

VARIATION OF PHYSICO-CHEMICAL PROPERTIES OF RADIATION CROSSLINKED RUBBER WITH STORAGE TIME

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Abstract The effect of storage on physico-chemical properties of non-irradiated natural rubber and radiation vulcanized natural rubber (RVNR) were evaluated. The rubber films were stored under two different conditions, namely in open air and sealed polyethylene bags. The antioxidant, tris(nonylated phenyl) phosphite (TNPP) was used for preventing degradation of RVNR films. Gel content, cross-link density, tensile strength at break and 500% elongation of rubber films were measured. The results show that the retention (%) of tensile properties of rubber films with TNPP is higher than that of rubber films without antioxidants. The rubber films stored in polyethylene bags also show better retention of tensile properties than those of rubber films stored in open air.

Keywords: Storage; Radiation; Tensile Properties; Antioxidant.

INTRODUCTION

The use of radiation vulcanized natural rubber (RVNR) in industry largely depends on the storage stability of its products. The natural antioxidants present in natural rubber latex (NRL) may be destroyed^[1, 2] when NRL is vulcanized by radiation. Leaching of the rubber films or products elutes water-soluble antioxidants. So the storage stability of RVNR products becomes poor. To improve thermal oxidative resistance of RVNR products additional antioxidant is needed. Wan Manshol *et al.*^[3] studied the storage stability of coagulant dipped RVNR films at room temperature and found that the mechanical properties like tensile strength decrease with the increase in the lengths of shelf time but the use of antioxidants like Arbostab Z, Ralox LC, Irganox 1520 and Irganox 1010 helps to protect the properties of rubber films. Rosa *et al.*^[4] investigated various properties of irradiated latex and its film after storing them up to 12 months and found that the viscosity of the latex as well as the tensile properties of rubber film decrease with the increased length in shelf time but remain within acceptable limits (22 MPa) even after storage for 12 months.

Antioxidants, tris(nonylated phenyl) phosphite (TNPP) and 2,5-di-*tert*-amylhydroquinone (DAHQ) were found to resist thermal oxidative degradation of RVNR films to some extent^[5, 6]. Yoshii *et al.*^[7] tested 12 different antioxidants and found that TNPP and DAHQ are the most effective antioxidants in preventing degradation of rubber films.

In the present investigation the properties of irradiated rubber films were evaluated after storing under two different conditions and compared to that with non-irradiated rubber films. The effects of the antioxidants, TNPP on the protection of the RVNR films from degradation were also studied.

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EXPERIMENTAL

Collection of Natural Rubber Latex (NRL)

The field NRL was collected from Satgaon Rubber Estate, Sylhet under Bangladesh Forest Industries Development Corporation (BFIDC). Immediately after collection of NRL from rubber trees, it was preserved with 20–25 mL/L of 25% ammonia solution (BDH, England). A laboratory scale centrifuge (model SPL-100, Saito Separator Ltd., Japan) was used for the concentration of latex to the extent of ~60% total solids content (TSC).

Irradiation of NRL

The concentrated NRL was diluted to 50% TSC by adding 1.5% dilute ammonia solution. Five parts per hundred rubber (phr) of *n*-butyl acrylate (*n*-BA) was used as radiation vulcanization accelerator (RVA). It was added to the diluted latex dropwise and mixed by stirring with a magnetic stirrer for 1 h. RVA mixed NRL was irradiated with cobalt-60 gamma source for the total radiation doses of 12 kGy^[8] at the dose rate of 5 kGy/h.

Addition of Antioxidant and Preparation of Rubber Films

Antioxidant, TNPP obtained from Seiko Chemical Co. Ltd., Japan, about 1 phr^[5] was added to the irradiated latex and stirred by the magnetic stirrer for 1 h. The irradiated rubber latex with and without antioxidant and non-irradiated rubber latex were cast on raised rimmed glass plates. The rubber films were dried in air until transparent. The air-dried rubber films were leached in tap water for 24 h and again dried in air till transparent and heated in an oven at 70°C for 1 h^[9].

Storage of Rubber Films

The rubber films were stored under two different conditions; (i) some were kept on the top of a wood bench and (ii) some were kept inside the sealed polyethylene bags (thickness of polyethylene was ~0.107 mm) and placed on the same bench. The temperature and relative humidity of the laboratory were 25–30°C and 45%–50%, respectively.

Measurement of Properties

The tensile properties were measured by using INSTRON testing machine (model 1011, England) interfaced with a personal computer. The ISO method, ISO 37–1977 (E) was used to measure tensile strength. British Standard (BS 1673: part 4, 1953) was then used to determine gel content. The degree of cross-linking of rubber film was determined by measuring the swelling ratio (*Q*). It was calculated on the basis of Flory and Rehner equation^[10].

RESULTS AND DISCUSSION

The gel contents of the irradiated rubber films containing added antioxidant and without antioxidant were measured according to the British Standard under the same storage condition. Figures 1 and 2 show the results of the gel contents of the rubber films stored in open air and polyethylene bags, respectively. The gel contents of the rubber films without and with antioxidant TNPP increase to some extent up to 3–4 months and then possess similar values up to about 15 months. After that period these start to decrease. The increasing trend of gel content may be attributed to the formation of hydrogen bond *i.e.* physical crosslinking between rubber molecules and proteins present in rubber during storage^[11]. Such physical crosslinking is supposed to arise from the oxidation of natural rubber (NR) to carbonyl and epoxide group on storage. The gel content is related to the crosslinking density in the rubber film. As the crosslinking increases the gel content also increases. The increased crosslinkages of the rubber molecules are responsible for the improved tensile properties of the films. The changes of crosslinking densities of the rubber films are presented graphically in Figs. 3 and 4. It is seen that the crosslinking density increases to some extent with the increase in lengths of storage time for a few months for these rubber films without antioxidants and containing TNPP. The reason for such increment of crosslinking is the same as stated above.

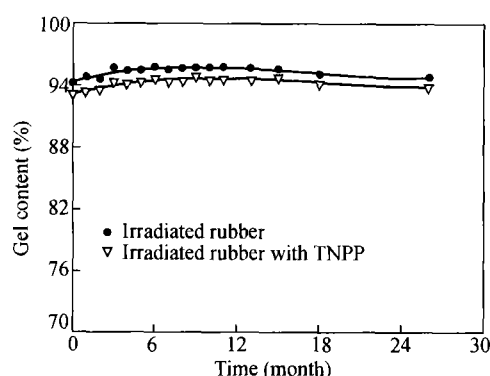


Fig. 1 Effect of storage time on gel content of rubber films in open air

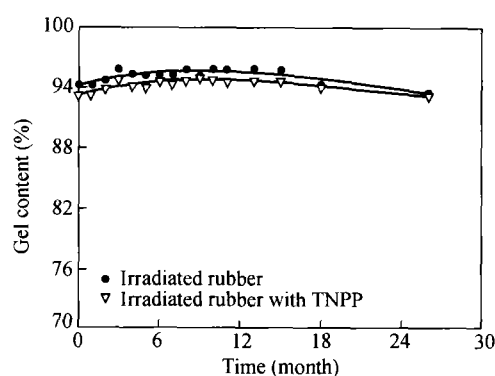


Fig. 2 Effect of storage time on gel content of rubber films in polyethylene bags

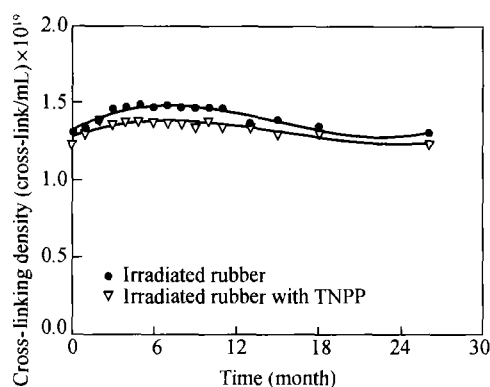


Fig. 3 Effect of storage time on cross-linking density of rubber films in open air

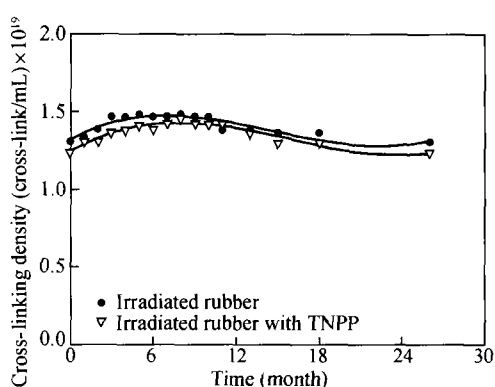


Fig. 4 Effect of storage time on cross-linking density of rubber films in polyethylene bags

Figures 5 and 6 show the effect of storage time on the tensile strength at break of various types of rubber films stored in the open air and polyethylene bags, respectively. It is found from these figures that the initial values of tensile strength at break of the irradiated rubber films are much higher than that of the non-irradiated rubber films. This is because of the cross-linkage between the molecules of rubber chain caused by the action of gamma rays^[12]. The rubber latexes were irradiated with a total radiation doses of 12 kGy. It is remarkable to note that the values of tensile strength at break of non-irradiated rubber films and RVNR films without and with antioxidant TNPP increase to some extent after storing the films under these conditions. The increase in tensile strength at break of rubber films continues up to 4–5 months of storage, remains almost unchanged up to about 15 months and then tends to decrease. The decreasing trend of tensile strength at break of stored films may be due to a breakdown of cross-linking caused by oxidation. But the lowering of tensile strength at break is not so rapid. After 26 months the values of tensile strength at break of the irradiated films without antioxidants are ~22 MPa and ~24 MPa in open air and polyethylene bags, respectively. The corresponding values of tensile strength at break of the rubber films containing TNPP are higher (~24 and ~26 MPa). It is consistent with the report that TNPP can resist degradation of the film^[5, 6, 7]. If a comparison is made among the rubber films stored separately in open air and polyethylene bags it is found that the tensile strengths at break of rubber films in two different conditions maintain the same trend of change for all types of rubber films. But the rubber films stored in polyethylene bags possess higher tensile strength at break than those of rubber films stored in open air. This may be due to limited oxygen and moisture in closed atmosphere than those of open atmosphere.

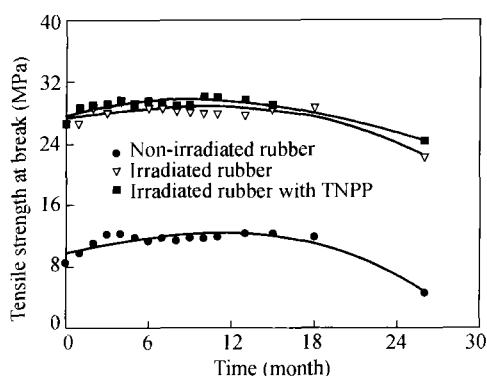


Fig. 5 Effect of storage time on tensile strength at break of rubber films in open air

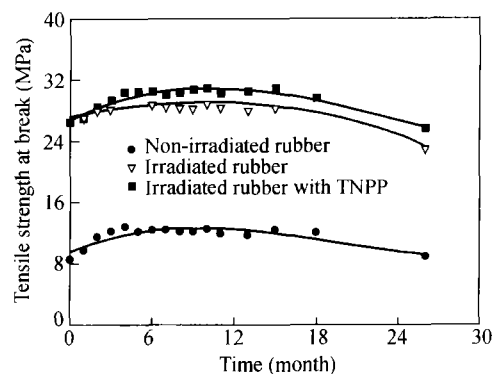


Fig. 6 Effect of storage time on tensile strength at break of rubber films in polyethylene bags

The strength at 500% elongation of these rubber films were measured at the same interval of time as for the tensile strength at break and the results are presented in Figs. 7 and 8. It is found that the strength at 500% elongation of the irradiated rubber films is much higher than that of the non-irradiated rubber films. Before storage it is ~1.5 MPa for non-irradiated rubber films and ~3 MPa for irradiated rubber films. As the tensile strength at break increases with the crosslinking of rubber molecules by radiation, the strength at 500% elongation also increases. After storage the strength is found to increase to some extent. As a matter of fact the nature of these curves is very much similar to that of the tensile strength curves. The strength at 500% elongation of the rubber films stored in polyethylene bags possesses higher values than that of the rubber films stored in open air.

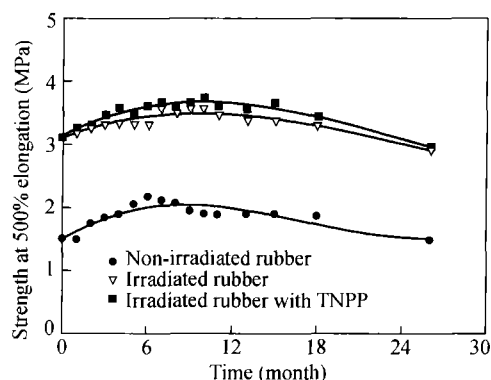


Fig. 7 Effect of storage time on strength at 500% elongation of rubber films in open air

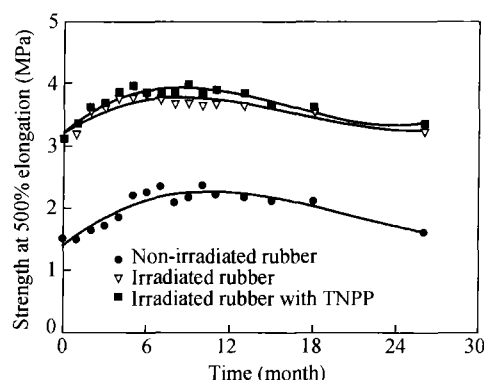


Fig. 8 Effect of storage time on strength at 500% elongation of rubber films in polyethylene bags

CONCLUSION

It can be concluded that higher tensile properties are obtained if the rubber films are stored in a sealed polyethylene bag. The rubber films with antioxidant TNPP also shows higher tensile properties than that of rubber films without antioxidants. According to Japanese Industrial Standard (JIS), American Standard of Test Method (ASTM) and British Standard (BS) the minimum values of tensile strength at break for dipped goods like hand glove should be ~24, ~21 and ~20 MPa, respectively. In this investigation it is found that the values of tensile strength at break of the rubber films remain within the prescribed limits for about 26 months of storage.

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