical forces driving rubber into the surface cavities/imperfections on silica particles and partly due to the presence of a protective layer of surface active materials on both rubber particles and dispersed filler particles preventing direct contact between the two particles. The extent of reduction in tensile strength of the films is in the order

SCL < LPL < DCL

at higher levels of filler addition.

Ageing of the three types of silica-filled radiation vulcanized latex films is accompanied by reduction in tensile strength. The aged tensile strength of LPL films are lower compared to SCL films and that of DCL films are the lowest. The extent of reduction in tensile strength with increasing silica content follows almost a linear relation. The fall in the tensile strength of the films on accelerated ageing is attributed to polymer degradation.

Addition of silica to the three types of radiation vulcanized latices reduces elongation at break of the dry films (Figure 5C.25). The reduction in EB varies linearly with silica content. The observed variations are in agreement with the modulus of the films. EB values are in the order

SCL < LPL < DCL

It is believed that addition of more silica imparts greater restriction to the relative movement of rubber molecular chains, leading to a reduction in elongation at
break. On ageing, three types of vulcanized films show slightly lower EB and at all levels of silica, EB of aged films follows the same order as that the unaged films. The reduction in EB on accelerated ageing is believed to be due to thermal degradation of rubber molecules.

**CONCLUSIONS**

Like ordinary centrifuged latex low protein latex also can be prevulcanized by gamma radiation, in presence of a sensitizer and the optimum dose is found to be 15kGy. Crosslink density of LPL films is only slightly lower than SCL films. Radiation-cured low protein latex films show good tensile properties, though slightly lower than that of standard centrifuged natural latex films. Optimum cured low protein latex films after extraction with water for 1h contains practically no residual extractable protein. Hence radiation vulcanized LPL films can provide high protection against latex protein allergy problem. Physical properties of radiation-cured low protein latex films are dependent on dry rubber content of the irradiated latex and the optimum properties are achieved when irradiated at 50% DRC. However, reasonably good physical properties are obtained for radiation-cured low protein latex films prepared from vulcanized latex irradiated at 58% DRC also. Leaching and post-cure heating of radiation cured low protein latex films improve their physical properties.

Since radiation vulcanized low protein latex films after leaching is almost free from residual extractable proteins, and exhibits good tensile properties it can be used for the production of articles like examination gloves, teats, soothers, balloons, condoms etc. which are almost free from type I allergic reactions.

Modulus of radiation vulcanized low protein latex films can be improved by incorporation of silica and the extent of increase is proportional to the silica content. This behaviour of LPL enables it to find application in products like catheter requiring high modulus.
REFERENCES


15. IS 3400 (Part 1) 1987: Methods of Test for vulcanized rubbers – tensile stress-strain properties.


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<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
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<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td></td>
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<tr>
<td>60% Natural Latex</td>
<td>100</td>
<td>167</td>
<td></td>
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<tr>
<td>10% Potassium hydroxide</td>
<td>0.3</td>
<td>3.0</td>
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<tr>
<td>50% n-Butyl acrylate</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>—</td>
<td>To 50%</td>
<td></td>
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Fig 5C.1. Effect of dose of radiation on crosslink density in radiation vulcanized latex films.
Fig 5C.2. Effect of dose of radiation on modulus of radiation vulcanized latex films.
Fig 5C.3. Effect of dose of radiation on tensile strength of radiation vulcanized latex films.
Fig 5C.4. Effect of dose of radiation on elongation at break of radiation vulcanized latex films.
Fig 5C.5. Effect of dose of radiation on extractable protein content in latex films before and after leaching.
Fig 5C.6. Effect of dose rate of radiation on crosslink density in latex films.
(Dose 15 kGy)
Fig 5C.7. Effect of dose rate of radiation on modulus of latex films. (Dose 15 kGy)
Fig 5C.8. Effect of dose rate of radiation on tensile strength of latex films. (Dose 15 kGy)
Fig 5C.9. Effect of dose rate of radiation on elongation at break of latex films (Dose 15kGy)
Fig 5C.10. Effect of dose rate of radiation on EP content in latex films. (Dose 15 kGy)
Fig 5C.11. Effect of solids content of irradiated latex on crosslink density of latex films.
Fig 5C.12. Effect of solids content of irradiated latex on modulus of latex films.
Fig 5C.13. Effect of solids content of irradiated latex on tensile strength of latex films.
Fig 5C.14. Effect of solids content of irradiated latex on elongation at break

Solids content of latex (%) vs Elongation at break (%) graph showing the relationship between solids content and elongation at break for different types of films.
Fig 5C.15. Effect of leaching on modulus of radiation vulcanized latex films.
Fig 5C.16. Effect of leaching on tensile strength of radiation Vulcanized latex films.
Fig 5C.17. Effect of leaching on elongation at break of radiation vulcanized
Fig 5C.18. Effect of leaching on extractable protein content in radiation vulcanized latex films.
Fig 5C.19. Effect of post-cure heating at 80°C on crosslink density of radiation vulcanized latex films.
Fig 5C.20. Effect of post-cure heating at 80°C on modulus of radiation vulcanized latex films.
Fig 5C.21. Effect of post-cure heating at 80°C on tensile strength of radiation Vulcanized latex films.
Fig 5C.22. Effect of post-cure heating at 80°C on elongation at break of radiation vulcanized latex films.
Fig 5C.23. Effect of addition of silica on modulus of radiation vulcanized latex films.
Fig 5C.24. Effect of addition of silica on tensile strength of radiation vulcanized latex films.
Fig 5C.25. Effect of addition of silica on elongation at break of radiation vulcanized latex films.