Effect of Water Soluble Polymers on Radiation Vulcanized Natural Rubber Latex Films

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Abstract

Water soluble polymers (WSP) such as poly(vinyl alcohol), Poly(ethylene oxide) etc. were mixed with radiation vulcanized latex and their vulcanizate properties were studied in detail. Most of the polymers showed a drastic increase in tear strength with water soluble polymer content and a reduction in tackiness of the vulcanized films. The properties of water soluble polymer incorporated vulcanizates depend mainly on the type of the polymer blended into the latex. Addition of water soluble polymer causes fast leaching of soluble proteins from the films, which reduces the prolonged leaching commonly adopted for rubber vulcanizates. Water soluble polymer incorporation improves the ageing properties of radiation vulcanized films and they were highly transparent.

INTRODUCTION

When rubber is irradiated by high energy radiation, hydrogen atoms of the trunk chain, mainly of methylene groups α to the double bonds are ejected and radical sites are formed and these radical sites are combined into C-C crosslinks.[1-4] Heat vulcanizing ingredients such as sulfur, accelerators, benzoylperoxide and other peroxides are known to have very little effect on this reaction,[5-6] but it is possible that these ingredients acting as radical acceptors[7] hinder the radicals from combining with each other and thus retard the radiation vulcanization. Since the radiation vulcanization is carried out in the absence of sulphur and accelerators the products can be obtained uncontaminated by poisonous residues, therefore the future of radiation curing looks bright.

Radiation vulcanized natural rubber latex (RVNRL) has many advantages over the conventional sulphur vulcanized latex, such as absence of nitrosamines, very low cytotoxicity, good degradability and low emission of gases when incinerated.[8-12] However, the technology has not yet been applied in industry on a large scale. The lack of interest of RVNRL in industry is due to the high initial investment and also due to its poor technological properties such as low tensile and tear strength. Processing factors such as leaching and drying can effect the qualities of the latex products. Tensile strength increases quite sharply on drying in heat. The sharp increase in tensile strength on heating is due to the better fusion of the rubber particles and increased chain entanglement of the rubber molecules. Tensile strength also increases upon leaching of the latex films due the better fusion of rubber particles caused by the removal of the water soluble non-rubber components adsorbed on the surfaces of the rubber particles. These effects are also observed in the conventionally pre-vulcanized NR latex[9]. Though radiation vulcanized latex articles are free from poisonous ingredients it is believed that some of the residual proteins can cause allergic reactions in humans. It requires several hours of leaching to remove the proteins completely from the products. Though incorporation of inorganic fillers like silica and talc can increases the modulus, such materials are of less importance. This is because the disposal of inorganic filler incorporated products is difficult due to the high ash content during incineration. In order to overcome the difficulties associated with vulcanized rubber films several methods such as grafting of monomers onto the NR chain, monomer coating, sensitization by new monomers, precipitation of latex proteins with different reagents and leaching of the vulcanizates in different solvents were employed[10].

In this paper organic fillers such as poly (vinyl alcohol) PVA, poly (ethylene oxide) PEO etc. have been tried to improve the technological properties of radiation vulcanized latex. These water soluble polymers (WSP) are incorporated into the irradiated latex and their technological properties are studied in detail.

MATERIALS AND METHOD

Radiation vulcanized films were prepared from the centrifuged latex obtained from Malaysia. The latex was first diluted to 50% total solids with 1% ammonia solution followed by 0.2 phr (parts per hundred rubber) of 10% KOH solution. The sensitizer, n-butyl acrylate, (5 phr) was then added with constant stirring. The irradiation was carried out with γ - rays from a Co^{60} source at a dose rate of 10 kGy/h for 2h. The irradiated latex is then mixed with different water soluble polymers, as 10% solutions, in different proportions. The films were then cast on raised glass plates and air dried till transparent. The dried films were leached, in 1% ammonia solution for 24h and post cured in an air oven at 80°C for 1h. Poly (vinyl alcohol), PVA supplied by Kurary Co. Ltd., Japan, has a degree of polymerization of 98 - 99%. Poly (vinyl alcohol) with saponification 78.5 - 81.5 % was supplied by Nippon Gohsei Ltd., Japan. Poly (ethylene oxide), PEO E-30 (mol.wt $3x10^5$-$5 x 10^5$) and PEO E-160 (mol. wt. $3.6x10^6$ - $4x10^6$) were supplied by Meisei Chemical Works, Ltd. Japan. Water soluble polymer solutions were prepared in an autoclave at 120 °C for 2 h. The tensile measurements were carried out using a tensile testing machine, Strograph-R1 (Toyoseki Co. Ltd). The tackiness of the films was measured using a probe Tackiness Tester model TAC II (Reshca Co. Ltd.). Transparency of the films was measured using a Direct Reading Hazemeter (Toyoseki Co. Ltd). IR studies were done using a FTIR-8100A machine (Shimadzu Corporation, Japan). An optical microscope of Nikon Ltd. Japan, was used for the observation of surfaces. Protein measurement was carried out as per ASTM D 5712. The precipitated protein was redissolved in minimum volume of 0.1 N NaOH and then analyzed using Pierce BCA method. For assessing the resistance to ageing of latex films, tensile test pieces were kept in an air circulated oven, maintained at a temperature of 100°C for 24h. The tensile properties of these samples were determined 24h. after the ageing period and compared with those of the original samples.

RESULTS AND DISCUSSION

Figure 1 shows the variation of tensile strength of two WSP namely, PVA and PEO (E-30) incorporated RVNRL films.

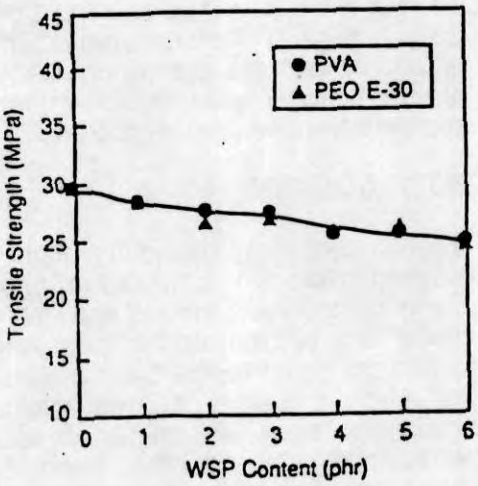

Figure 1: Variation of tensile strength with water soluble polymer.

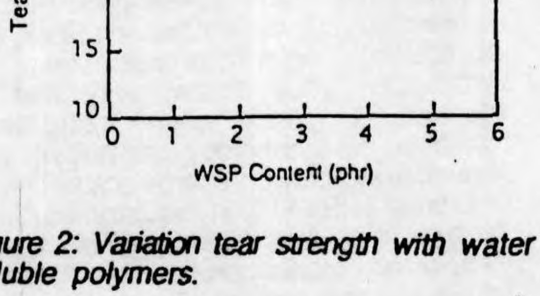

Figure 2: Variation tear strength with water soluble polymers.

Though we have conducted experiments with a number of polymer solutions only important results are shown here. It is observed that irrespective of the nature of the polymer, WSP incorporation decreases the tensile strength of RVNRL films. In the case of PEO E-30, for a WSP content of 6 phr, TS remains more or less constantafter an initial decrease. The initial decrease is due to the hindrance of strain crystallization of NR by the addition of WSP. Variation of tear strength with water soluble polymer content is also shown in Figure 2. Tear strength increases continuously with both the polymers. Here the effect is more pronounced in the case of PVA incorporated RVNRL films. The FTIR spectra of NR and WSP incorporated NR showed that absorption at 3280 cm $^{-1}$ is considerably high (data not given). This is due to the presence of hydroxyl groups from PVA. The shifting of this peak towards the lower wave number shows the possibility of hydrogen bonding. The continuous increase in tear strength with WSP may be due to hydrogen bonding between WSP and NR. This also indicates that water soluble polymers are present in RVNRL films even after the long (24 h) leaching process.

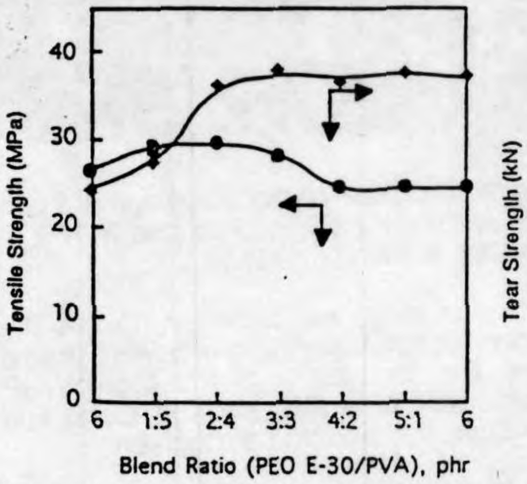

Figure 3: Variation of tensile strength and tear strength with blends water soluble polymers.

Further evidence for the presence of WSP in RVNRL films after the leaching can be seen from the optical photos of the surfaces and also from the enhanced ageing properties of WSP incorporated films which will be discussed later. Since we found each polymer has its own characteristic effect on the physical properties of RVNRL films, in order to get an optimum balance of almost all properties we blended different WSP before adding the same into the RVNRL. The blends were prepared by mixing PVA and PEO (E-30) in different proportions. Figure 3 shows the effect of TS and tear strength. At equimolar composition these blends have a balanced variation in tensile and tear properties. PEO E-160, a high molecular weight poly (ethylene oxide), also showed the same effect (Figure 4). Due to the processing difficulties with PEO E-160 we selected only PEO E-30 for further studies.

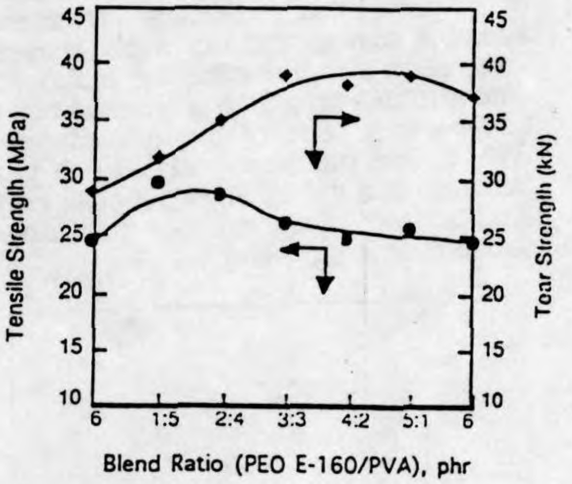

Figure 4: Variation of tensile strength and tear strength with blends of water soluble polymers.

Figure 5 shows the variation in tensile strength with an equimolar composition of PVA and PEO E-30. These equimolecular

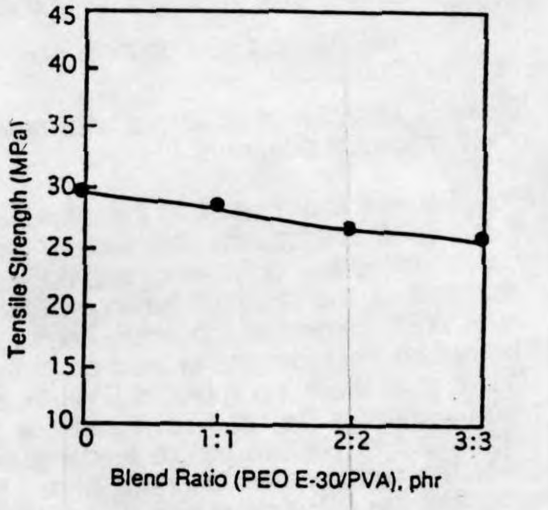

Figure 5: Variation of tensile strength with blends of water soluble polymer.

blends incorporated RVNRL films showed almost constant variation in tensile strength upto 6 phr of WSP content though it is less than the control sample.

Dipping factories are facing a serious problem with the high tack of the products from RVNRL latex and also from conventionally vulcanized latex. The ackiness is often too high to permit stripping of the products from the former. The tackiness depends largely on the origin of the latex and seems unrelated to the degree of crosslinking. Surface chlorination, hydrogel coating and tap water immersion have been tried to reduce the tackiness of natural rubber films.[13-15] It is reported that the transparency, one of the advantages of RVNRL films has been reduced due to the formation of a thin layer of deposits on the film surface due to the dissolved substances in tap water[16].

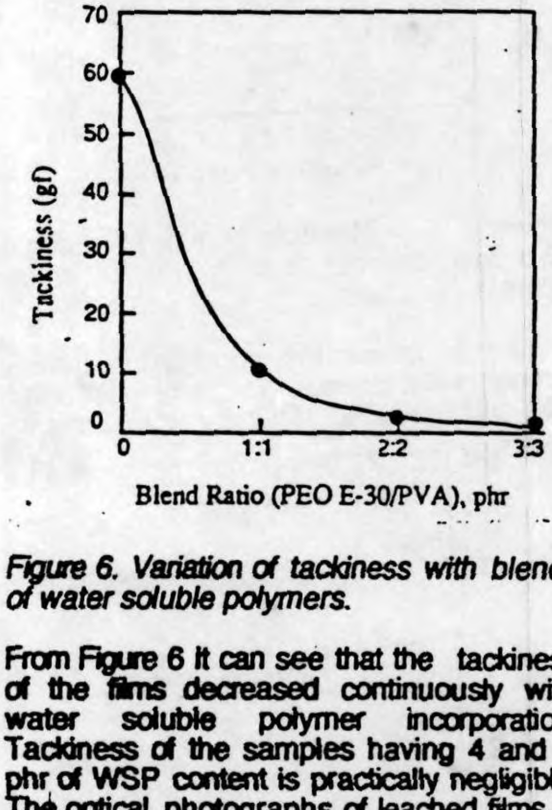

Figure 6. Variation of tackiness with blends of water soluble polymers.

From Figure 6 it can see that the tackiness of the films decreased continuously with water soluble polymer incorporation. Tackiness of the samples having 4 and 6 phr of WSP content is practically negligible. The optical photographs of leached films of RVNRL and WSP incorporated RVNRL are given in Figures 7a and 7b. Figure 7a is the surface of NR film before leaching and 6b is the surface after leaching. It can be seen that the NR surface being smooth is very tacky. On the contrary

Figure 7 (a). Optical photomicrograph of RVNRL film before leaching (X 40).

7b is the optical photograph of RVNRL film incorporated with 3 phr each of PVA and PEO E-30 after leaching. This

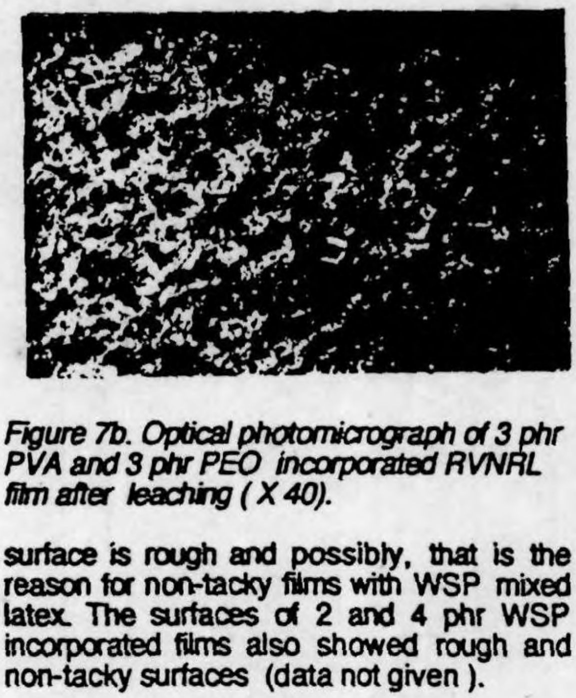

Figure 7b. Optical photomicrograph of 3 phr PVA and 3 phr PEO incorporated RVNRL film after leaching (X 40).

surface is rough and possibly, that is the reason for non-tacky films with WSP mixed latex. The surfaces of 2 and 4 phr WSP incorporated films also showed rough and non-tacky surfaces (data not given).

We found that mixing of WSP in to latex causes fast leaching of soluble proteins. The WSP mixed RVNRL films are leached for different extraction periods in distilled water and the soluble protein content are given in Table 1. Before leaching WSP incorporated films have an extractable protein content of 3.30 mg per gram of rubber. However, after leaching for 5 minutes 90% of the soluble proteins are leached away which results in a film with residual protein 0.35 mg and after 15 minutes leaching there is no detectable

Table 1: EFFECT OF LEACHING TIME ON EXTRACTABLE PROTEIN

Leaching Time (Min.)	Extractable Proteins (mg/g)
0	3.30
5	0.35
10	0.20
15	Not detected
20	Not detected
25	Not detected
30	Not detected
35	Not detected
40	Not detected

protein in the films. However in the case of RVNRL films with out WSP it takes 2 h to leach 97% of soluble protein [16]. After 24 h of leaching the residual protein content is 50µg. This means that water soluble polymers in RVNRL facilitates the fast leaching of soluble proteins. A possible reason for this fast leaching is that soluble proteins have more affinity towards water soluble polymers than the rubber hydrocarbon. When water soluble polymers are mixed with latex the soluble protein forms complex with WSP, from there it goes into the water during leaching. Since WSP incorporation causes fast leaching of latex proteins, the prolonged leaching time of latex products can be reduced considerably. This will reduce the loss of natural antioxidants present in natural rubber latex.

The transparency of the RVNRL films is also important in the medical field as these materials can be used as endoscopic balloons for internal examinations. The transmission of Ng-Yag laser through the balloon is higher (98%), than that of the sulfur vulcanizate (65%). The balloon is thin and transparent enough to perform endoscopic examinations and laser treatment throughit[17]. The high transparency of the balloon is also favourable for laser treatment to prevent accidental burning and destruction of the optical laser tip. It is found that the transparency of the films depend on the type of the WSP incoporated into the RVNRL. The RVNRL films mixed with 75.5 to 81.5% saponified PVA has low haze and high transparency. The results are shown in Figure 8. Though the reason for the low haze is unknown, it is possibly due to the formation of a complex of WSP with the non-rubber components, which impart haze to natural rubber film.

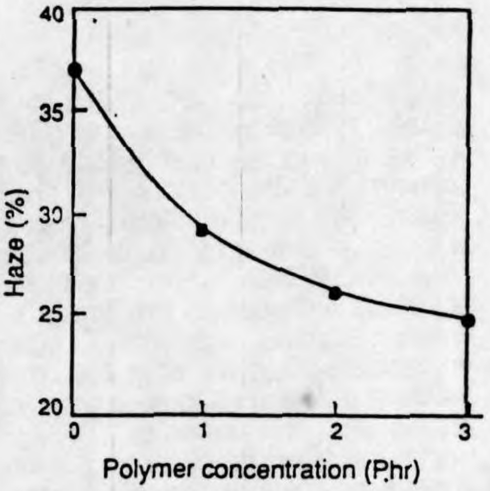

Figure 8: Variation of Haze with water soluble polymer content.

The ageing properties of WSP incorporated RVNRL are shown in Figure 9. As C-C bonds have higher bond energies than C-S bonds, the heat stability of the RVNRL films is superior to that of a sulphur vulcanizate [15]. However the ageing properties of the radiation vulcanizate is deteriorated by leaching with ammonia solution compared to those of the sulfur vulcanizate. One of the reasons for the poor ageing properties of the radiation vulcanizate is the absence of dithiocarbamates that function as strong

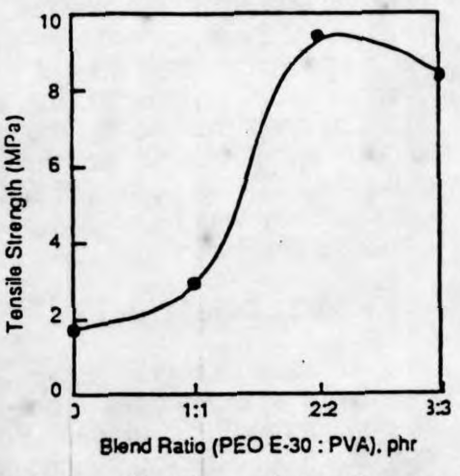

Figure 9: Variation of tensile strength after aging at 100°C of RVNRL films with water soluble polymer.

antioxidants. However, WSP incorporated RVNRL films show better ageing resistance. A five fold increase in tensile strength is obtained with the addition of 4 phr of WSP (Figure 9). Another reason for the poor resistance to thermal-oxidative degradation of leached RVNRL latex is due to the elution of natural antioxidants present in it[15]. Since water soluble polymer incorporated vulcanizate requires only few minutes of leaching retention of some amount of natural antioxidants is possible. The saturated backbone structure of these polymers also contributes towards the high thermal ageing resistance of WSP incorporated films.

CONCLUSIONS

Mixing of water soluble polymers such as PVA and PEO E-30 into the irradiated natural rubber latex will increase the tear strength while tensile strength shows only a small decrease. Irradiation increases the soluble protein content in the serum phase where as that in the rubber phase decreases. WSP incorporated RVNRL has a fast leaching rate of soluble proteins and the films are almost free of soluble proteins after 15 minutes of leaching at room temperature. WSP is found to be retained in the rubber film even after the long leaching in water which imparts better ageing resistance to the rubber films. The surfaces of WSP incorporated RVNRL films being rough have very low tackiness and a few minutes leaching in water will result in surfaces which are not at all tacky. Transparency of the radiation vulcanized films can be increased by the addition of suitable water soluble polymers into the latex. Addition of PVA (78.5 to 81.5% saponification) was found to produce highly transparent RVNRL films.

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