

Degradability Testing of Radiation-Vulcanized Natural Rubber Latex Films

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SYNOPSIS

The degradability under various conditions of five kinds of radiation-vulcanized natural rubber latex (RVNRL) films was studied. The treatments were leaching in methanol, leaching in 1% ammonia solution, mixing with tris(nonylated phenyl)phosphite (TNP) antioxidant, blending with poly(methyl methacrylate) (PMMA), and grafting with PMMA. Comparisons were made with sulfur-vulcanized natural rubber latex (SVNRL) film. RVNRL films and SVNRL film can be kept for a long time when indirectly exposed to sunlight at room temperature. However, the former degraded much more rapidly than did the latter. TNP was found to be very suitable as an antioxidant to prolong the life of RVNRL films under dry conditions. PMMA, either blended or grafted with RVNRL, was ineffective in the prevention of deterioration of RVNRL films. The rapid degradation of RVNRL products could be an advantage over SVNRL products in environmental and wildlife conservation.

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INTRODUCTION

Radiation-vulcanized natural rubber latex (RVNRL) products have been shown to have the following advantages over conventional sulfur-vulcanized natural rubber latex (SVNRL) products¹: the absence of carcinogenic nitrosamines,² low cytotoxicity,³ transparency, and softness. These properties are due to the absence of sulfur, zinc oxide, and dithiocarbamates that occur in conventional SVNRL. However, the strength and aging properties of RVNRL products has been reported to be inferior to those of SVNRL. The poor aging of RVNRL is due to the absence of dithiocarbamates, which function as antioxidants, and to the elution of naturally occurring antioxidants during the leaching process.[†] RVNRL products degraded more rapidly than did the SVNRL products.⁴ This may actually be advanta-

geous for the manufacture of products such as balloons. It is believed that the release of toy/advertising balloons that are not degradable might be harmful to the environment and wild animals when they return to the ground.

In this work, the degradability of five kinds of RVNRL films in comparison with SVNRL film was tested, using both natural degradation and accelerated degradation by a weather meter machine.

EXPERIMENTAL

Materials

Highly stabilized concentrated natural rubber latex (60% dry rubber content) was obtained from Sri Lanka. Sulfur prevulcanization of natural rubber latex was supplied from the Fuji Latex Co. Technical-grade monomer of methyl methacrylate (MMA) was passed through an alumina Woelm B-super 1 column to remove the inhibitor before use. TNP was supplied by the Seiko Chemical Co. All chemicals were used as received without further purification.

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† The aging properties of RVNRL products can be improved by the immobilization of the natural antioxidant with alcohol.⁵

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Sample Preparation and Irradiation

RVNRL Films Without Antioxidant

Natural rubber (NR) latex was diluted with 1% ammonia solution to a 50% dry rubber content (DRC). *n*-Butyl acrylate (*n*-BA), 5 phr, was added to the diluted NR latex while stirring. Stirring was continued for 1 h and the mixture was then irradiated with gamma rays from the Co-60 source at a total dose of 1.5 Mrad. The irradiation was conducted at a constant dose rate of 1 Mrad/h at room temperature. Films were then cast.

RVNRL Films with 2 phr of Tris(nonylated phenyl)phosphite (TNP) Antioxidant⁶

RVNRL was prepared as described in the above procedure and 50% TNP emulsion was prepared according to formula in Table I (using a Yamato Ultradisperser Model LK-22 at high speed: 2400 rpm). Fifty percent TNP emulsion was added to the irradiated latex as specified and stirred about 15 min. Films were then cast.

RVNRL Films Without Antioxidant and Leached in Methanol or 1% Ammonia Solution

RVNRL films were leached in methanol or in 1% ammonia solution for 24 h at room temperature.

RVNRL Blended with PMMA⁷

The emulsion polymerization of MMA was first prepared by a redox system: $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{NaHSO}_3$ as the initiator and with sodium lauryl sulfate as the emulsifier, at a polymerization temperature of 50°C. The emulsion polymerization procedure followed was that set out by Sonsuk and modified from Egusu and Makuuchi.^{7,8} Emulsion polymerization was carried out in a 500 mL stainless-steel vessel that was thermostated to 50°C. MMA, 180 g, deionized water, 320 g, and sodium lauryl sulfate, 1.2 g, were poured into the reaction vessel and brought to the polymerization temperature. The mixture was stirred by a paddle-type stirrer at 150 rpm with ni-

trogen gas bubbling and then left for 40 min to attain temperature equilibrium and to remove oxygen from the system. $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.2 g, and NaHSO_3 , 0.2 g, each dissolved in 10 mL of water, were added to the system at 30 min intervals. After 3 h, the temperature of the vessel was lowered to room temperature. The obtained latex was passed through a stainless-steel 200 mesh to remove coagulum. An ammonia solution was added to the emulsion to bring the concentration of ammonia in the serum to 1%. The total solid content in the emulsion was 33%, determined by drying. The emulsion latex was then mixed with RVNRL at 25% v/v (18 phr) (suggested by Sonsuk⁷ for optimum tensile strength).

RVNRL-grafted PMMA⁷

RVNRL was prepared as described above. The obtained RVNRL was diluted with 1% ammonia solution to 30% total solid content (TSC). MMA monomer, 40 phr (suggested by Sonsuk⁷ for optimum tensile strength), was emulsified using oleic acid (0.5 phr) and then mixed thoroughly with the diluted RVNRL and kept overnight. The mixture was irradiated by gamma rays at total dose of 1 Mrad.

Film Preparation

Films were prepared by casting 25 mL of latex on a level 17×11 cm glass mold and dried at room temperature. The resulting dried films were immersed in distilled water[†] for 24 h to leach out water-soluble components and dried subsequently at room temperature until transparent. They were then dried again at 80°C for 1 h.

Degradability Testing

1. Preparation of the films for testing was done in the following ways:
 - (a) Naturally degraded: Rubber films were placed outdoors in three positions:
 - (i) On the ground, for exposure to natural air and sunlight; the maximum and minimum temperatures were 23 and 1°C, respectively; films were tested at 7 day intervals.

Table I Formula for 50% TNP Emulsion

Ingredient	Weight (g)
TNP	100
20% sodium dodecyl sulfate	10
10% ammonium casein	20
Bentonite	0.5
Distilled water	70

[†] In the case of RVNRL without an antioxidant, rubber films were immersed in methanol, which acts as a natural antioxidant fixer; others were immersed in 1% ammonia solution, which acts as a strong leaching agent.

- (ii) Ten centimeters below ground, where maximum and minimum temperatures were 9 and 3°C, respectively; films were tested at 7 day intervals.
- (iii) Suspended 1 m above the ground; maximum and minimum temperatures were similar to those observed at ground level. Films were tested at 15 day intervals.
- (b) Degradation by a weather meter machine: Films were degraded with a Sunshine Xenon Long Life Weather Meter (Suga Test Instrument Co.). Films were fixed on a sample holder inside the weather meter, irradiated with light from a xenon lamp, and held at various temperatures, both with and without wall-cooling water, under the following conditions:
- 30°C/light from the xenon lamp, with cooling water.
 - 30°C/light from the xenon lamp, without cooling water.
 - 50°C/light from the xenon lamp, without cooling water.

Films were taken out for testing at controlled times, depending on the prescribed conditions (set out above).

- (c) Control films: Films were hung at room temperature as a control group (i.e., unexposed to degradation factors). The maximum and minimum temperatures were 24 and 13°C, respectively; films were tested at 15 day intervals.
- (d) Aging Properties Test Group: Films were aged in a geeroven at 70°C over a 10 day period; films were tested daily.
2. Test Procedures: The mechanical properties of the original and degraded rubber films were measured with a Toyoseiki tension meter (Strograph-R1) according to the Japan Industrial Standard (JIS) K6301 method. The research was carried out at the Radiation Processing Development Laboratory, TRCRE, JAERI, from December 1991 to April 1992.

RESULTS AND DISCUSSION

Tensile Strength of the Original Rubber Films

The tensile strength of the original rubber films are summarised in Table II. The RVNRL film leached

Table II The Tensile Strength of the Original Rubber Films

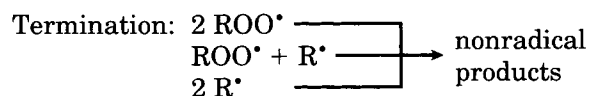
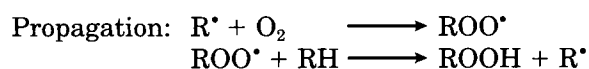
Type of Rubber Film	Average Tensile Strength (kg/cm ²)
RVNRL leached in MeOH	309
RVNRL leached in 1% NH ₄ OH	242
RVNRL with TNP antioxidant	303
RVNRL + PMMA (18 phr)	336
RVNRL-g-PMMA (40 phr)	330
SVNRL	371

in MeOH has a tensile strength similar to that of RVNRL with TNP antioxidant film; the tensile strength of both types of rubber film are higher than that of RVNRL film leached in 1% NH₄OH. This is due to the presence of some nonrubber substances, such as proteins, which were removed from the rubber film with a strong leaching agent: 1% NH₄OH. The proteins act as a binder between rubber molecules through hydrogen bonding and result in increased tensile strength of the rubber film. PMMA, in RVNRL film, acts as a reinforcement filler for RVNRL film and makes the tensile strength of the rubber film greater than that of the unfilled RVNRL film.

Degradation of Natural Rubber Film

Natural rubber (NR), like any other polymer, is susceptible to oxidative degradation, which is accelerated mainly by heat, humidity, light, oxygen concentration, etc. Chain scission may occur as a result of the following reaction mechanism:

Initiation: Production of R[•] or RO₂[•] radicals



Chain scission can be detected by a number of physical method techniques, such as a fall in molecular weight, stress relaxation, sol-gel analysis, and stress-strain measurements. The last technique was chosen to characterize the degradation of rubber film in this experiment.

Degradation by oxygen causes NR to soften, predominantly through cutting of the elastomer chain,

which causes the tensile strength to drop very rapidly and the surface to become soft and sticky.

Effect of Leaching Agents on Degradability of RVNRL Film

Leaching in 1% NH_4OH

NR films are normally leached in 1% ammonia solution to remove impurities. Data on degradability testing obtained from these rubber films indicates a rapid degradability property. A sharp decrease in tensile strength was observed after a few days in field studies.

NR latex is known to contain several natural antioxidants. Among these, tocotrienols, phospholipids, amino acids, phenols, and betaines are reported to have these functions.⁹ Previous experiments in our laboratory indicated that those substances were removed during the leaching process with 1% ammonia solution, and the aging property of the leached rubber film was correspondingly poor.¹⁰

Leaching in MeOH

Data on degradability testing obtained from these rubber films indicated that the degradability property was slightly slower than was RVNRL leached in 1% ammonia solution, because MeOH denaturizes the proteins (natural antioxidants), resulting in their precipitation and in being less soluble in aqueous media during the leaching process. This meant that protein was retained in the rubber films and affected the degradability property of these films, making it slightly slower than that of films leached in 1% ammonia solution.

Natural Degradation

Rubber Films Degraded on the Ground (Fig. 1)

RVNRL film without antioxidant, those leached in methanol and leached in 1% ammonia solution, and those with TNP antioxidant were cracked and softened and the surfaces tackied after 2, 2, and 3 weeks' exposure, respectively. RVNRL films blended and grafted with PMMA were cracked and hardened after 3 weeks' exposure, whereas surface cracking was observed in SVNRL films after 6 weeks.

There was a sharp decrease, approaching zero kg/cm^2 , in the tensile strengths of RVNRL films leached in methanol, in 1% ammonia solution, and with TNP antioxidant, after 4, 2, and 3 weeks' exposure, respectively; subsequent tests of tensile strength could not be made because of the stickiness

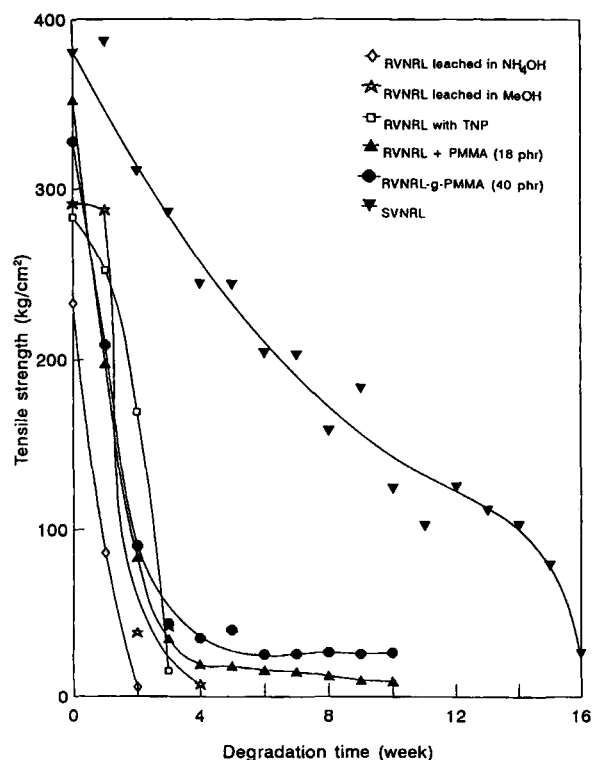


Figure 1 Relationship between tensile strength and degradation time of rubber films placed on the ground.

of the degraded films. Tensile strengths of RVNRL films with PMMA also sharply decreased over an exposure period of 4 weeks; strengths remained almost constant thereafter at levels of $16 kg/cm^2$ (5% retention of tensile strength) and $25 kg/cm^2$ (8% retention of tensile strength), respectively. The tensile strength of SVNRL film decreased steadily at the beginning of the test period and more sharply toward the end, to $26 kg/cm^2$ (7% retention of tensile strength), after 16 weeks.

Notable among these results is the fact that all RVNRL films degraded more rapidly than did SVNRL films and that TNP antioxidant is ineffective in prolonging the life of RVNRL films.

Rubber Films Placed 10 cm Below Ground (Fig. 2)

Hardening, due to exposure to low temperatures, was observed on RVNRL films, while some brown color points were observed on SVNRL films. This was thought to be due to the decomposition of some chemical additive in the rubber latex.

Only slight degradation was observed. The rubber films proved relatively stable 10 cm below ground and are not affected by soil conditions over periods of this duration.

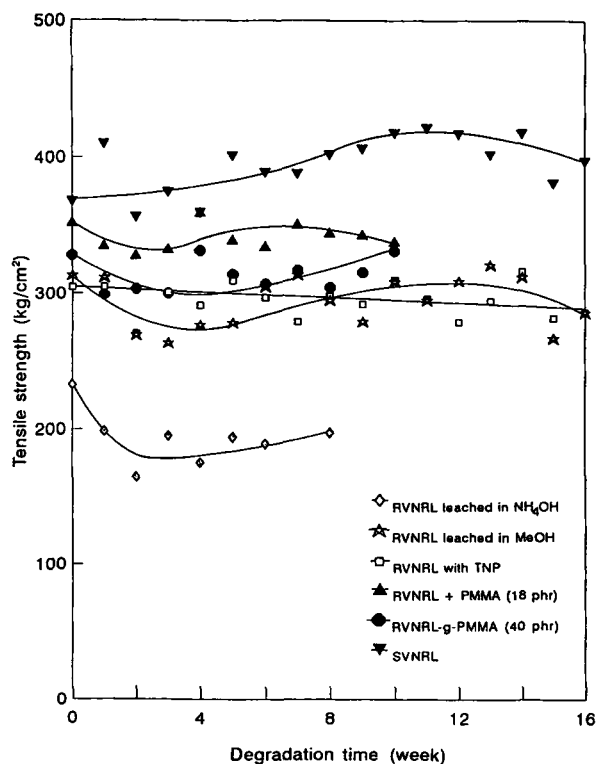


Figure 2 Relationship between tensile strength and degradation time of rubber films placed 10 cm below ground.

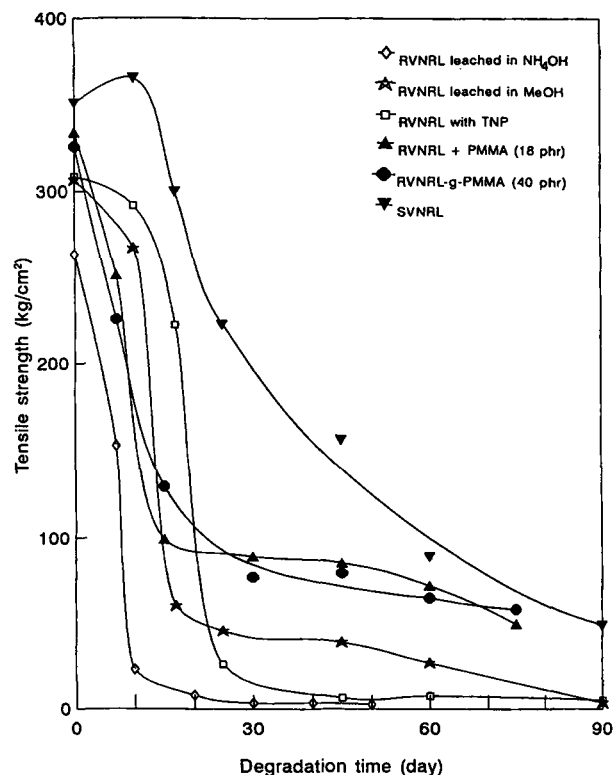


Figure 3 Relationship between tensile strength and degradation time of rubber films suspended 1 m above ground.

Rubber Films Suspended 1 m Above Ground (Fig. 3)

The tensile strength of all RVNRL films rapidly decreased and they were quite degraded after 30 days of exposure, whereas that of SVNRL film decreased at a somewhat slower rate, to 48 kg/cm² (14% retention of tensile strength) after 90 days' exposure.

Rubber Films at Room Temperature (Fig. 4)

The tensile strengths of these films were only slightly changed from the original state; it appears that these films are stable in this environment, which has important implications for storage of products made from these materials.

Degradation by Weather Meter Machine

30°C/Xenon Light/With Cooling Water (Fig. 5)

The tensile strengths of all RVNRL films rapidly decreased and they were quite degraded after 4 days (9 days for RVNRL film with TNP antioxidant). The tensile strength of SVNRL film decreased more slowly, and at the end of this test (9 days), tensile

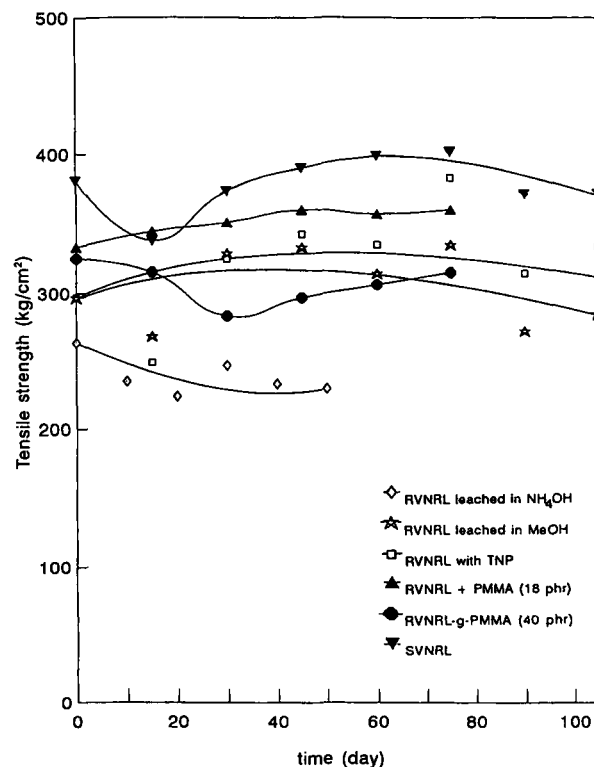


Figure 4 Relationship between tensile strength and time of rubber films at room temperature.

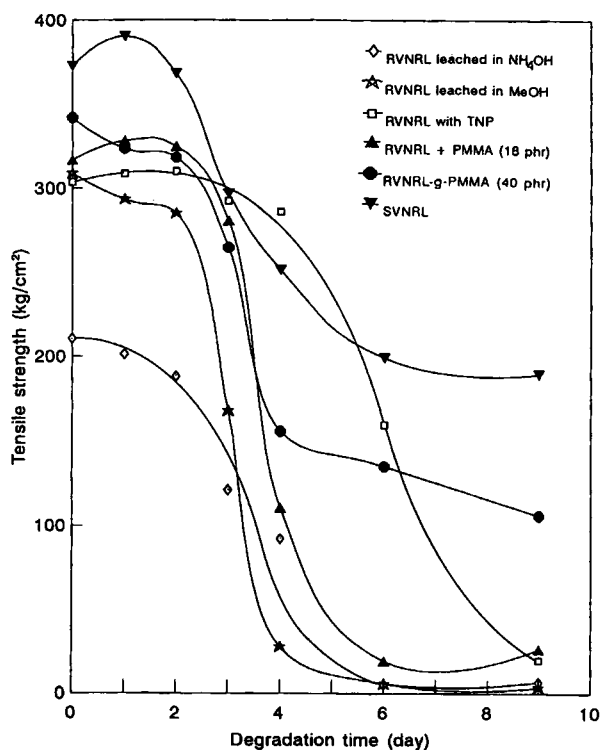


Figure 5 Relationship between tensile strength and degradation time of rubber films in a weather meter at 30°C/light from a xenon lamp and wall-cooling water.

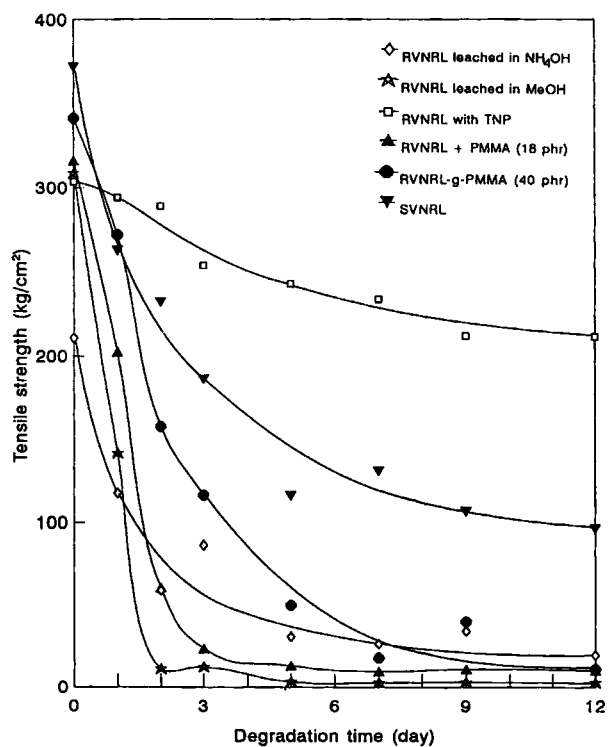


Figure 6 Relationship between tensile strength and degradation time of rubber films in a weather meter at 30°C/light from xenon lamp and without wall-cooling water.

strength was still at 190 kg/cm² (51% retention of tensile strength).

30°C/Xenon Light/Without Cooling Water (Fig. 6)

All films except RVNRL with TNP antioxidant and SVNRL returned similar results as those obtained on the 30°C test with cooling water. The tensile strength of RVNRL film with TNP antioxidant decreased much more slowly; the retained tensile strength was still 70% after 9 days. It appears that TNP antioxidant is effective in dry conditions and can be used to prolong the life of RVNRL films.

50°C/Xenon Light/Without Cooling Water (Fig. 7)

The tensile strength tests of all RVNRL films gave the same results as those obtained at 30°C; that of SVNRL film rapidly decreased and the film was quite degraded after 7 days. These results confirmed both the effectiveness of TNP antioxidant and the longer life of RVNRL films over SVNRL film.

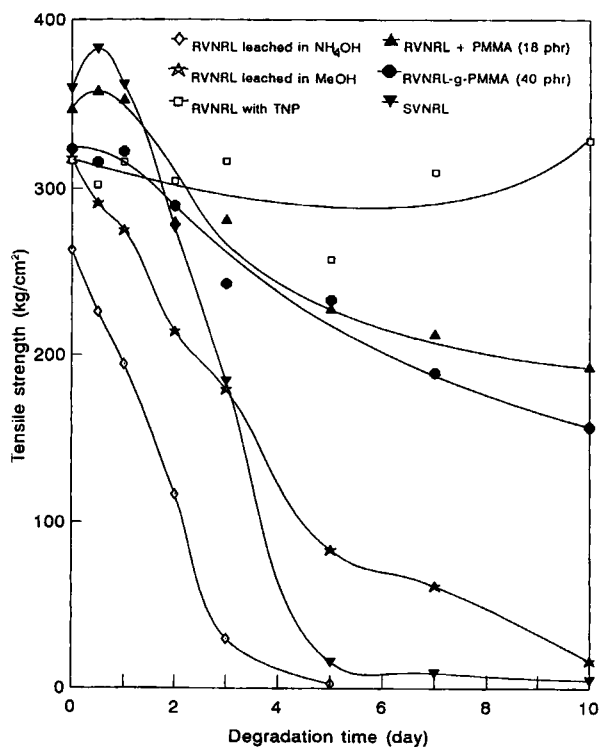


Figure 7 Relationship between tensile strength and degradation time of rubber films in a weather meter at 50°C/light from a xenon lamp and without wall-cooling water.

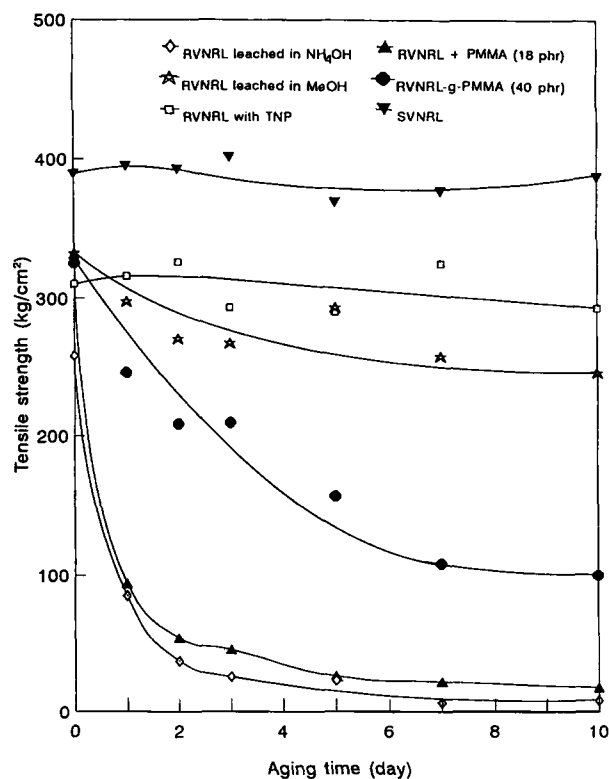


Figure 8 Relationship between tensile strength and aging time of rubber films at 70°C.

Aging Properties (Fig. 8)

The tensile strengths of RVNRL film that has been leached in 1% ammonia solution and RVNRL film blended with PMMA rapidly decreased and the material was quite degraded after 2 days. Those of RVNRL film leached in methanol and RVNRL grafted with PMMA slightly decreased and were still high at 246 kg/cm² (74% retention of tensile strength) and 100 kg/cm² (31% retention of tensile strength), respectively; those of RVNRL with TNP and SVNRL film were unchanged.

By comparing the results for the test at 50°C/xenon light/without cooling water, it is clear that light greatly affects the degradation rate of SVNRL film and not of RVNRL film with TNP antioxidant.

CONCLUSIONS

1. RVNRL films degraded rapidly, much more than did SVNRL films, in the environment

2. The degradation can be retarded in dry conditions and unexposed to sunlight.
3. TNP antioxidant is very suitable for RVNRL products. However, the product must be kept in dry conditions.
4. RVNRL products should be kept in the presence of a drying agent such as silica gel. In this case, the life of RVNRL products will exceed that of SVNRL products; when the RVNRL products are exposed into the environment, they will rapidly degrade.
5. PMMA, blended or grafted, is not effective in terms of the prevention of aging of RVNRL products.

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