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Effect of Gamma Irradiation and Leaching Conditions on Residual Extractable Protein Content in Radiation Vulcanized Natural Rubber Latex Films

By Valsa George, M. Sunny Sebastian, I. John Britto and E. V. Thomas.
Dept. of Processing and Product Development, Rubber Board, Kottayam.

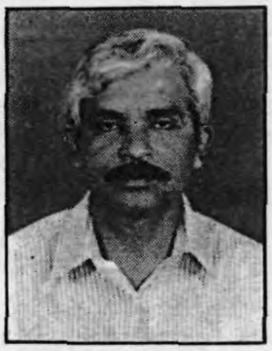
Abstract

Gamma irradiation of natural rubber latex degrades the proteins associated with rubber particles and makes them water extractable to some extent. These degraded proteins can be removed from latex films by leaching. Duration of leaching can be reduced by using hot water. Post-heating of radiation vulcanized natural rubber latex (RVNRL) films, further degrades the proteins and can be removed by very short leaching in water.

Key words: RVNRL, Extractable proteins, Leaching, Post-heating.

Introduction

Radiation vulcanization of natural rubber latex is a process in which rubber molecules are crosslinked by irradiation with gamma rays to get prevulcanized latex(1). Radiation vulcanization process has been standardised to achieve acceptable physical properties to latex films prepared both by casting or dipping(2-4). Ammonia preserved concentrated natural latex contains proteins to the extent of about 1% on the weight of latex, part of which is dissolved in the aqueous phase and the remaining is adsorbed at the rubber serum interphase(5). From dry natural latex films part of the proteins can be extracted by sweat or water. It has been reported that these extractable proteins in latex products can cause type I allergic reactions in sensitized people(6-9). Out of the total proteins in latex films, only a small fraction is extractable(10). There are reports that gamma irradiation of latex degrades the proteins to some extent and are made water soluble (11,12). Similarly irradiation of natural latex with electron beam also degrades proteins and make them more extractable(13). Leaching is an important process in dipped latex goods manufacture to remove non-rubber materials and to improve physical properties of films by better particle integration(13-15). This paper reports the effect of dose and dose rate of gamma ray irradiation of natural



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latex, the effect of leaching conditions, post-heating and heat ageing of latex films on residual extractable protein content in them.

Experimental

Natural latex was compounded as per formulation given in table 1. After maturing for 6 hrs, latex compound was irradiated to produce radiation vulcanized natural rubber latex (RVNRL). Gamma rays emitted from a Cobalt 60 source using Gamma Chamber 5000, designed and errected by the Board of Radiations and Isotope Technology (BRIT), Dept. of Atomic Energy, Mumbai was used for irradiation. Dose of irradiation was varied by varying the duration of exposure and dose rate was varied by the use of attenuators. Latex films were prepared by casting in levelled glass plates[16] and dried in air at ambient temperature. To impart protection to the films against heat and oxidation 2 phr of trisnonylated phenyl phosphite (TNPP) was added as antioxidant (prepared as 50% emulsion) to the irradiated latex. Leaching of the dry films in water was carried out at different temperatures for predetermined periods. Leaching was also carried out using 1% aqueous ammonia solution. Ageing of films was carried out by heating in air at 70°C for 7 days. Extractable protein content in films was determined by RRIM modified Lowry method[17] using distilled water as the extractant.

Table 1
Latex compound for irradiation

Ingredient	Parts by weight	
	Dry	Wet
60% Natural latex	100	167
10% Potassium hydroxide	0.3	3.0
50% n-Butylacrylate(nBA)	5.0	10.0
Water	---	50% solids content

Results and Discussion

Effect of dose of irradiation on extractable protein content in RVNRL films

Dry films prepared from unvulcanized latex contain some extractable proteins. During RVNRL processing latex compound is irradiated by gamma rays for crosslinking the rubber molecules to a desired state of prevulcanization, with a view to achieve the required level of physical properties. During irradiation, simultaneous to crosslinking, proteins undergo degradation and become water soluble. Figure 1 shows the effect of dose of irradiation on EP content in unleached latex films. It is seen that EP content increases almost linearly with dose of irradiation in the range of dose covered in the present study. It is believed that during high energy gamma irradiation, the proteins adsorbed at the rubber serum interface are degraded to such an extent that the degraded fragments dissolve in the aqueous phase.

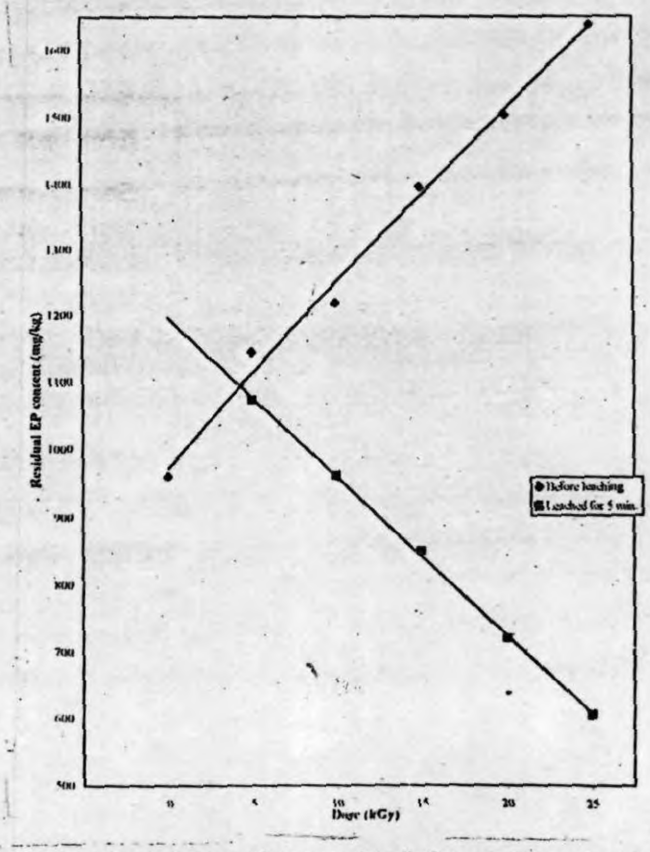

Fig 1 - Effect of dose of gamma irradiation on EP content in RVNRL films before and after short term leaching

Effect of short term leaching

The cast films, prepared from latex irradiated to various doses were subjected to short term leaching of 5 minutes to simulate the conditions of on-line leaching in a typical dipping process. The residual extractable proteins left in the leached films also are given in figure-1. It is seen in the leached films the residual EP is highest when dose of irradiation is least, and lowest EP for the highest dose films even though EP was highest with the highest dose in the case of unleached films. Also on short term leaching the residual EP decreases linearly with dose of irradiation. This is probably because during irradiation at high doses, proteins are very thoroughly degraded and can migrate very easily to the surface of the film, and are leached off even during a short leaching period.

Effect of dose of irradiation and duration of leaching on residual EP

Figure 2 shows the effect of dose irradiation on EP content in RVNRL films leached for different intervals. It is seen that residual EP varies linearly with dose for all leaching periods. The longer the leaching period the lesser is the residual EP in the leached film.

The slopes of the curves are negative for short leaching, they increase with leaching period, becomes almost parallel to dose axis when duration of leaching is about 1 hr, beyond which the slope becomes positive. At higher doses of irradiation more proteins are degraded and made water extractable. However, residual EP content of films leached for long periods increases with dose when leaching period exceeds one hour. This is contrary to the behaviour of films leached for short intervals. It is believed that latex films containing high levels of EP when subjected to leaching in static water, an equilibrium is attained between proteins in aqueous phase and proteins in latex film, so that soluble proteins can no longer be extracted into the aqueous phase, with the result that residual EP retained in leached films will increase with dose. Figure 3 shows the effect of duration of leaching on residual EP in the extracted films. It is seen that there is a drastic reduction in residual EP even by leaching for short intervals, and the rate of reduction in EP decreases with leaching time. Protein levels with minimal allergen content/activity have been identified to be about 100 mg/kg or lower[18]. Generally latex is irradiated at 15 kGy in RVNRL processing. Leaching for a period of about 3 hrs. is required to reduce residual EP content to less than 100 mg/kg.

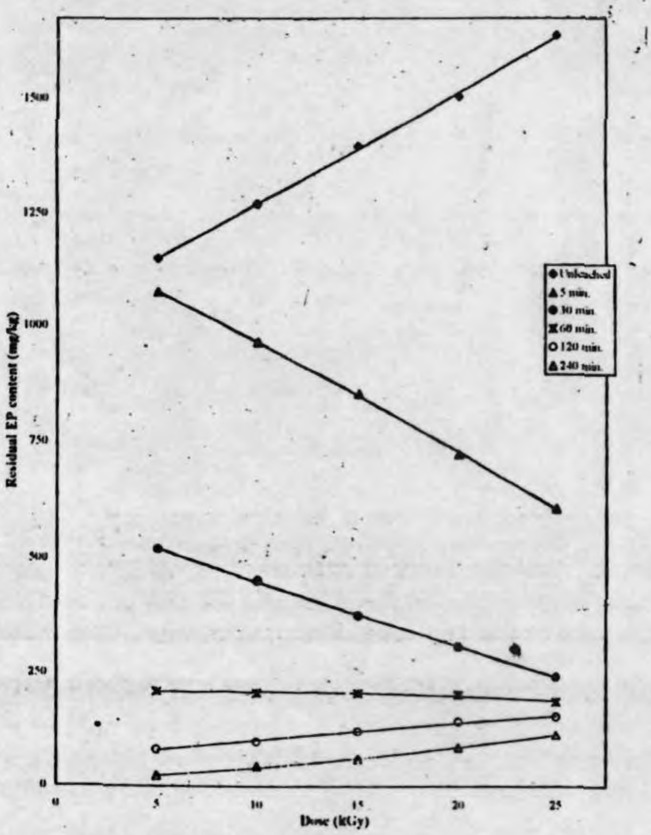

Fig 2 - Effect of dose of irradiation on residual EP in RVNRL films leached for different intervals

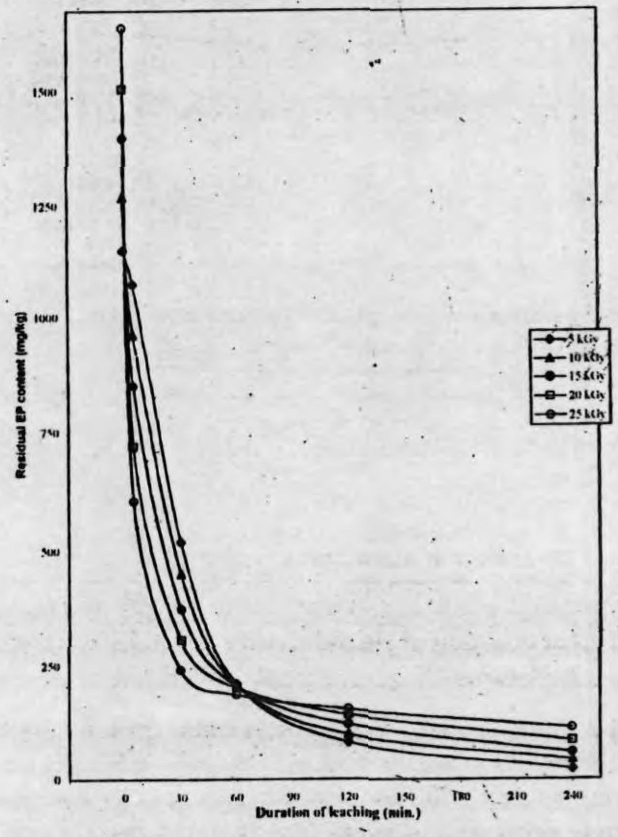

Fig 3 - Effect of duration of leaching on residual EP content in RVNRL films prepared from films irradiated to different doses

Effect of dose rate

Figure 4 shows the effect of dose rate of irradiation on residual EP content in unleached RVNRL films and films leached for various intervals. The latex was irradiated at a total dose of 15 kGy. It is observed that dose rate has little effect on residual EP content in the range of dose rates studied. All the curves are almost paralled to dose rate axis. It appears that the degradation occurring to proteins is proportional to the total dose delivered, rather than the rate at which the dose is delivered.

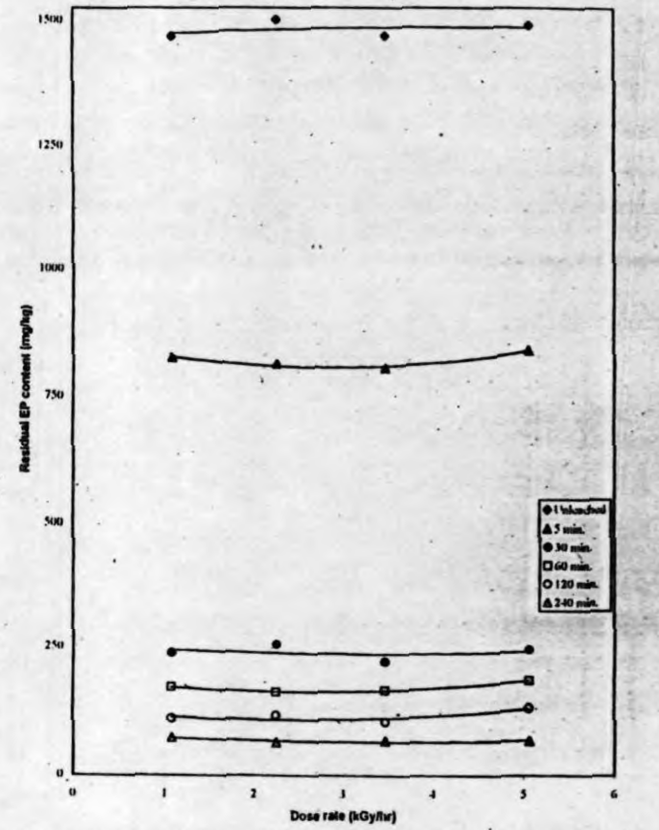

Fig 4 - Effect of dose rate of irradiation on EP content in RVNRL films

Effect of duration of leaching on residual EP content in RVNRL films

Leaching of dipped latex articles is an important processing step in latex industry. The residual EP content in RVNRL films depends on the duration of leaching. Figure 5 shows the effect of duration of leaching on residual EP content in RVNRL films, prepared from latex irradiated to a total dose of 15 kGy at different dose rates. It is seen that for all dose rates, short leaching for about 5 min. removes about 50% of the total extractable proteins and leaching for a period of 30 min. removes about 85%. However, further continued leaching for a total of 4 hours reduces residual EP content to below 100 mg/kg, which is considered to be a rather safe limit[18]. However, only shorter leaching periods are required to bring down residual EP in post vulcanized latex films using sulphur and accelerator[19]. But it may be noted that total EP content in vulcanized latex films before leaching is much higher in RVNRL films compared to sulphur vulcanized latex films[19], due to protein degradation during irradiation.

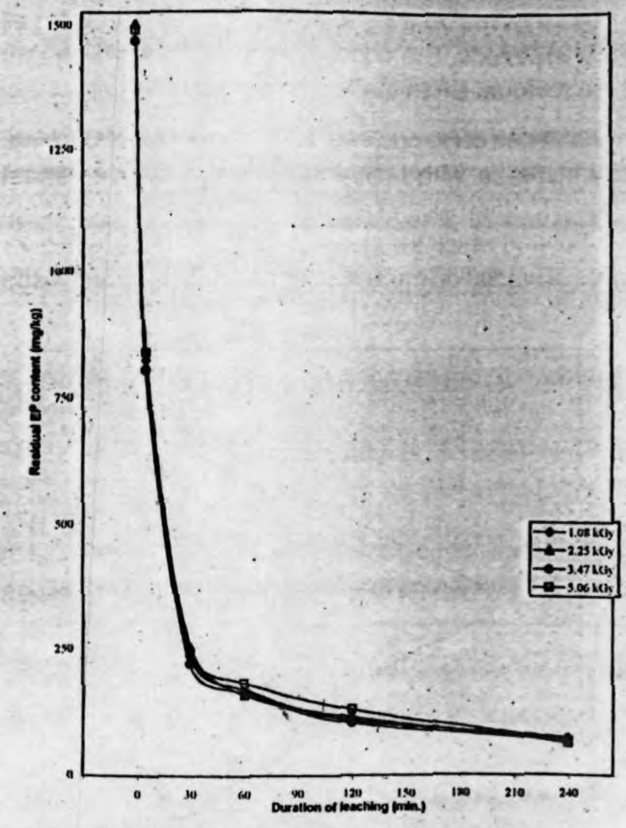

Fig 5 - Effect of duration of leaching on residual EP content in RVNRL films prepared from latex irradiated at different dose rates

Effect of temperature of leaching water

Long leaching periods are necessary for proper removal of non-rubber materials and proteins from latex films. However long leaching is generally inconvenient. Solubility and rate of dissolution of proteins and non-rubber materials are enhanced by increasing the temperature of leaching water. Short term leaching in hot water has been suggested as an alternate to long term leaching in cold water as a means of improving the physical properties of RVNRL[14]. Figure 6 shows the effect of temperature of leaching water on residual extractable proteins when leaching was conducted for 5 minutes on films made from latex irradiated to 15 kGy at various dose rates. Practically not much difference is seen between latex films irradiated at different dose rates. It is seen that as the temperature of leaching water increases, more proteins are leached off from the films, so that residual EP is less; ie rate of protein removal increases with rise in temperature of leach water. RVNRL films initially leached in water at 80°C for 5 minutes retained only 50% of the extractable proteins compared to those films leached at 30°C for 5 minutes. After leaching, the wet films have to be invariably dried before packing. Drying will be easier for those films which were leached at higher temperature.

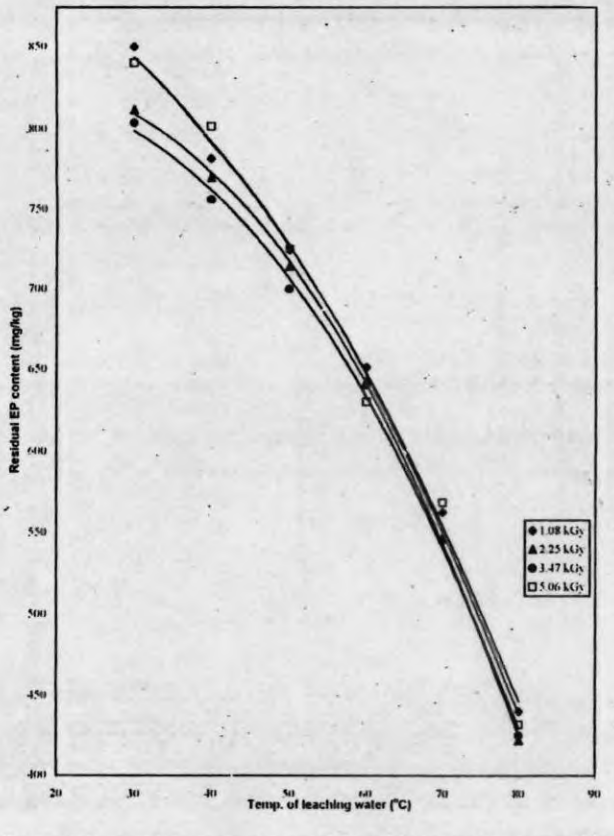

Fig 6 - Effect of temperature of leaching water on residual EP content in RVNRL films, prepared from latex irradiated at 15 kGy at different dose rates

Residual extractable protein content in aged RVNRL films after leaching

Unleached RVNRL films were heat aged. The aged films were leached for different intervals and residual EP content in aged films were estimated. The data obtained are presented in figure 7. It is seen that in the unleached film after ageing, there is an increase in EP. This is believed to be due to degradation of some more proteins, which were initially unextractable. The aged films after leaching, even for short interval of 5 min. show very low EP values. This is because the extractable proteins were still further degraded very throughly, and thus probably easily migrated to the surface of the film, so that they would be easily extracted. Thus heat ageing followed by leaching of RVNRL films reduced EP to low levels, about 50 mg/kg. even by short leaching of 5 minutes or so. By longer leaching there is only small further reduction in residual EP, showing that EP in aged films have migrated to the surface of latex film[20].

Eventhough heat ageing for 7 days at 70°C followed by leaching is thus found to be a good method for reducing EP, it cannot be implemented on a practical scale due to the prolonged heating period. Hence further studies were conducted by heating RVNRL films at higher temperatures for shorter intervals.

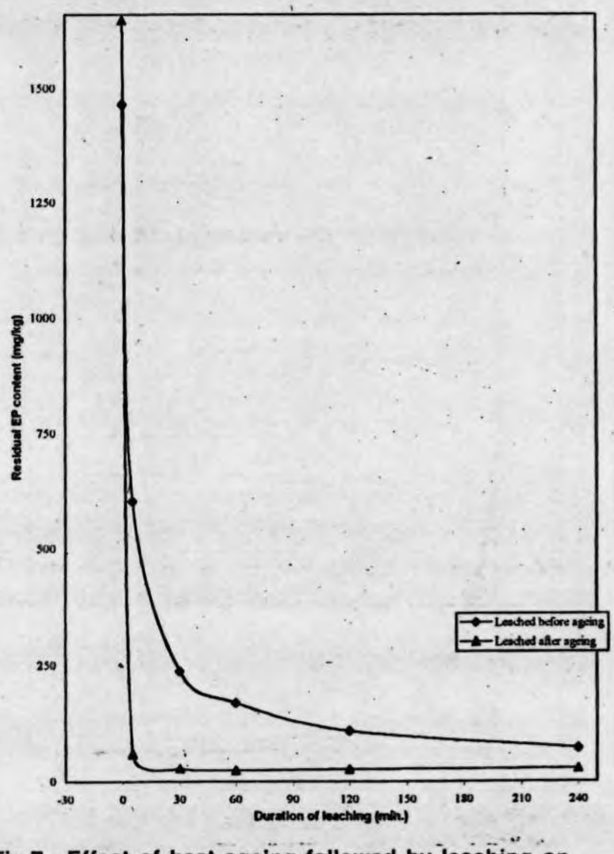

Fig 7 - Effect of heat ageing followed by leaching on residual EP in RVNRL films

Post-heating of dry RVNRL films

It is a general practice in latex industry to post-heat dry latex films prepared from sulphur prevulcanized latices for the purpose of improving physical properties[20]. Physical properties of RVNRL films are also improved by post-heating[14]. It is found that in addition to improvement in physical properties post-heating of dry films makes the proteins more extractable and the residual EP left after leaching is less compared to a non-heated films. Data obtained in this study are presented in figure 8. An increase in total EP in unleached films indicates that more proteins are degraded and converted to EP, the films heated at 100°C shows little more EP than the film heated at 80°C. Residual EP in films leached for short intervals, say 5 min. indicates that proteins already extractable and made more easily water leachable, either by further degradation or bringing them to the surface or both. However in prolonged leaching, the difference between post-heated films at 80°C and non post-heated films becomes marginal, even though post-heated films show slightly lower EP. However, the film post-heated at 100°C, show very low residual EP even after short leaching of 5 min. Thus RVNRL films, post-heated at 100°C for 1 hour and subjected to short leaching of 5 min. reduces residual EP to less than 100 mg/kg, which is considered to be an approximate limit below which the films are considered to be non-alergic[18].

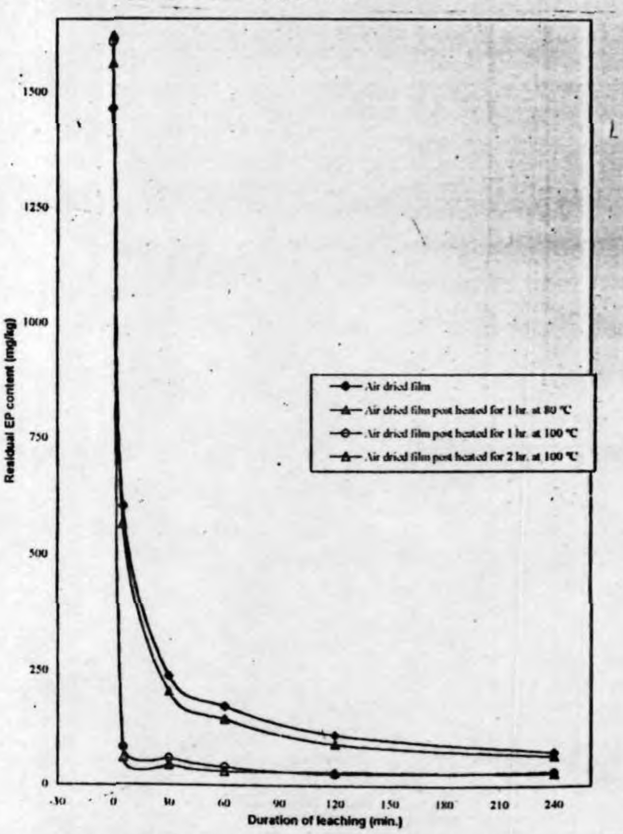

Fig 8 - Effect of post-heating of RVNRL films followed by leaching on residual extractable protein content

Effect of leaching medium on residual EP content in RVNRL films

Figure 9 shows the effect of leaching medium on the residual EP content in films, leached for different intervals. Water and 1% aqueous ammonia solution were used for leaching RVNRL films. There are earlier reports that 24 hours leaching of RVNRL film in 2% aqueous solution can remove 90% of the total EP[22]. It is seen that for short duration of leaching, water is more effective in removing EP from latex films. However, beyond two hours, ammonia solution is found to be marginally better. However the overall performance of water is better than that of 1% aqueous ammonia solution.

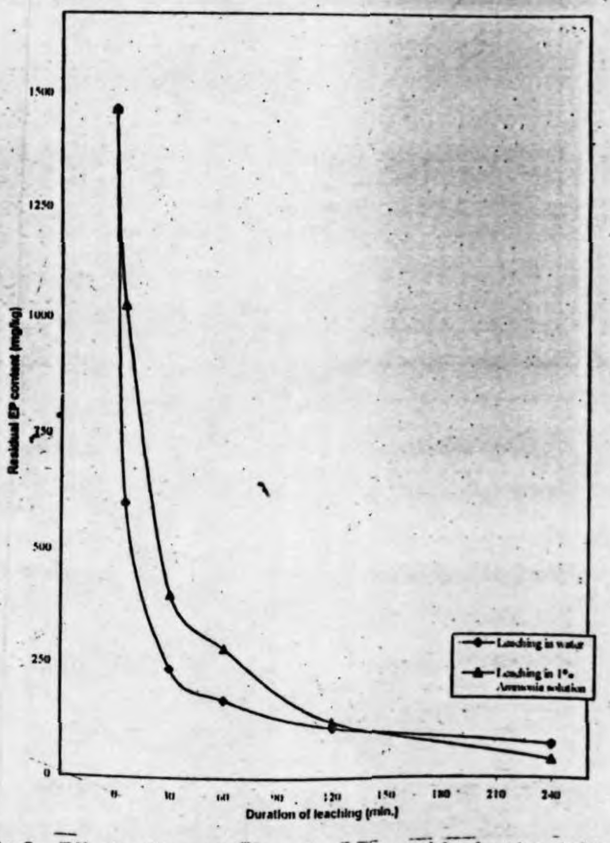

Fig 9 - Effect of leaching medium on residual extractable protein content in RVNRL films

Conclusions

During RVNRL processing, naturally occurring proteins in latex undergo degradation and are made more water soluble. Higher the dose of irradiation the higher is the extent of protein degradation and more effectively they are removed by leaching. Longer the leaching of the film, lesser is the quantity of residual EP. When dose of irradiation is 15 kGy, which is the normal dose of RVNRL processing 4 hours of leaching at room temperature is necessary to reduce EP to acceptable levels. Dose rate has practically no effect in protein degradation and removal. Proteins are more effectively removed from RVNRL films by leaching with hot water. By increasing the temperature of leaching bath from 30°C to 80°C, residual EP is reduced to approximately half for short leaching. Post heating of RVNRL films at 100°C for 2 hours followed by leaching for 5 minutes reduces EP to low levels (less than 60 mg/kg.). Leaching of RVNRL films in 1% aqueous ammonia solution has no advantage over water for protein removal.

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