RADIATION VULCANIZATION OF PHILIPPINE NATURAL RUBBER LATEX

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Abstract

The response of Philippine natural rubber latex to radiation vulcanization and the stability of the irradiated natural rubber latex (INRL) upon storage and aging were investigated. Commercially available high ammonia (HA) concentrated latices obtained from various rubber plantations in Mindanao Island were treated with 5 phr of n-butyl acrylate (nBA), and gamma-irradiated at the PNRI ^{60}Co Irradiation Facility at a dose rate of 2.57 kGy/hr. Unirradiated cast latex films gave different green strengths which varied from 2 - 11 MPa. Cast films from INRL exhibited maximum tensile strengths of 25 - 32 MPa at a radiation dose of 15 kGy. Higher tensile strengths were obtained from cast films with low Mg and high nitrogen contents. Thermal analysis using thermogravimetry (TG) revealed one major decomposition product at 374° - 377°C. Its rate of decomposition decreased to a minimum at 15 kGy, then increased as radiation dose was increased. This trend correlated well with the tensile strength measurements. The stability of the INRL upon storage and aging is an essential parameter to the rubber latex industry. For storage studies, INRL was stored for various periods of time. It was found that the pH and total solids content of the stored INRL did not change significantly after 12 months of storage; the MST values remained at above 1000 seconds, and the viscosity decreased with time. The cast films exhibited a decline in tensile strength, modulus$_{100\%}$ and crosslinking density upon storage. While there were observed changes in the physical properties of the INRL during the storage period, the data indicate that these properties were within values acceptable to the latex industry. Tests on the aging properties of INRL films were undertaken. It was shown that among the chemical antioxidants presently used by the latex industry, TNPP demonstrated the highest antioxidant property, followed by Antage DAHQ and Vulcanox BKF. Our data indicate that the natural rubber latex produced and processed in the Philippines is suited for radiation vulcanization.

INTRODUCTION

Radiation vulcanization of natural rubber latex (RVNRL) is an emerging technology whereby radiation is used in place of sulfur in the conventional prevulcanization process for the manufacture of dipped natural rubber latex products (Minoura etal. 1961; Makuuchi etal. 1991). The radiation process involves the irradiation of NRL in the presence of sensitizers resulting in the improved properties of the latex. The products obtained have shown to have noticeable advantage over the conventionally vulcanized NRL due to the absence of the carcinogenic nitrosamines derived from the common accelerators of the sulfur vulcanized NRL, lower levels of cytotoxicity and allergic reaactions, faster degradation in the enviironment, and absence of acid combustion gases (Gazeley etal. 1989; Nakamura etal. 1989; Tsuchiya etal. 1992; Makuuchi etal. 1992). The rise in the environmental consciousness among consumers has boosted the potential for RVNRL. This paper presents our data on the response of Philippine natural rubber latex to radiation vulcanization, the properties of irradiated NRL (INRL) and the effect of some antioxidants on the aging properties of the INRL.

Rubber plantations in the Philipppines are found in Mindanao, the southern island of the country (Fig. 1). These plantations started as small-scale holdings before World War II. The area planted to rubber expanded gradually from 3,400 ha in 1950 to 88,100 ha in 1993 (Fig. 2) (PCARRD 1993; BAE 1980 to 1993). About 75% of the rubber farms are less than five hectares indicating that rubber farming is in the hands of smallholders (PCARRD 1993). Table I presents the rubber clones used in Mindanao. The annual rubber production has increased from 76,700 MT in 1980 to 181,150 MT in 1995 (BAE 1980 to 1995). Centrifuged latex, however, is produced in a limited scale of roughly 10% of the annual natural rubber production.

MATERIALS

Samples of locally processed, high ammonia (HA) concentrated latices with an average of 64% total solid content (TSC) and a mechanical stability test (MST) of 1000+ sec as well as HA latices imported from Malaysia and Thailand were obtained from the different industrial rubber producers/processors through the Philippine Rubber Industries Association (PRIA). Field latices with a TSC of 32% were obtained from Cotabato through the University of Southern Mindanao. The sensitizer, n-butyl acrylate, was provided the Resins, Inc., and by Dr. K. Makuuchi of TRCRE, JAERI. The antioxidants used in the aging experiments were provided by Dr. K. Makuuchi of TRCRE, JAERI (TNPP, tris-nonylated phenylphosphite, and Antage DAHQ, 2,5-di-tert-amylhydroquinone), and by the local rubber manufacturing companies (Vulcanox BKF, 2,2'-methylene bis-(4-methyl-6-tertbutylphenol, Permanax HD/SE, alkylated diphenylamine, BHT, 3,5-di-tert-hydroxytoluene, and Aminox, of unknown structure).

METHODS

A. Characterization of Philippine Natural Rubber Latex

Percent TSC, dry rubber content(DRC) and volatile fatty acids were analyzed using the ASTM procedure Nos. D1076-88 (ASTM 1994). Elemental content of the samples was analyzed by AAS (ASTM D 1278). Kjeldahl analysis was used to analyze the nitrogen content of the rubber samples (ASTM D3533-90). The tensile strength and elongation at break of the cast films, cut into dumbbell pieces, were measured using the Instron testing machine (Model 1011). Thermal analyses were performed using the Shimadzu TGA-50 thermogravimetric analyzer.

B. Irradiation of NRL Samples

NRL was diluted to 50% TSC with NH_4OH and mixed with 0.2 phr KOH and 5 phr n-BA as sensitizer. NRL was irradiated at the PNRI ^{60}Co Irradiation Facility for different radiation doses (0, 5, 10, 15, 20, 30 kGy) at a dose rate of 2.57 kGy/hr.

C. Preparation of Cast NRL Films

Twenty five (25) mL of INRL was cast onto a glass plate, 19cm x 13cm, to make a film of 0.4 - 0.6mm thickness. The sample was air-dried. The film was removed from the glass plate, leached in 1% NH_4OH overnight, washed with tap water, air-dried for 24 hr, and cured at 70°C for two hr.

D. Permanent Set

A 10 cm distance (Li) was marked on film strips measuring 12L x 1W cm. The strips were fastened to a board with the 10 cm mark stretched to a 100 % distance for one hour. The strips were loosened and allowed to stand for 30 min. The final length (L_f) for the marked distance was then measured and the permanent set was computed as follows:

$$PS = \frac{L_f - L_i}{L_i}$$

E. Swelling Ratio and Crosslinking Density

A 0.1g film strip was immersed in toluene for 48 hr. The sample was taken out and blotted quickly with filter paper and weighed. The swelling ratio was computed using the following formula:

$$Q = 1 + (d_r/d_s)(W_2/W_1) - d_r/d_s$$

where :

W_1 = weight of film before immersion

W_2 = weight after immersion

d_r = density of rubber latex

d_s = density of toluene

Crosslinking density was computed using the Flory & Rehner equation:

$$V_o = K \times Q^{-5/3}$$

where:

V_o = crosslinking density

$K = 4.71 \times 10^{20}$

Q = swelling ratio.

F. **Aging Test**

Antioxidant emulsions/dispersions were prepared using the formulation below and ballmilled for three days.

Antioxidant	50%
20% emulsifier	10%
10% by wt. casein in 10% by wt. NH_4OH	10%
Distilled water	30%

Different concentrations (0. 0.5, 1.0, 1.5, 2.0 and 2.5 phr) of the antioxidant emulsion/dispersion were added to irradiated NRL and stirred for 2 hr. The latex was made into films and aged at 100°C for 22 hr using a Geer oven. Tensile strengths were measured before and after aging.

RESULTS AND DISCUSSION

A. Properties of Phhilippine NRL

Commercially available latices vary in their physico-chemical and mechanical propeties depending on such factors as the rubber clone used, conditions of tapping and processing of latex, preservatives used, storage time, and non-rubber components of latex. These properties have been found to affect the response of NRL to radiation. Different sources of latices give distinct radiation responses as measured by the vulcanization dose , Dv , and the tensile strength, Tb. These variations in radiation response have been attributed mainly to the differences in composition and quantity of their non-rubber components (NRC). Dv is said to decrease with increasing green strength which is directly associated with protein content in the rubber phase(Pansa etal. 1987). Metal ions also affect RVNRL. Large amount of Mg decreases the tensile strength of radiation vulcanized natural rubber (Makuuchi etal. 1993). Mg and the volatile fatty acids (VFA) are known to have an adverse effect on the stability of NRL. Tensile strength of of NH4OH-leached irradiated latex film increases upon the addition of latex serum proteins (Abad 1993). Thus, for a good RVNRL product, latex with higher green strength , low Mg content , and higher nitrogen content is the latex of choice for RVNRL.

Some physical and chemical properties of the Philippine NRL investigated are shown in Table II. The field latex from Cotabato exhibited higher NRC, which was expected, because these samples were not centrifuged. Centrifugation removes most of the NRC in NRL. The centrifuged latices varied in their NRC. The Mg contents of the latices from Zamboanga in Western Mindanao and Agusan in Northern Mindanao are 14-77 ppm and 12-13 ppm, respectively. For the same latex samples, the nitrogrn contents are 0.18-0.71% and 0.32%, respectively. The VFA number is within the minimum set value of ISO 2004 which is 0.2ppm. The latices are quite stable with MST of 1000+ sec, values greater than the minimum set limit of 800 sec. The green strengths of the latices (7-11 MPa) exceed the limit of 7 MPa except for Zam 2-1 which has only a green strength of 2 MPa. This low value could be attributed to its nitrogen content which is only 0.18% .

B. Properties of Irradiated NRL (INRL)

The dose -effect response curves for the different Philippine latices are shown in Fig.3. Cast films exhibited maximum tensile strengths of 25 - 32 Mpa at a radiation dose of 15 kGy. The tensile strengths decreased at higher radiation doses. Higher tensile strengths were observed from latices of Zam1-2 and Agu 1-2 with a Tb above 30 MPa at this dose. The characteristics of latex Agu 1-2 indicate a low Mg content and a high nitrogen content. On the other hand, latex sample Zam-3-2 with the lowest green strength and nitrogen content exhibited a maximum tensile strength of 25 Mpa only. The data show that samples with lower green strengths gave lower tensile strengths at the vulcanization dose. The lower tensile strengths obtained could be due to high Mg content and/or low nitrogen content. The cast films formed from all latices would be able to meet the standard requirements of ASTM for the mechanical properties of examination gloves (21MPa) and finger cots (20MPa). The typical properties of the Philippine INRL and the cast films are shown in Table III.

The degree of radiation vulcanization was measured from the swelling ratio and crosslinking density of the cast films. As observed by other workers (Parinya etal. 1989), the swelling ratio decreased with increasing radiation dose while the crosslinking density increased with increasing dose (Table IV). It was further found that while the level of crosslinking in the rubber network continued to increase after 15 kGy, the tensile strength decreased indicating that there is an optimum number of crosslinks required to attain the maximum tensile strength of the INRL.

Thermogravimetric analysis (TGA) was used to study the thermal behavior of the INRL as a function of radiation dose. As shown in Fig. V, the TGA curves of the unirradiated and irradiated NRL revealed only one major decomposition product which underwent thermal degradation at 374° to 377°C. Its rate of decomposition, was affected by radiation dose as shown in Fig. 5 and Table V. Thermal decomposition decreased and reached a minimum at 15 kGy, then increased as radiation dose was increased to 30 kGy. This trend is consistent with the negative correlation between rate of decomposition and tensile strength up to 15 kGy. These observations indicate that the NRL irradiated up to the vulcanization dose of 15 kGy are more thermally stable than the unirradiated NRL and those irradiated above the vulcanization dose.

C. The Effect of Antioxidants on the Aging Properties of Philippne INRL

The thermal oxidative resistance of RVNRL is inferior to that of the conventionally processed NR due to the absence of dithiocarbamates that function as strong antioxidants. This aging property can be improved by the addition of some external antioxidants. The effectiveness of different antioxidants (TNPP, Vulcanox BKF, Permanax HD/SE, BHT, Antage DAHQ, and Aminox) was tested on the Philippne INRL. Table VI presents the chemical structures of the antioxidants and their respective effects on the aging properties of INRL. Figure 6 shows that among the antioxidants, TNPP was found to be the most effective. Percent retention was quite high (88%) even at a concentration of only 0.5phr. Vulcanox BKF and Antage DAHQ also demonstrated strong antioxidant properties with percentages retention of 85% and 76%, respectively, at 0.5phr. However, Vulcanox BKF leaves a red staining effect on the radiation vulcanized natural rubber. The effectiveness of the other antioxidants are quite poor with tensile strength retentions of less than 50%.

D. Storage Experiments

The storage stability of INRL would be an important factor to consider in the commercialization of RVNRL. Table VII shows some of the physical and mechanical properties of INRL after a storage period of 12 months. The Philippne latex showed similar trends with the Malaysian and Thai latices. No significant changes have been observed with the MST, pH, %TSC, and Permanent Set for the three INRLs. Their viscosities decreased with time. This reduction may be due to the evaporation of n-BA which has been observed to increase the viscosity of natural rubber latex. The RVNRL films formed from these latices indicated a decrease in Modulus $_{100\%}$ and tensile strength with time (Fig. 7). A sharp drop in Tb was observed after four months of storage from 27 MPa to 22 MPa for the Malaysian latex, 26 MPa to 22 MPa for the Thai latex and 26 MPa to 22 MPa which remains stable up to a period of 12 months for the Philippine latex . This decrease could be associated with the decrease in crosslinking density as seen in Fig 9. These values are, however, still within the acceptable limit for the mechanical properties of examination gloves and finger cots.

CONCLUSION

The Philippine latex is compatible for RVNRL. The cast films from the INRL have good mechanical properties which remain within acceptable limits even after storage of 12 months. The aging properties of the INRL can best be improved with the addition of TNPP as antioxidant. Improved handling and processing of the Philippine NRL can reduce the Mg content and VFA of the latices for an even better quality INRL.

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Table I. RUBBER CLONES IN MINDANAO[a]

REGION	CLONES
IX	RRIM 600, TJIR-1, PR-86, PB-280, AVROS 1328, GT-1
X	RRIM 600, RRIM 501, RRIM 606, RRIM 605, PB-86, GT-1, TJIR-1, HARBEL, IAM
XI	RRIM 600, GT-1, TJIR-1
XII	RRIM 600, TJIR-1, PB-86, PB-300

[a]Philippine Industrial Crops Research Institute, 1991

Table II. Characterization of Philippine Natural Rubber Latex

Samples	% TSC	% DRC	% Nitrogen Content	Green Strength (Mpa)	% Ash	Elemental Analysis (ppm)			
						Mg	Ca	Cu	Mn
Zam 1-1	60.90	60.00	0.71	7	0.27	26.31	11.02	0.77	n.d.
Zam 2-1	62.00	61.50	0.18	2	0.34	13.98	15.78	1.12	n.d.
Zam 3-2	66.00	---	0.36	10	0.28	77.27	12.15	0.93	n.d.
Agu 1-1	64.27	62.95	0.32	10	0.25	12.19	7.24	0.94	n.d.
Agu 1-2	64.65	62.30	0.32	11	0.26	13.48	10.14	1.39	n.d.
Cot 1-1	31.65*	26.10	1.11	---	0.28	72.39	32.69	2.21	n.d.
Cot 1-3	33.17*	27.55	1.73	8	0.45	---	21.80	1.07	n.d.

* not centrifuged
n.d - not detected

Samples	MST	VFA Number
A	1600	0.1724
B	1740	0.0187
C	1851	0.0294

Table III. Typical Properties of Philippine Irradiated Natural Rubber Latex

Latex	
Total Solids Content (TSC)	50.03 %
Dry Rubber Content (DRC)	49.08 %
Non-rubber Component (TSC-DRC)	1.05 %
Viscosity	25.0 Cp
pH	10.3
Mechanical Stability Time (MST)	1000+ sec

Cast Film		
	Before Aging	*After aging
Modulus 300%, (MPa)	1.5	0.8
Tensile Strength, (MPa)	28.0	25.0
Elongation at Break, %	990	990
Permanent Set, %	4.32	3.57
Swelling Ratio in Volume	7.63	7.14

* aging was done at 100°C for 20 hours in a Geer oven

Table V. Thermal Stability of INRL vs Radiation Dose

Temp. Rate (°C/min)	Degradation Rate (mg/min)* Dose (kGy)					
	0	5	10	15	20	30
10	-0.577	-0.691	-0.825	-0.910	-0.868	-0.867
15	-0.977	-1.110	-1.114	-1.341	-1.093	-1.135
20	-1.265	-1.329	-1.610	-1.936	-1.684	-1.654

* Obtained from the TGA Curves

Table IV. Swelling Ratio, Crosslinking Density and Tensile Strength vs Radiation Dose

Dose (kGy)	Swelling Ratio	Crosslinking Density x 10^{19}	Tensile Strength (MPa)
0	45.3	0.08	13.1
5	9.87	1.04	21.2
10	7.49	1.64	28.6
15	7.20	1.75	30.3
20	6.63	2.01	29.0
30	3.32	6.37	28.7

Table VI. Effect of different antioxidants on Philippine Irradiated Natural Rubber Latex

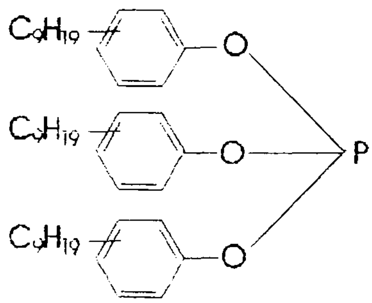
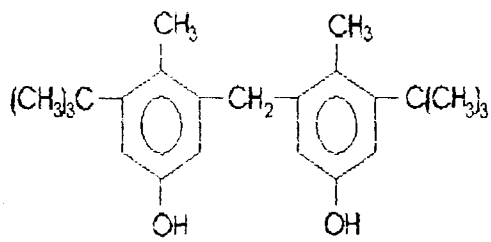
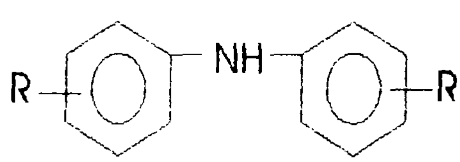
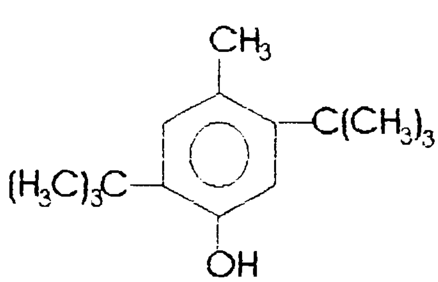
Antioxidants	Chemical Name/Structure	Concentration (phr)	% Tb Retention
TNPP		0	24
		0.5	88
		1.0	95
		1.5	99
		2.0	100
	tris-nonylated phenyl phosphite	2.5	100
Vulkanox BKF		0	37
		0.5	85
		1.0	85
		1.5	96
		2.0	96
	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)	2.5	84
Permanax HD/SE		0	23
		0.5	38
		1.0	38
		1.5	46
	alkylated diphenylamine	2.0	46
		2.5	55
BHT		0	35
		0.5	45
		1.0	45
		1.5	39
		2.0	50.10
	3,5 di-tertiary butyl-4-hydroxy toluene	2.5	46.16

Table VI. Effect of different antioxidants on Philippine Irradiated Natural Rubber Latex (continuation)

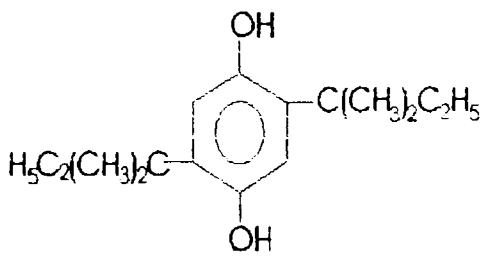
Antioxidants	Chemical Name/Structure	Concentration (phr)	% Tb Retention
Antage DAHQ	 2,5 -Di-tert-amylhydroquinone	0	37
		0.5	76
		1.0	79
		1.5	86
		2.0	88
		2.5	91
Aminox		0	45
		0.5	54
		1.0	56
		1.5	61
		2.0	58
		2.5	56

Table VII. Storage Studies on Philippine Irradiated Natural Rubber Latex

A. Latex Parameters

Sample	pH							Viscosity (cps)						
	Storage Interval (month)							Storage Interval (month)						
	0	2	4	6	8	10	12	0	2	4	6	8	10	12
with TNPP	10.02	9.05	9.56	9.83	9.54	9.58	9.45	20.0	15.8	---	---	15.0	---	---
w/o TNPP	9.90	9.38	9.67	9.83	9.76	9.65	9.43	22.7	16.4	---	---	15.0	---	---

Sample	% TSC							% DRC						
	Storage Interval (month)							Storage Interval (month)						
	0	2	4	6	8	10	12	0	2	4	6	8	10	12
with TNPP	49.5	49.5	49.4	49.7	49.5	47.2	48.2	47.8	47.6	47.8	48.3	47.7	46.1	47.1
w/o TNPP	49.6	49.8	49.6	49.6	49.9	47.9	47.9	47.9	47.7	47.8	48.2	48.7	46.3	46.0

Sample	MST (sec)							VFA Number						
	Storage Interval (month)							Storage Interval (month)						
	0	2	4	6	8	10	12	0	2	4	6	8	10	12
with TNPP	1820	846	1162	1221	1183	1082	938	0.345	0.429	0.356	0.444	0.331	0.364	0.339
w/o TNPP	1850	756	1185	1127	1033	938	885	0.401	0.19	0.360	0.518	0.361	0.389	0.386

B. Film Parameters

Tensile Strength

Sample	Storage Interval (month) 0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	32	21	26	21	26	20	22	18	22	20	25	20	22	20
w/o TNPP	28	---	26	13	26	17	20	16	21	18	20	17	19	17

% Elongation at Break

Sample	Storage Interval (month) 0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	985	950	950	950	1000	1046	1000	940	1000	1000	1000	1000	950	950
w/o TNPP	989	---	970	950	1000	1050	1000	930	1000	1000	1000	1000	950	950

Modulus [illegible]

Sample	Storage Interval (month) 0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	1.10	0.63	1.15	0.59	1.12	0.72	0.43	0.53	0.47	0.77	0.55	0.58	0.65	0.60
w/o TNPP	1.47	---	0.54	0.44	1.61	0.54	0.72	0.48	0.42	0.76	0.42	0.63	0.66	0.64

Permanent Set														
	Storage Interval (month)													
Sample	0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	3.5	---	4.0	3.0	3.0	4.0	5.0	2.0	3.0	2.0	3.0	2.0	3.5	2.0
w/o TNPP	4.5	---	3.0	5.0	4.0	4.0	5.0	2.0	4.5	3.0	3.0	2.0	4.0	2.0

Swelling Ratio														
	Storage Interval (month)													
Sample	0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	7.56	7.85	8.00	8.62	7.44	8.00	8.00	8.00	8.62	8.62	7.41	8.62	8.00	8.00
w/o TNPP	7.71	---	8.00	9.26	7.44	8.00	8.00	8.00	8.62	8.62	7.41	8.63	8.00	8.00

Crosslinking Density x 10^{19}														
	Storage Interval (month)													
Sample	0		2		4		6		8		10		12	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
with TNPP	16.2	15.2	14.7	13.0	16.6	14.7	14.7	14.	13.0	13.0	16.7	13.0	14.7	14.7
w/o TNPP	15.7	---	14.7	11.5	16.6	14.7	14.7	14.7	13.0	13.0	16.7	13.0	14.7	13.0

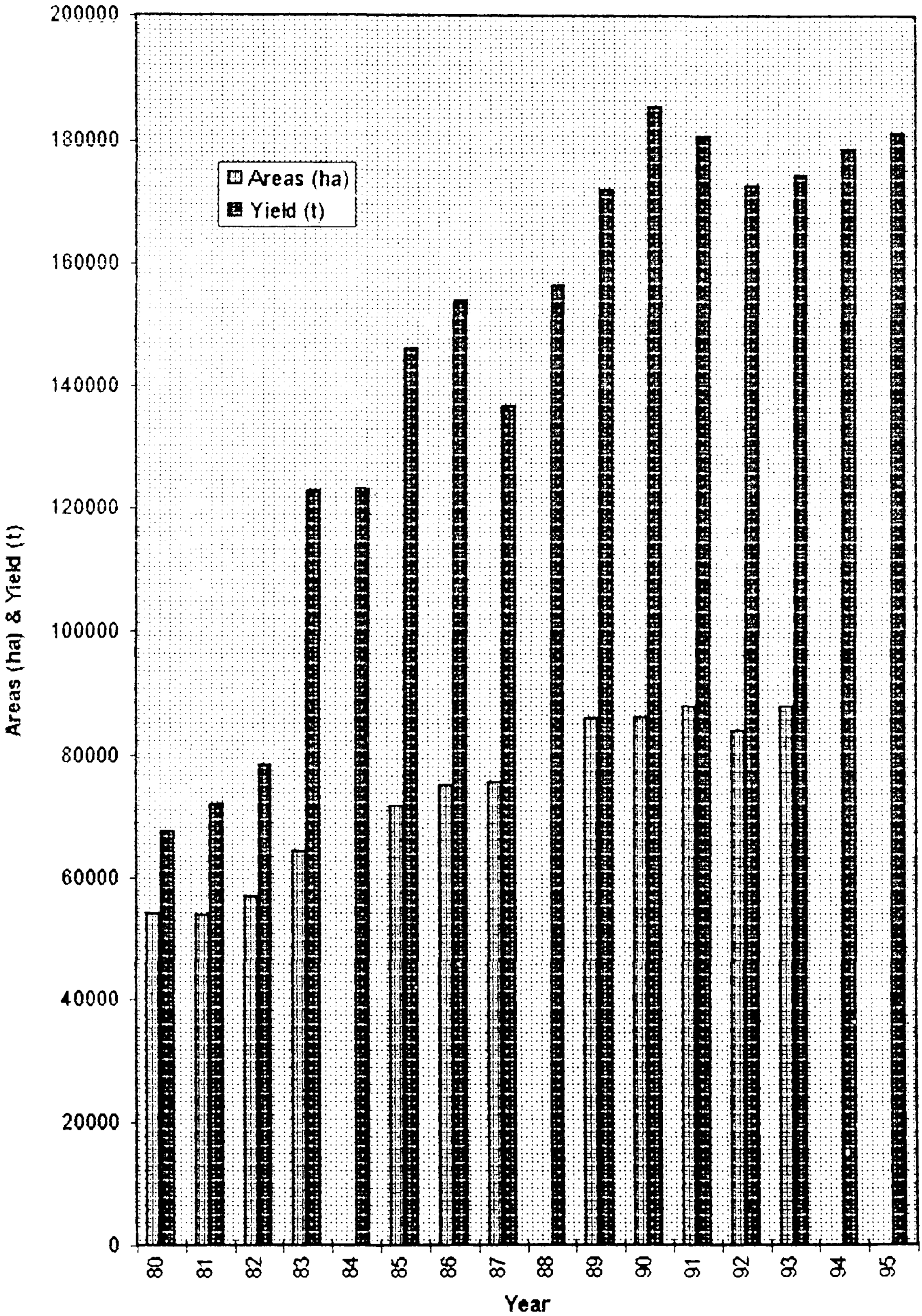


Figure 2. AREAS AND YIELD OF RUBBER IN THE PHILIPPINES
(1980-1995)

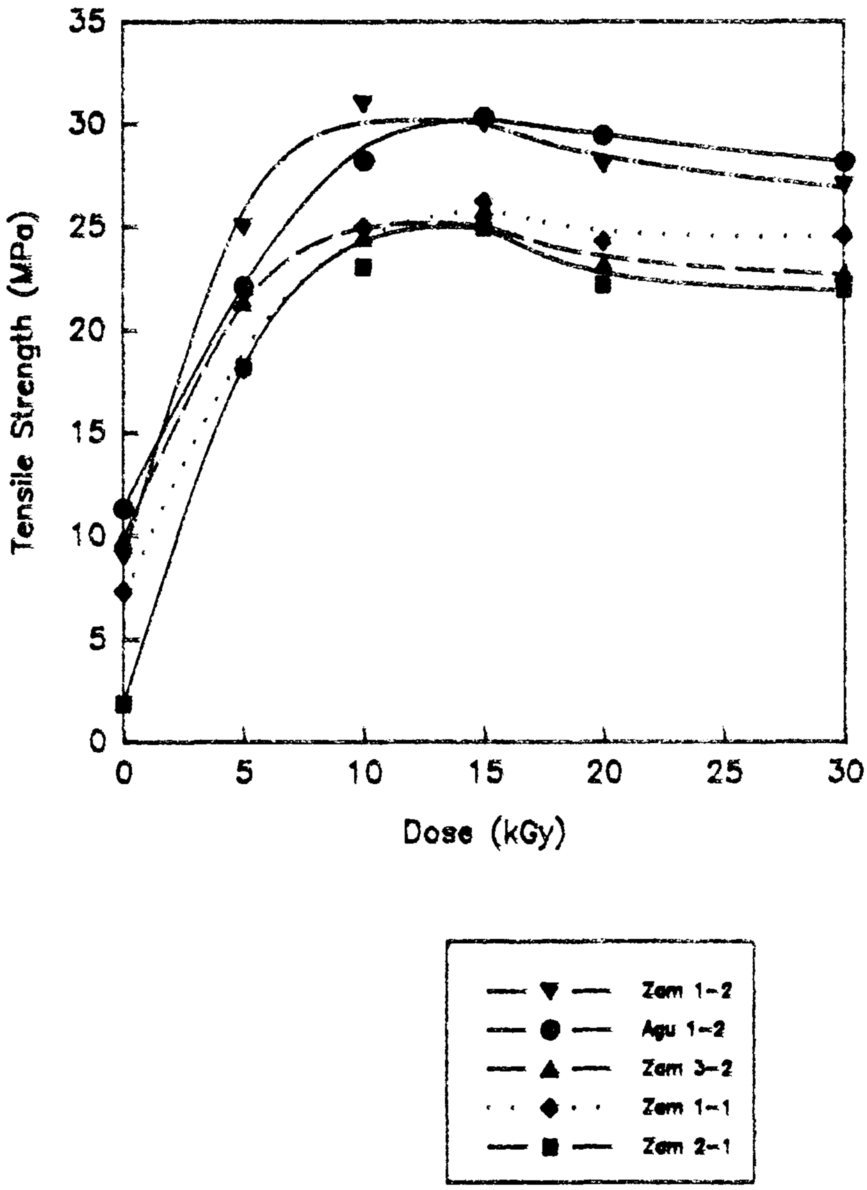


Figure 3 Dose Response Curves of the Philippine NRL

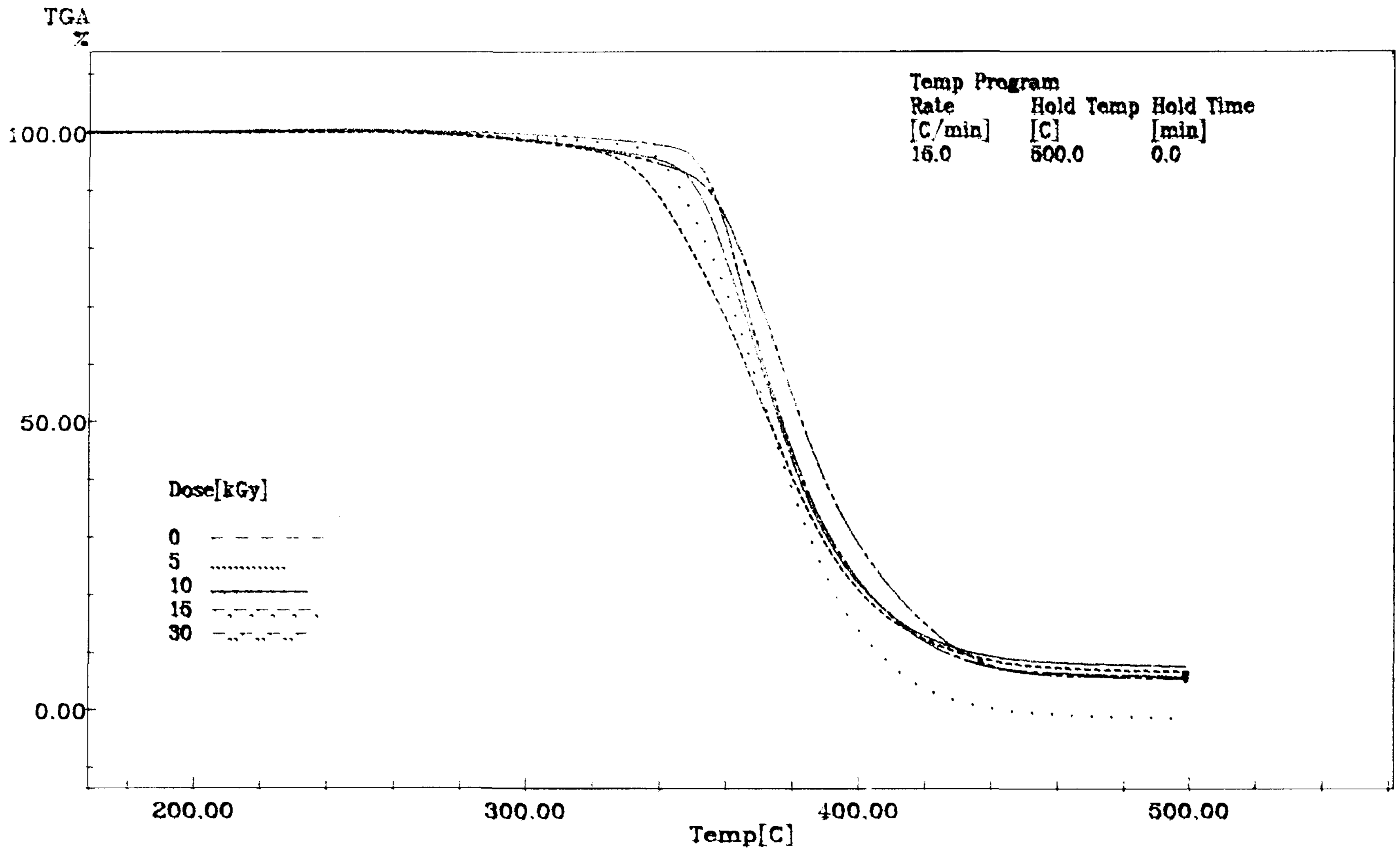


Figure 4. Thermal degradation curve of INRL at different doses

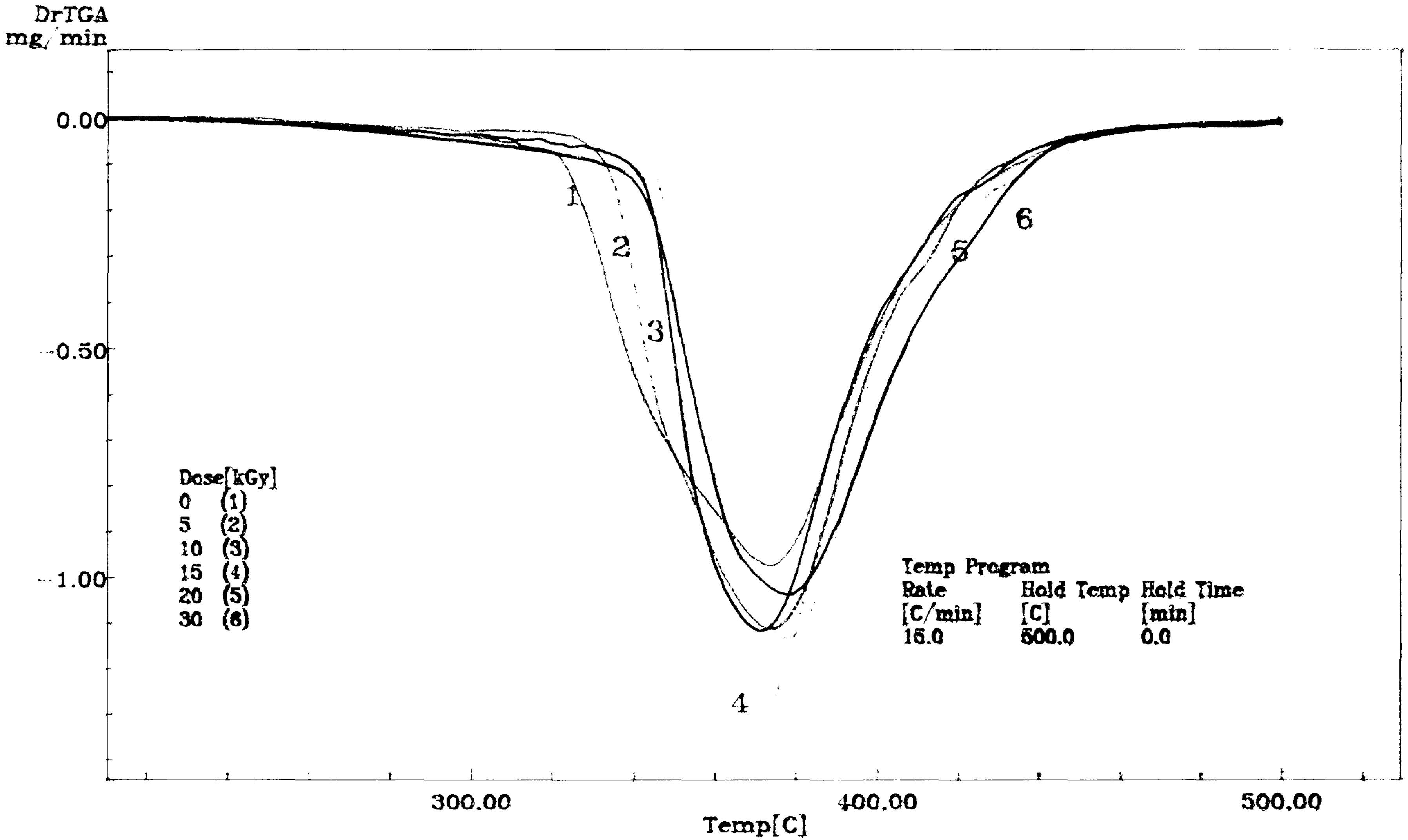


Figure 5. Thermal degradation rate of INRL at different doses

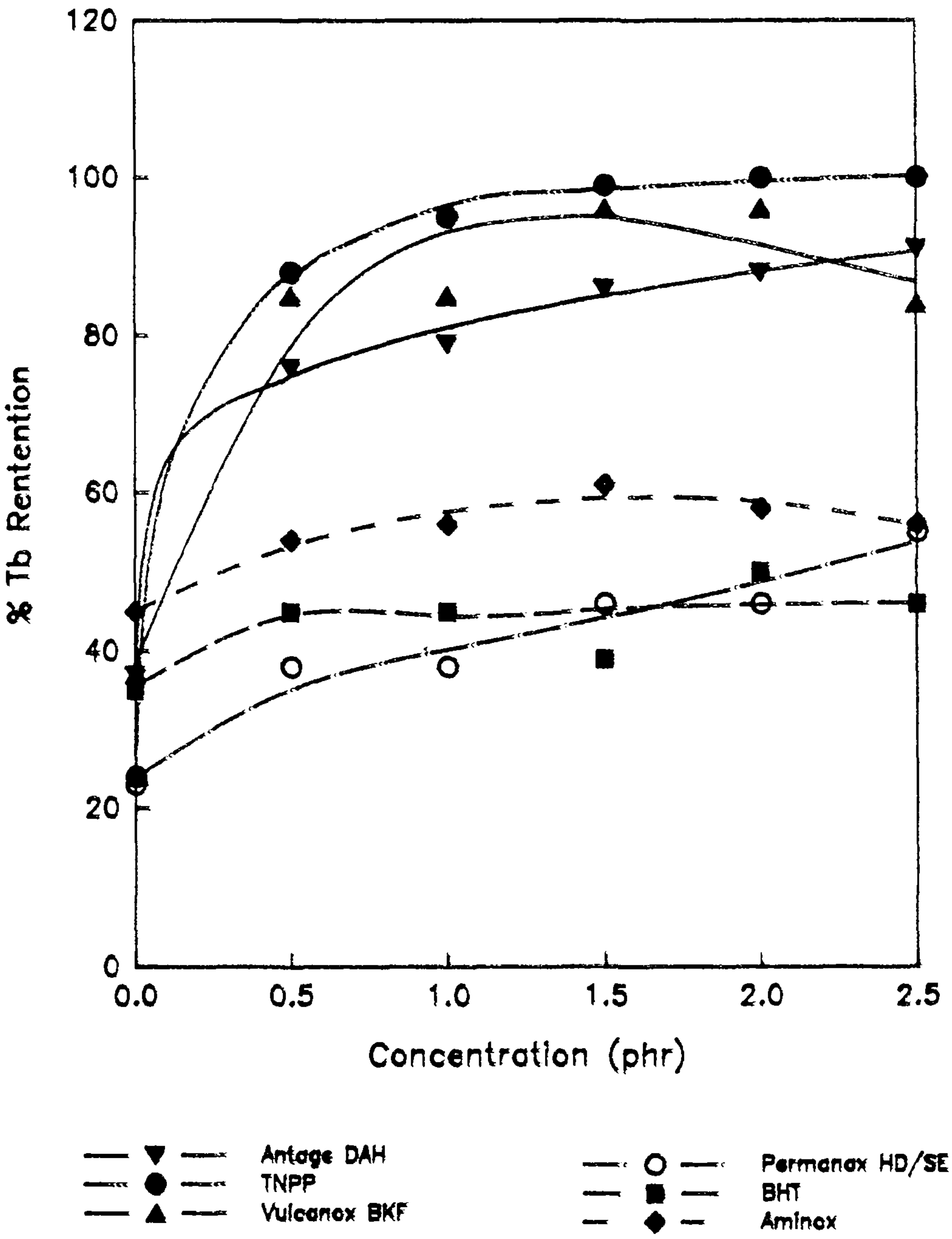


Figure 6 The Effect of Antioxidants on the Aging Properties of INRL Films

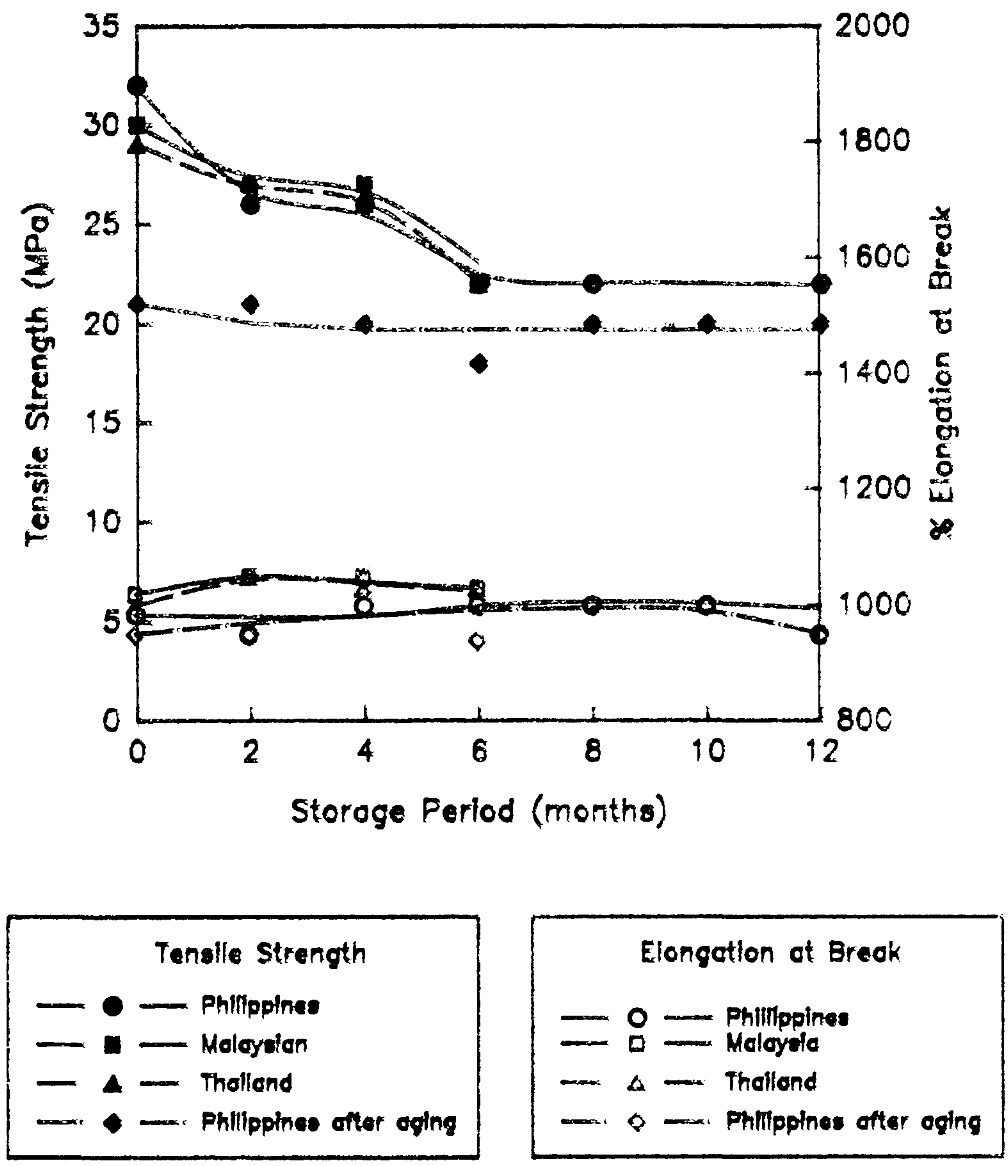


Figure 7 Tensile Strength of INRL with Storage Time

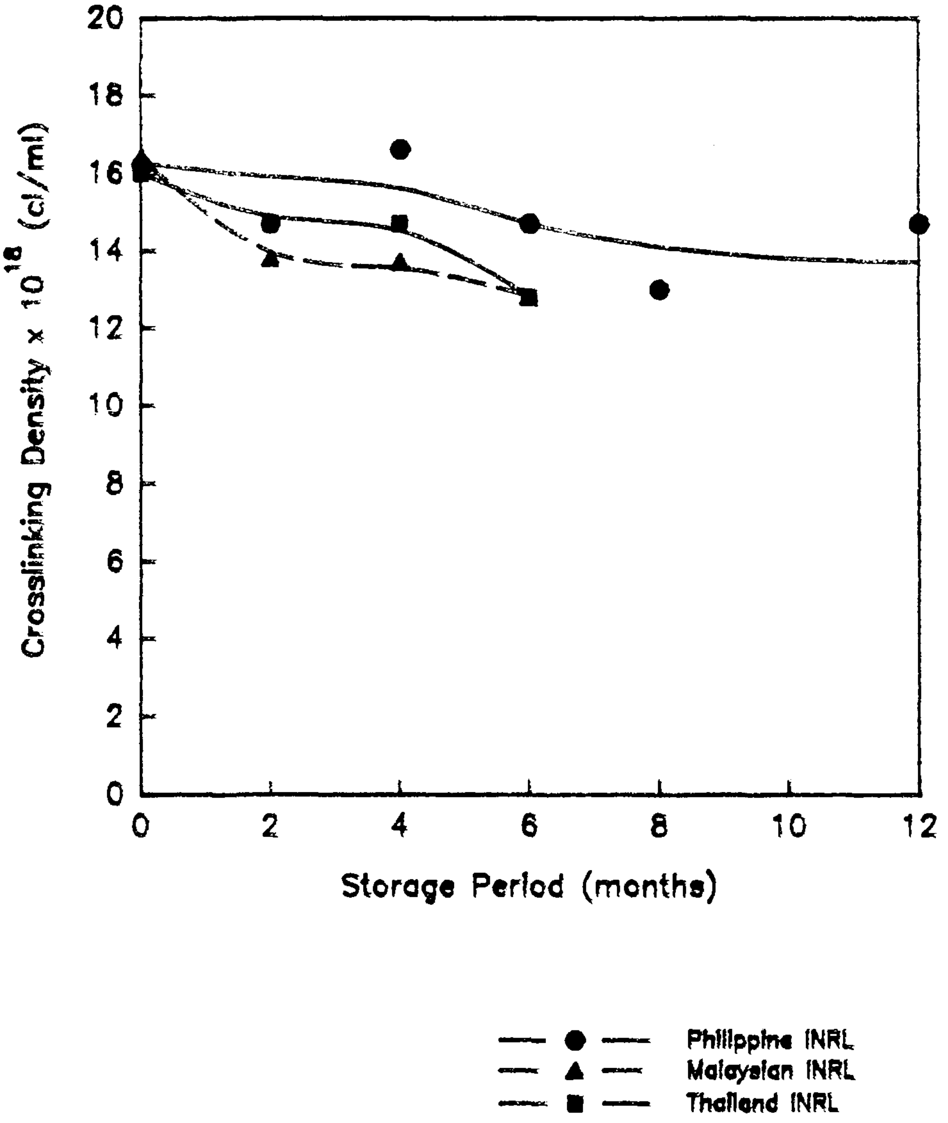


Figure 8 Crosslinking Density of INRL with Storage Time