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QUALITY IMPROVEMENT OF RADIATION VULCANIZED NATURAL RUBBER LATEX BY ADDITION OF POLYVINYL ALCOHOL AND CENTRIFUGATION

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ABSTRACT

Effect of polyvinyl alcohol (PVA) on extractable soluble protein content, and on mechanical and physical properties of radiation vulcanized natural rubber latex (RVNRL) was studied with the view of improving properties of RVNR latex. Concentrated natural rubber latex was irradiated at the rate of 10 kGy/h for 2 hrs in the presence of 5 phr of n-BA and 0.5 phr of KOH. PVA solution was added to the RVNR latex at three different stages and different time periods were used for leaching to find out the most suitable process to produce soluble protein less RVNR latex. Present results indicate that combined treatments of PVA addition and centrifugation followed by leaching were more effective compared to single treatment to reduce soluble protein content in RVNR latex films. It could be further observed that, the tear strength was increased whereas tensile strength and tackiness were decreased with PVA concentration. However when the PVA incorporated RVNRL was centrifuged, tensile and tear strength were not changed up to 2 phr of PVA. Fourier Transform Infrared spectrophotometer (FTIR) measurements showed that when PVA added RVNRL was centrifuged, most of the PVA could be removed with the serum phase. According to the Horizontal Attenuated Total Reflectance (HATR) measurements, PVA concentration on the upper and lower surfaces of the latex films (i.e. the exposed and unexposed surfaces of the films when drying) was not equal.

INTRODUCTION

Natural rubber latex extracted from *Hevea brasiliensis* after treatment and processing is widely used to produce dipped products such as condoms, examination

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and surgical gloves and large number of medical devices. It was found that sulfur vulcanization system created some problems in final product due to non rubber constituents in latex as well as due to chemicals added during the process. Radiation vulcanization technique was developed to over come the disadvantages found in conventional sulfur vulcanization system. Radiation vulcanization of natural rubber latex has following advantages over the conventional sulfur vulcanization system (Makuuchi, 1997).

1. Absence of N-nitrosoamine
2. Very low cytotoxicity.
3. Less allergy response
4. Degradability
5. Transparency and softness
6. Low emission of $S0_2$ and less formation of ashes when burned

Absence of accelerator (which is necessary for sulfur vulcanization) has caused a great reduction of type IV allergy in RVNRL (Geertsma *et al.*, 1996). However irradiated latex does not inhibit type I allergy reaction (Bez, 1996). Soluble protein the cause for Type I allergy reaction could not be removed completely during the irradiation process. Radiation can cause destructive effect on protein in latex and increase the solubility which may have an effect on Type I allergy reaction (Geertsma *et al*, 1996). Varghese *et al* (1999) have reported that addition of water soluble polymer enhanced the leaching of soluble protein from RVNRL films and also reported that centrifugation of RVNRL could effectively reduce soluble protein (Varghese *et al*, 1997, Varghese *et al*, 1999). They also reported that mixing water soluble polymer with irradiated NR latex increased the tear strength where as tensile strength showed small decrease. This paper discusses the effect of combined treatment of PVA addition and centrifugation on extractable protein of RVNRL. Extractable protein of three different processes which are PVA addition only, centrifugation followed by PVA addition and PVA addition followed by centrifugation were compared in order to find out the most suitable process to produce soluble protein free RVNR latex. This paper also discusses how properties of RVNR latex will change when PVA was mixed with RVNR latex and centrifuged.

MATERIALS AND METHODS

Materials

High ammonia concentrated latex (60% dry rubber content) was supplied by Dunlop Malaysia. n-butyl acrylate and 10% KOH were used as radiation vulcanization accelerator and stabilizer respectively. PVA degree of polymerization

2000 was prepared using autoclave and used as 10% aqueous solution. RVNR latex was centrifuged using SPL-100 SAITO centrifuge machine.

Experimental methods

Preparation of latex films

Concentrated latex was diluted up to 50% dry rubber content (DRC) using 1% ammonia solution. 0.5 phr of 10% KOH was added to the latex while stirring followed by 5 phr of n-Butyl acrylate. The irradiation was carried out by gamma rays from a Co 60 source at a rate of 10 kGy/h for 2 hrs. The irradiated latex was mixed with PVA as 10 % solution at different proportions and at three different stages as shown in figure 1. Latex films were caste on glass plates using PVA incorporated RVNR latex. Latex films were dried in an air until transparent. Dried latex films were leached in 1% ammonia solution at room temperature for various lengths of time periods and post dried in air and in an oven at 80 ° C for 1 hr.

Protein assay

After leaching of PVA added RVNR latex films, remaining soluble protein content was measured using Bicinchonic acid (BCA) method. One gram of latex film sample was extracted with 10 ml of distilled water at 37 °C for 2hrs. Interference substances were precipitated by centrifugation (Brown *et al.*, 1989). The precipitated protein was dissolved directly with BCA working reagent. Enhanced protocol of BCA method (at 60 °C for 30 min.) was used to increase the minimum detection level up to 5μg/ml. The protein concentration was measured at 562 nm using Shimadzu 800 uv-visible spectrophotometer.

IR measurements

The latex films for IR measurement were prepared by dipping small glass slides in to the PVA incorporated RVNR latex. Latex films were dried in an air oven at 100° C to constant weight. IR measurements were carried out with FTIR-800 Shimadzu instrument. Due to the difficulty of preparing same thickness samples, height ratio of two peaks which belong to C-H bending of rubber hydrocarbon (1449 cm^{-1}) and N-H stretch vibration of RVNRL protein, O-H stretch vibration of PVA (3300 - 3330 cm^{-1}) was calculated in order to quantitatively measure, remaining PVA in the RVNR latex after leaching and centrifuging.

HATR attachment was used to measure the concentration of PVA on the upper surface which is exposed to air during drying of RVNR latex films and the lower surface which is not exposed to air.

Mechanical and physical properties

After leaching 30 minutes in 1% ammonia solution the films were dried in an oven at 80 °C for 1hr, Tensile measurements and tackiness were measured using tensile machine StrographRI (Toyoseki Co. Ltd) and Probe tackiness tester model TAC II respectively.

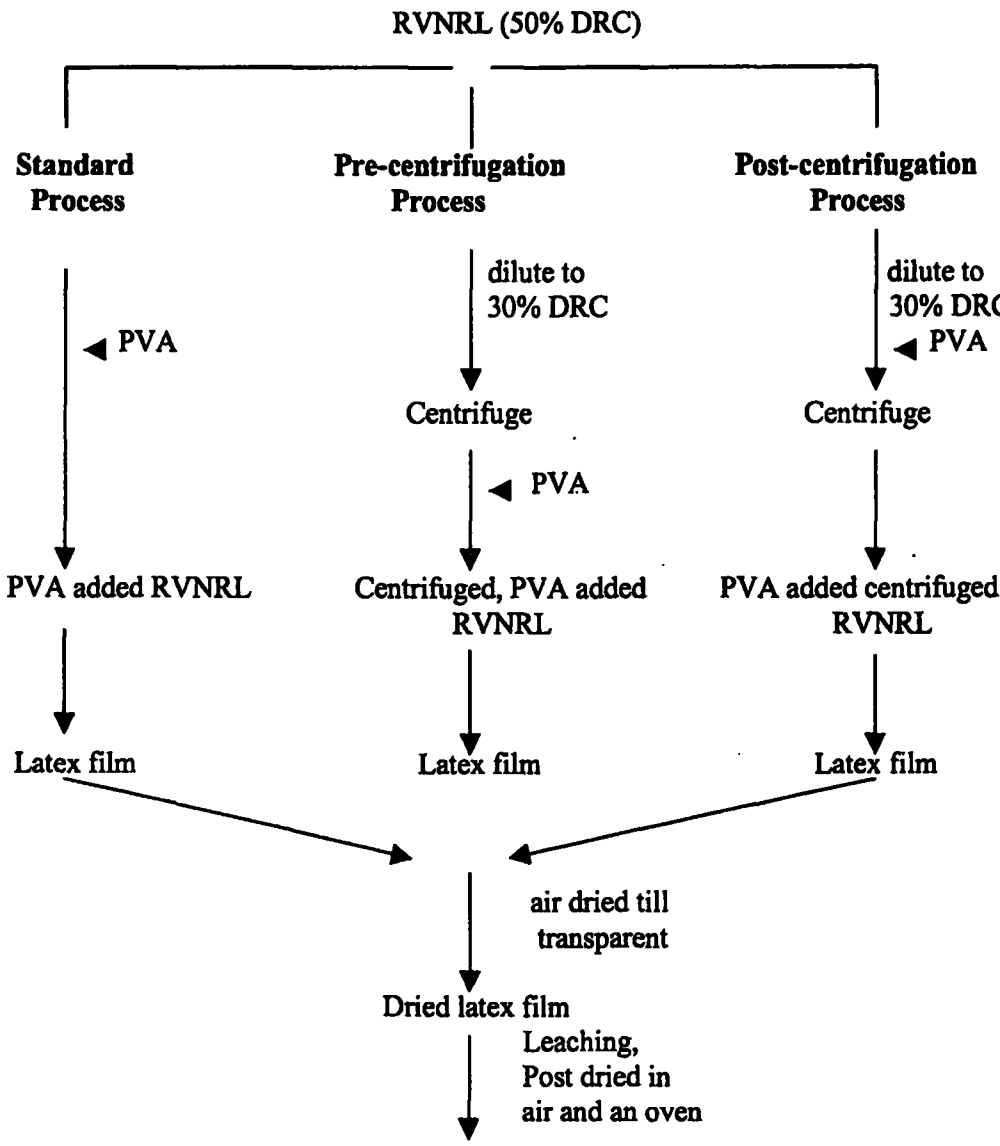

Figure 1

RESULTS AND DISCUSSION

Protein measurement

Proper leaching of the final product made from RVNRL as well as Sulfur vulcanized natural rubber latex (SVNRL) is essential to reduce soluble protein to a lower level (Zin *et al.*, 1996, Said *et al.*, 1996). However even after 24 hr. leaching all extractable protein could not be removed from the RVNR latex films (Bez, 1996). In this experiment, effect of leaching time on soluble protein content of PVA added RVNR latex films was studied.

As shown in figure 2, soluble protein content was reduced with increasing leaching time and PVA concentration. When PVA is incorporated with RVNRL (Standard Process), fast leaching of soluble protein could be achieved. These results are in agreement with the results found by Varghese *et al.* (1999) using water soluble polymers. However this standard process could not produced soluble protein free RVNR latex hence small amount of soluble protein (0.065mg/g) was remained even after 30 minutes leaching of 3phr PVA added RVNR latex films.

Figure 3 shows the leaching effect on soluble protein, when RVNR latex was centrifuged and PVA was added to the centrifuged RVNR latex (Pre-centrifugation Process). RVNRL was subjected to dilution and then centrifuged. This process removes the soluble protein with the serum from RVNRL (Varghese *et al.*, 1997). When RVNRL was centrifuged, the soluble protein content could be reduced from 1.02mg/g to 0.11mg/g when compared to non centrifuging process (Standard Process I). Based on this result, by centrifuging about 90% of soluble protein could be removed. Possible explanation for this is that during irradiation latex protein undergo disintegration and reduction in molecular weight. This can contribute to enhanced solubility and the protein is removed with the serum phase when latex is centrifuged. Remaining protein of the latex could be further reduced by adding PVA followed by leaching.

Figure 4 shows the leaching effect on extractable protein when PVA was mixed with RVNRL and then centrifuged (Post-centrifugation Process). Comparing the soluble protein content of Post-centrifugation process having 3phr of PVA with Pre-centrifugation process having same amount of PVA, the soluble protein can be reduced by about 50% by the former process compared to latter one (figure 5). This may be due to the soluble protein having more affinity towards the PVA phase than the rubber phase. Most of the leachable protein is removed during the first 10 minutes of leaching (Hashim, 1993). When Post-centrifugation process was used, about 60% of extractable protein was removed during the first 10 minutes of leaching of latex films. Extractable protein was further removed at a comparatively slow rate when leaching time was increased.

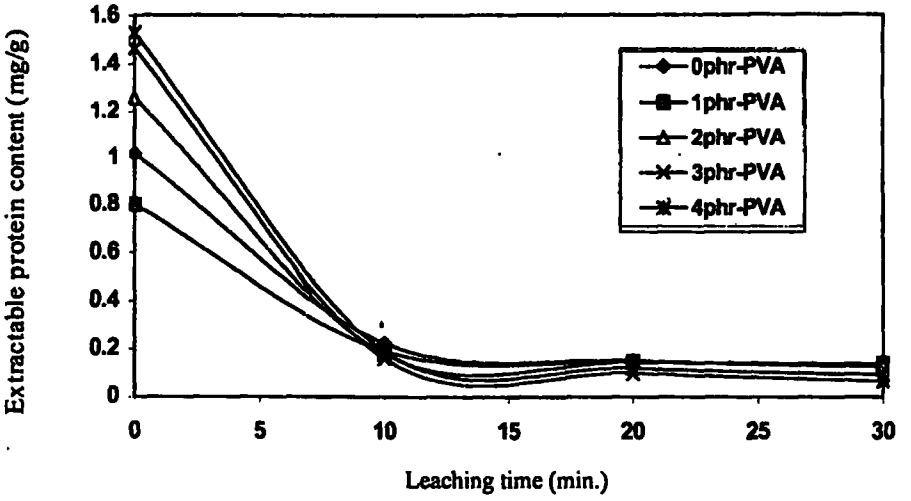

Fig. 2. Effect of leaching time on extractable protein – Standard process

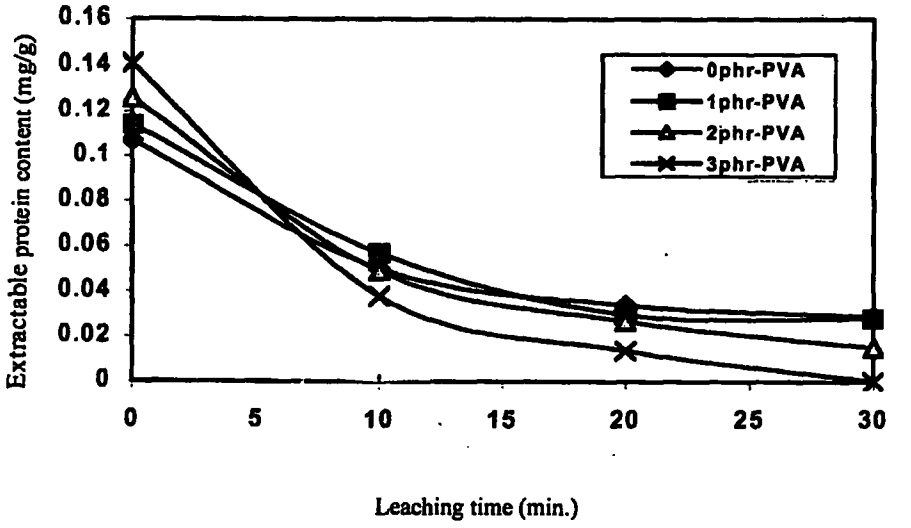

Fig. 3. Effect of leaching time on extractable protein – Pre-centrifugation process

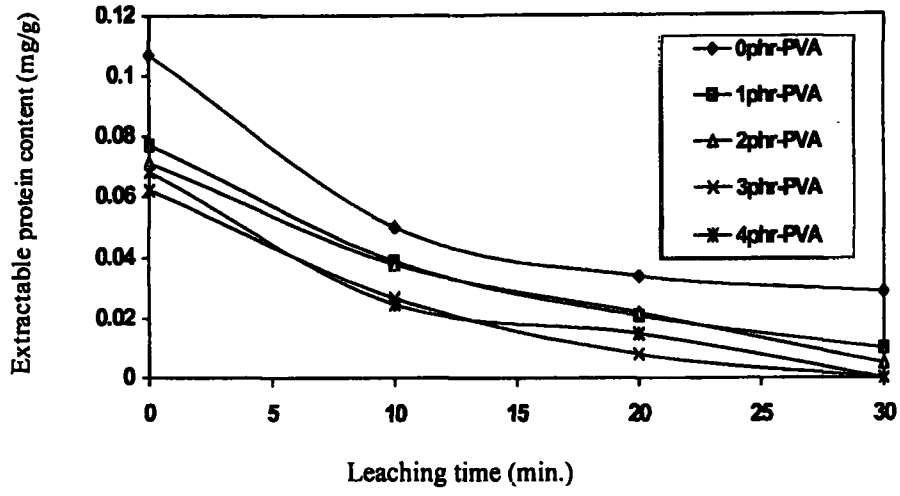

Fig. 4. Effect of leaching time on extractable protein – Post-centrifugation process

Comparing the three processes (Figure 5), the results indicate that combined treatment of centrifugation and PVA addition was more effective than single treatment to reduce soluble protein in RVNR latex. Based on these results addition of 3phr of PVA and 30 minutes leaching was sufficient to produce soluble protein free RVNRL films when Pre-centrifugation Process and Post-centrifugation process were used.

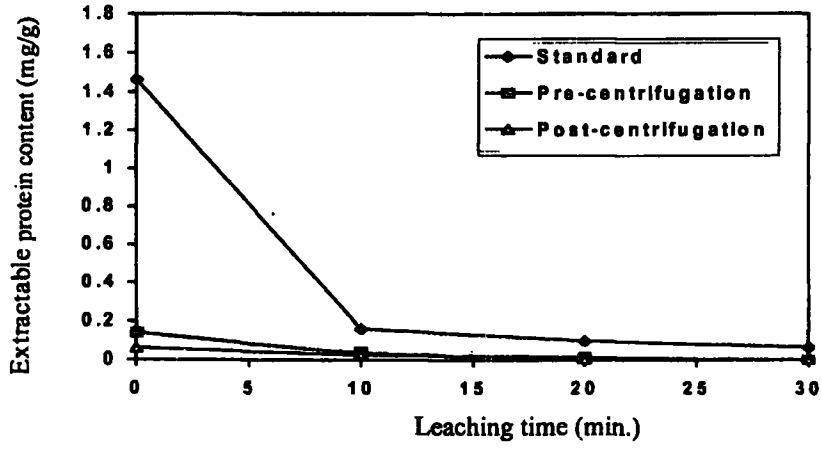

Fig. 5. Comparison of extractable protein content of the three process containing 3phr of PVA

Mechanical properties

As shown in figure 6, tensile strength decreases with PVA concentration for both standard process and post-centrifugation process. However when PVA was added to RVNRL and centrifuged (Post-centrifugation Process), tensile strength was almost constant up to 2phr PVA. This is due to removal of the PVA almost completely with serum phase when RVNRL is centrifuged. This was confirmed by analyzing IR spectrum of PVA added centrifuged RVNR latex films. Even after increasing the PVA concentration more than 2phr, rate of decrease was smaller when compared to standard process.

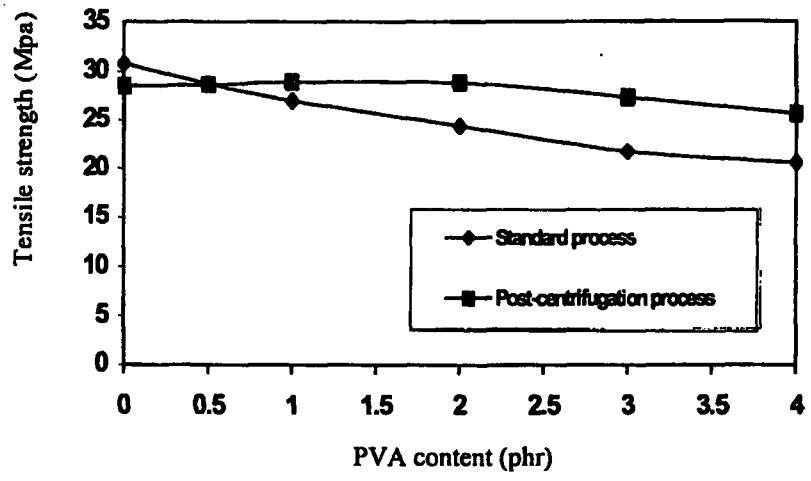

Fig. 6. Effect of PVA on tensile strength

Figure 7a shows the IR spectrum of the RVNRL films. The peak height ratio of A to B is 0.03 . When Post-centrifugation process with 2phr of PVA is used (figure 7b), the same peak height ratio (0.02) is smaller than Figure 7a. because of removal PVA as well as RVNRL protein. However Figure 7c shows, when 4phr of PVA was used and centrifuged, the peak height ratio (0.052) is higher than that of figure 7a. These results reveal that PVA could be removed completely from RVNRL when low PVA percentage was used but it could not be removed when high PVA percentage was used. Figure 7d shows the IR spectrum of 2phr PVA added RVNR films after 30 minutes leaching. The peak height ratio (0.10) indicates that PVA could not be removed completely by leaching. These spectrum results and tensile measurement show that tensile strength was affected due to PVA incorporation. However mixing PVA up to 2phr, tensile strength was not affected because PVA was completely removed from RVNRL when it was centrifuged.

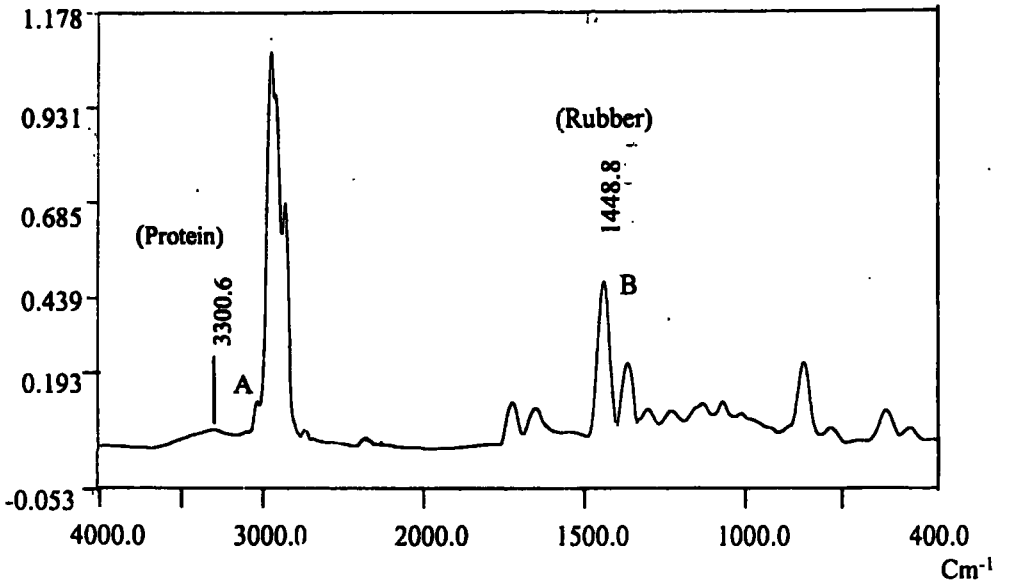

Fig. 7a. FTIR spectrum of RVNR latex

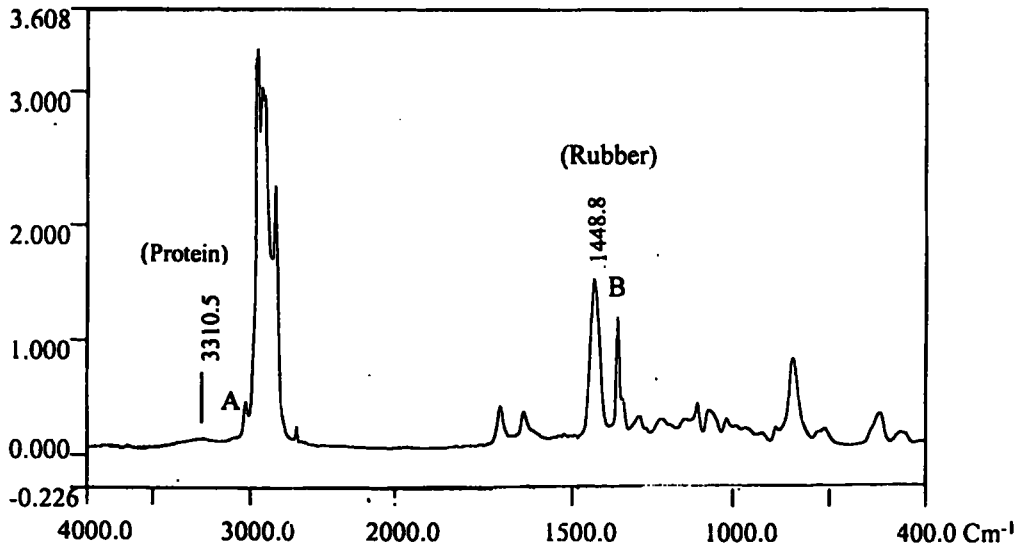

Fig. 7b. FTIR spectrum of 2phr PVA mixed and centrifuged RVNR latex

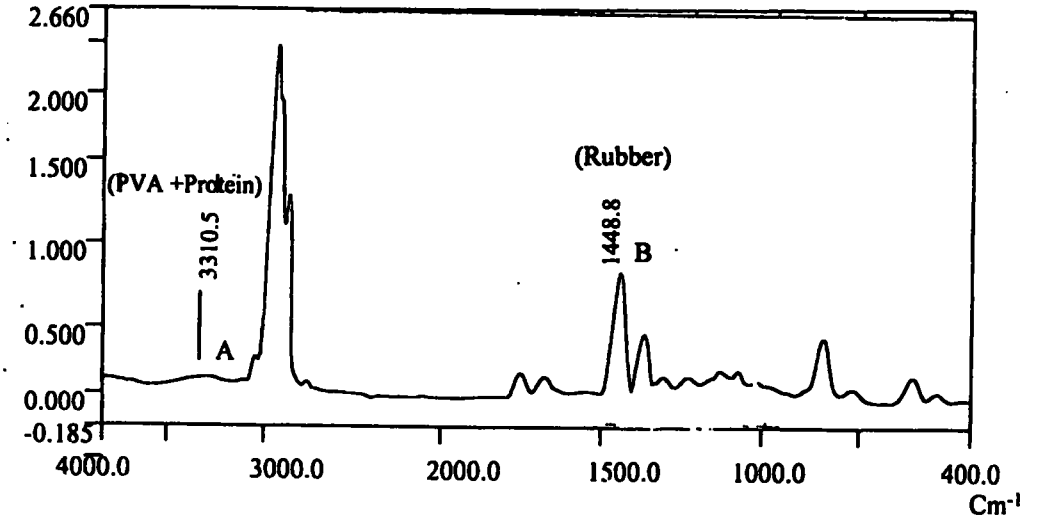

Fig. 7c. FTIR spectrum of 4phr PVA mixed and centrifuged RVNR latex

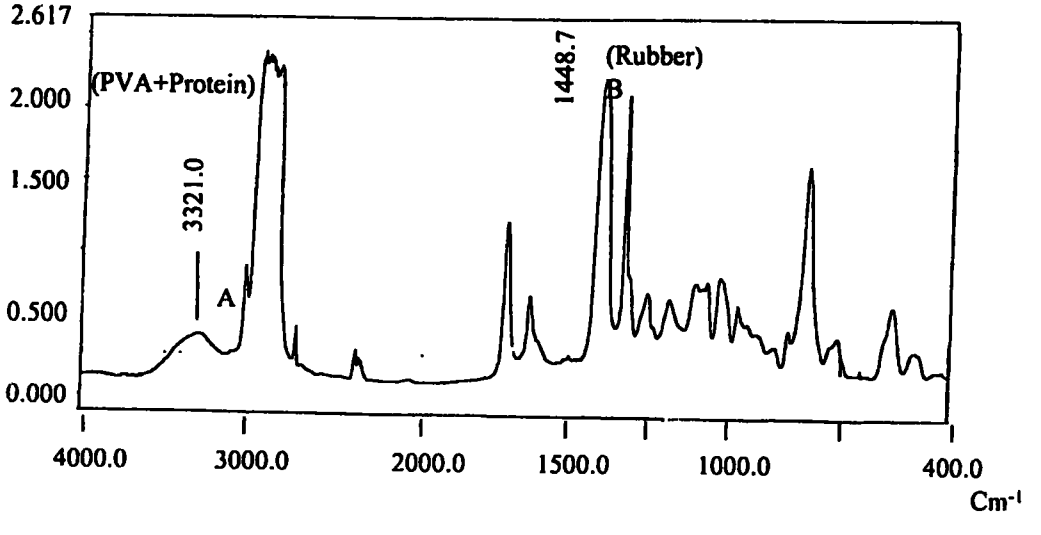

Fig. 7d. FTIR spectrum of 2phr of PVA added RVNRL after 30 min. leaching

Figure 8 shows that the tear strength is increased with increasing PVA concentration for standard process whereas there is not much variation in tear strength when Post-centrifugation process is used.

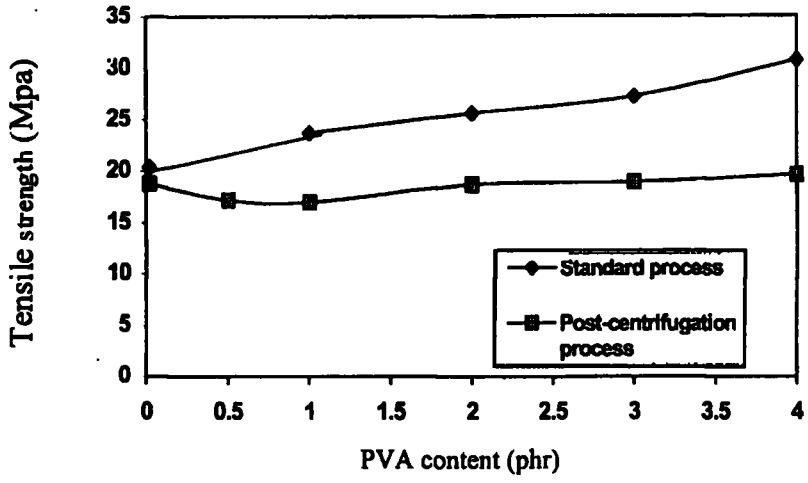

Fig. 8. Effect of PVA on tear strength

Tackiness

Incorporation of water soluble polymer (WSP) showed the drastic decrease of tackiness (Varghese *et al.*, 1999). According to figure 9 tackiness was reduced with increasing PVA concentration. However tackiness of the upper surface and lower surface of the latex films was not same. Upper surface has less tackiness when compared to lower surface. This could be explained as due to migration of PVA and accumulation on the upper surface during drying of latex films. After PVA added latex films were leached, tackiness showed slight increment in both surfaces. This is due to removal of surface PVA during the leaching process. These results were further confirmed by analysing IR spectrums of both surfaces obtained from HATR attachment.

Figure 10a and 10b show the surface spectrum of the upper and lower surface of 3phr of PVA added RVNRL films. Figure 10a. has a higher peak height ratio (0.42) than the peak height ratio (0.32) of figure 10b. This spectrum results showed that upper surface has higher concentration of PVA than the lower surface.

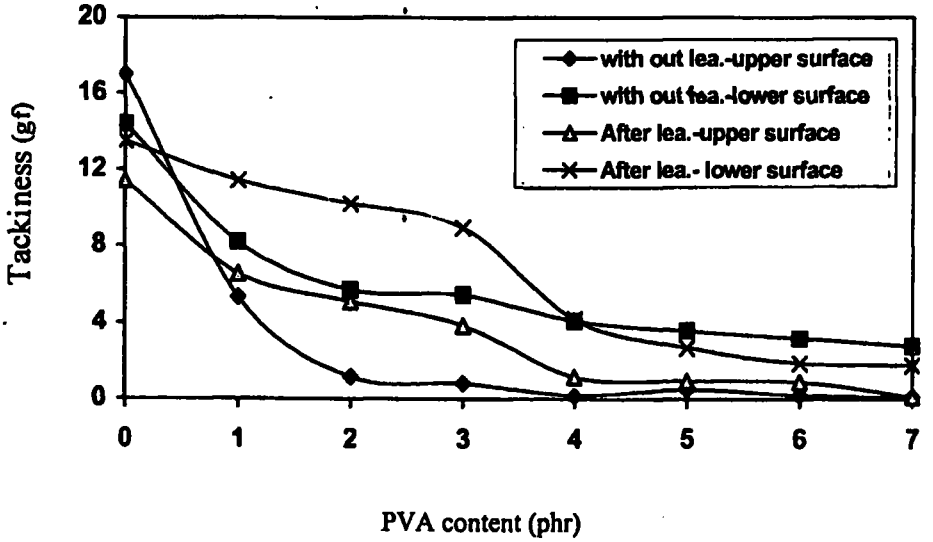

Fig. 9. Effect of PVA on tackiness

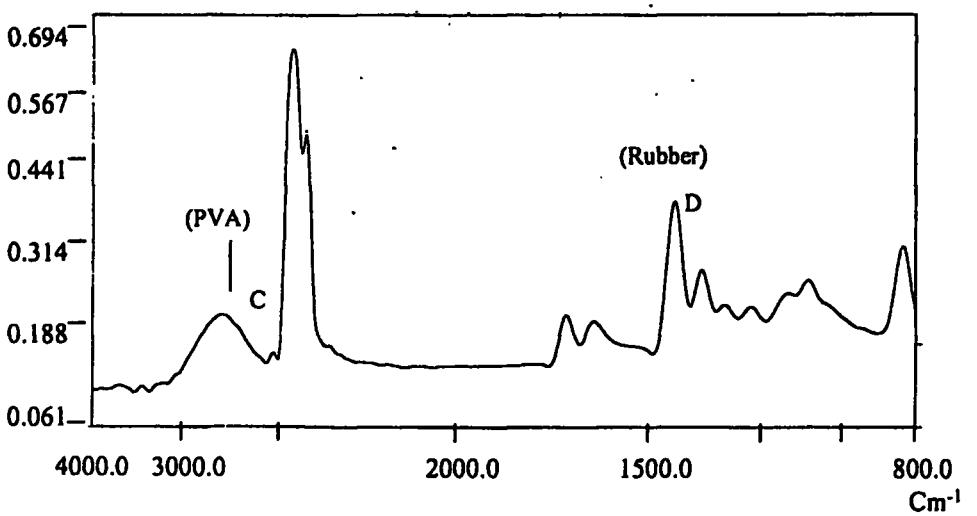

Fig. 10a. HATR spectrum of upper surface of 3phr PVA added RVNRL

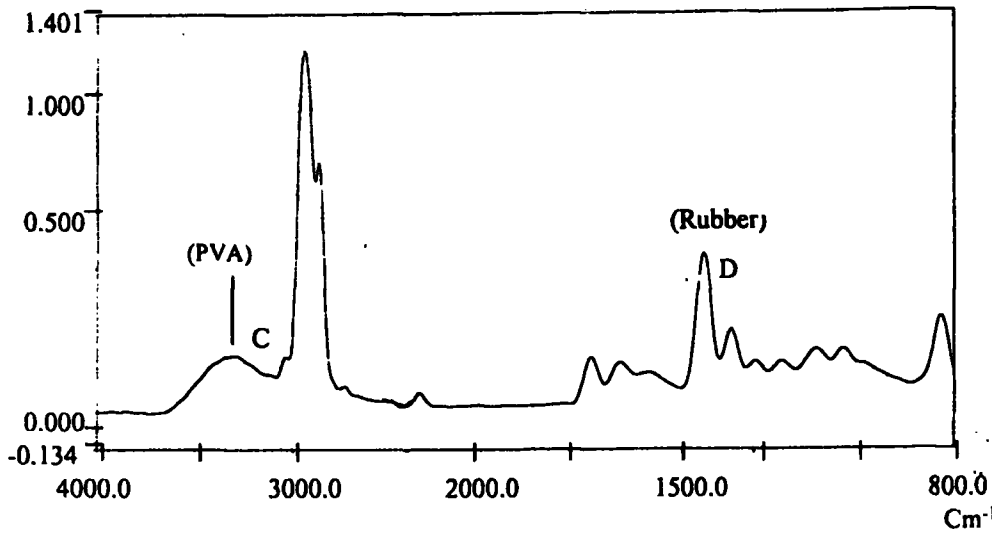

Fig. 10b. HATR spectrum of lower surface of 3phr PVA added RVNRL

CONCLUSION

Based on experimental results following conclusions can be made:

1. Soluble protein content of RVNRL films is reduced more effectively by combined treatment of PVA addition and centrifugation followed by leaching. 3phr of PVA is the optimum concentration to produce almost soluble protein free RVNR latex films.
2. Mixing of PVA with RVNR latex, tear strength is increased whereas tensile strength is decreased with PVA concentration. However tensile and tear strength are almost constant up to 2phr PVA added to RVNR latex followed by centrifugation.
3. Tackiness of the RVNR latex films is decreased with increasing PVA concentration. PVA migrates to the upper surface when latex films are dried and causes a reduction in the tackiness of the RVNR latex films.

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