Epoxidized Linseed Oil-Free Fatty Acids Modified with Substituted Anilines as Antioxidants and Antirads for SBR Vulcanizates

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SYNOPSIS

Epoxidized linseed oil-free fatty acids were reacted with aniline and three isomers of toluidine, anisidine, and chloroaniline in such a manner that the carboxylic groups remained free. The prepared adducts were evaluated as antioxidants and antirads for styrene butadiene rubber (SBR) vulcanizates. It was found that 2 phr of orthotoluidine, paraanisidine, orthochloroaniline, and aniline adducts were the best antioxidants and/or antirads. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The use of high molecular weight additives; especially antioxidants and antirads for rubber vulcanizates, is a useful trend to avoid the drawbacks of simple organic compounds. The use of such additives as antioxidants is well known,[1-2] and a number of these have been synthesized by the authors.[3-9]

In the present work, epoxidized linseed oil-free fatty acids were reacted with aniline and three isomers of toluidine, anisidine, and chloroaniline in such a manner that the carboxylic groups remained free. The prepared adducts were incorporated in SBR formulations to study their effect as antioxidants and antirads.

Kaolin was used as a filler in order to use the final vulcanizates as electrical insulators in further work.

EXPERIMENTAL

Raw Rubber: Styrene–butadiene copolymer SBR-1502 (nonstaining).

Rubber Ingredients: As customarily used in industry (See Table II).

Aniline and Substituted Anilines: Products of Aldrich Chemical Co. Inc. (pure grade).

Linseed Oil: Egyptian alkali-refined linseed oil (Iodine value 173).

Dowex 50W–8X: A sulfonated poly(styrene divinyl-benzene).

Hydrogen Peroxide: 30% strength.

Preparation of the Laboratory Compound

Linseed oil was alkali hydrolyzed and was then neutralized. The liberated free fatty acids were epoxidized by preparing peracetic acid in situ.[6] The epoxidized linseed-free fatty acids were reacted with aniline, and the three isomers of toluidine, anisidine, and chloroaniline, stoichiometrically, that is, one mole amine per epoxy group. The reaction was carried out at 130°C for 3 h in sealed ampoules under inert atmosphere (N₂ gas).
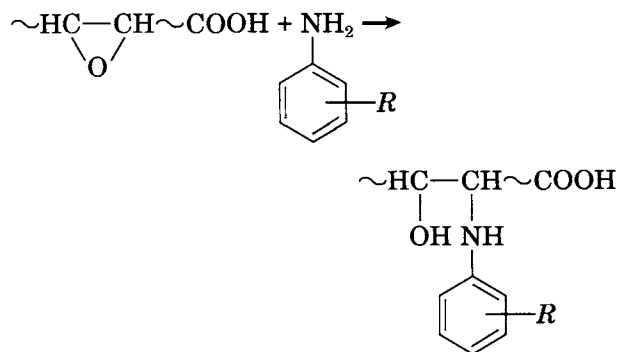
Where R is H, CH_3, OCH_3, or Cl.

All reaction products were viscous, dark brown, and freely soluble in benzene, toluene, xylene, and acetone. The measurements of acid value proved that not less than 80% of the carboxylic groups remained free, the others reacted with amines to form corresponding amides. The prepared adducts are listed in Table I.

Preparation of the Rubber Vulcanizates

The prepared compounds were incorporated in SBR mixes, using a laboratory roller mill with an outside diameter of 460 mm, a working distance of 250 mm, a speed of the slow roll of 16 r.p.m., and a gear ratio of 2.

The rheometric characteristics were determined using an oscillating disc rheometer model 100 at 152°C ± 1°C.[10]

The rubber mixes were vulcanized in a hydraulic press at 152°C for the optimum cure time.

The physicomechanical properties were determined using a tensile testing machine (Zwick 1101).[11]

Aging was carried out by the oven method.[12] In this method, thermal oxidative aging of rubber vulcanizates was carried out in an oven at 90°C for different periods of time. The retained values of the physicomechanical properties were determined.

A Cobalt-60 gamma irradiator, type 6500, supplied by the Atomic Energy of Canada Ltd., was used for irradiating the specimens. The exposure was carried out in air at room temperature while the absorbed doses were measured by using a standard calibrated perspex dosimeter.

Table I The Amine Content and Acid Value of the Prepared Adducts

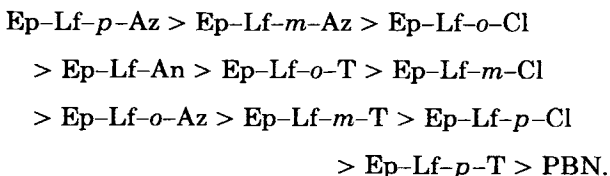| Adduct	Acid No.	Amine Content (%)
Ep–Lf	207.0	—
Ep–Lf–An	165.6	45.8
Ep–Lf–o–T	170.6	49.3
Ep–Lf–m–T	167.3	49.3
Ep–Lf–p–T	171.0	49.3
Ep–Lf–o–Az	178.0	52.8
Ep–Lf–m–Az	172.0	52.8
Ep–Lf–p–Az	169.3	52.8
Ep–Lf–o–Cl	179.2	53.7
Ep–Lf–m–Cl	175.0	53.7
Ep–Lf–p–Cl	171.6	53.7

(Ep–Lf) Epoxidized linseed oil-free fatty acids, (T) Toluidine, (Az) Anisidine, (Cl) Chloroaniline, (An) Aniline, (o) ortho, (m) meta, (p) para.

RESULTS AND DISCUSSION

The prepared adducts were incorporated in SBR mixes. Table II shows the SBR formulations, the rheometric characteristics of the rubber mixes, and the physicomechanical properties of their vulcanizates. It is obvious that the laboratory compounds improve the physicomechanical properties of the vulcanizates, but their effect on the cure time (tc 90) and the cure rate index (CRI) can be neglected, except for the formulation containing Ep–Lf–p–Az, where the optimum cure time is decreased by 2.5 min and CRI is the maximum among all adducts, which means that the Ep–Lf–p–Az adduct has a secondary accelerating effect.

Evaluation of the Laboratory Compounds as Antioxidants

The rubber vulcanizates were subjected to thermal oxidative aging at 90°C for different periods of time up to 7 days. Figures 1, 2, and 3 show the dependence of the relative change in tensile strength on aging time. The aniline adduct, as well as the commercial antioxidant (PBN), are taken for comparison with the other amines (o-, m-, p-toluidines, o-, m-, p-anisidines, and o-, m-, p-chloroanilines). It can be seen that the prepared compounds protect SBR vulcanizates against thermal oxidative aging and their efficiencies follow the descending order:

Ep–Lf–p–Az > Ep–Lf–m–Az > Ep–Lf–o–Cl

> Ep–Lf–An > Ep–Lf–o–T > Ep–Lf–m–Cl

> Ep–Lf–o–Az > Ep–Lf–m–T > Ep–Lf–p–Cl

> Ep–Lf–p–T > PBN.

Figures 4, 5, and 6 show the relative changes in elongation at break vs. aging time. The curves indicate that the adducts possess good heat resistance and gave better results than PBN.

The lower efficiency of the Ep–Lf–o–Az adduct than that predicted may be attributed to steric hindrance and/or the hydrogen bond that may arise between the methoxyl group and the —NH, which decreases the lability of the hydrogen atom of —NH— group.
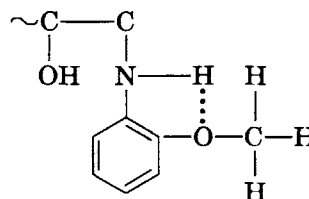
Table II Rubber Formulations, the Rheometric Characteristics, and the Physicomechanical Properties

| Ingredient / Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
SBR	100	100	100	100	100	100	100	100	100	100	100	100
Stearic Acid	2	2	2	2	2	2	2	2	2	2	2	2
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Kaolin	50	50	50	50	50	50	50	50	50	50	50	50
Processing Oil	3	3	3	3	3	3	3	3	3	3	3	3
MBTS	2	2	2	2	2	2	2	2	2	2	2	2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PBN (phr)	—	1	—	—	—	—	—	—	—	—	—	—
Ep–Lf–An (phr)	—	—	2	—	—	—	—	—	—	—	—	—
Ep–Lf–o–T (phr)	—	—	—	2	—	—	—	—	—	—	—	—
Ep–Lf–m–T (phr)	—	—	—	—	2	—	—	—	—	—	—	—
Ep–Lf–p–T (phr)	—	—	—	—	—	2	—	—	—	—	—	—
Ep–Lf–o–Az (phr)	—	—	—	—	—	—	2	—	—	—	—	—
Ep–Lf–m–Az (phr)	—	—	—	—	—	—	—	2	—	—	—	—
Ep–Lf–p–Az (phr)	—	—	—	—	—	—	—	—	2	—	—	—
Ep–Lf–o–Cl (phr)	—	—	—	—	—	—	—	—	—	2	—	—
Ep–Lf–m–Cl (phr)	—	—	—	—	—	—	—	—	—	—	2	—
Ep–Lf–p–Cl (phr)	—	—	—	—	—	—	—	—	—	—	—	2
Rheometric Characteristics												
M_L ($dN \cdot m$)	12.0	10.5	10.2	10.0	9.5	10.0	9.0	10.0	9.0	9.0	10.0	10.3
M_H ($dN \cdot m$)	47.0	50.0	54.0	55.0	59.0	61.5	59.0	60.3	67.0	52.5	52.5	55.0
M_{C90} ($dN \cdot m$)	43.5	46.0	49.6	50.5	54.0	56.4	54.0	55.3	61.3	48.2	48.3	50.5
t_{S2} (min)	15.0	15.3	13.5	14.5	14.0	14.5	14.0	12.8	13.5	12.5	14.0	14.0
t_{C90} (min)	48.0	50.0	49.5	50.0	51.0	51.0	51.0	51.5	47.5	49.0	50.0	50.0
Cure Rate Index (min^{-1})	3.03	2.88	2.74	2.82	2.70	2.74	2.70	2.85	2.94	2.67	2.78	2.78
Rate Constant, K	0.075	0.067	0.055	0.060	0.048	0.049	0.052	0.048	0.057	0.079	0.060	0.063
Initiation Time, t_i (min)	10.01	15.81	13.15	15.45	13.06	12.86	13.67	13.56	13.84	15.48	13.95	13.50
Physicomechanical Characteristics												
Tensile Strength, MPa	4.46	4.54	4.56	4.36	4.65	4.60	4.74	4.77	4.43	4.18	4.59	4.40
Modulus at 300%, MPa	3.27	3.07	3.21	3.13	3.09	3.13	3.52	3.50	3.47	3.02	3.10	3.24
Elongation at Break, %	594	534	490	494	490	517	478	482	502	472	504	478
Equilibrium Swelling, %	256	255	248	250	248	239	252	255	252	257	236	237
M_C	2994	2974	2839	2882	2835	2663	2902	2957	2902	3004	2613	2629
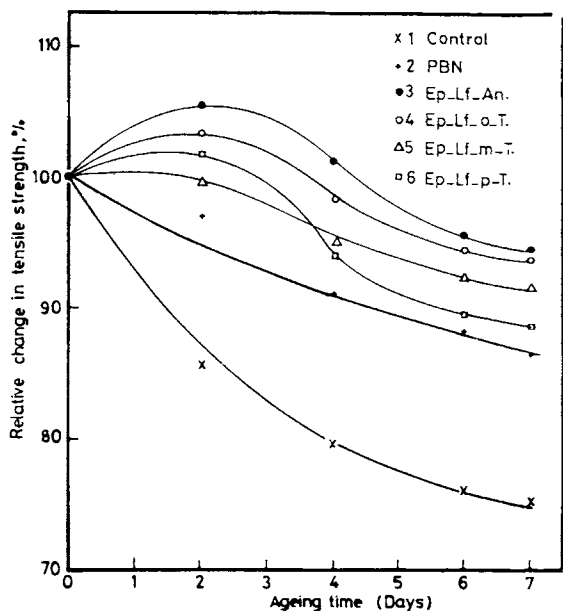
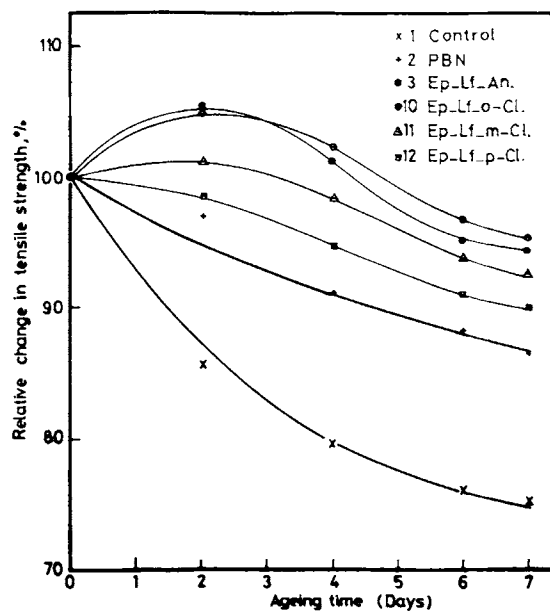**Figure 1**   Relative change in tensile strength vs. aging time.

Figure 3   Relative change in tensile strength vs. aging time.

Effect of the Chemical Structure of the Prepared Compounds on Their Efficiencies as Antioxidants

The curves of the physicomechanical and physico-chemical properties against aging time obey the power relationship of the formula:
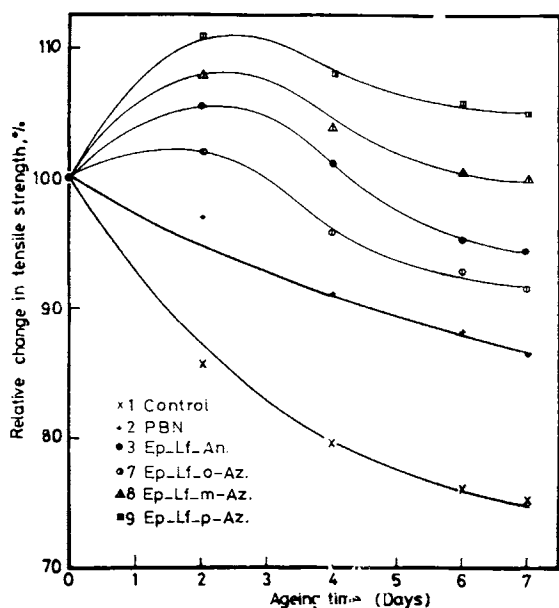
$$C = at^b, \quad 2 \le t \le 7$$

Where C is the relative change of the property, t is the aging time in days, and a, b are constants listed in Table III, with a degree of fitting $\ge$ 0.98.

The correlation between the chemical structure

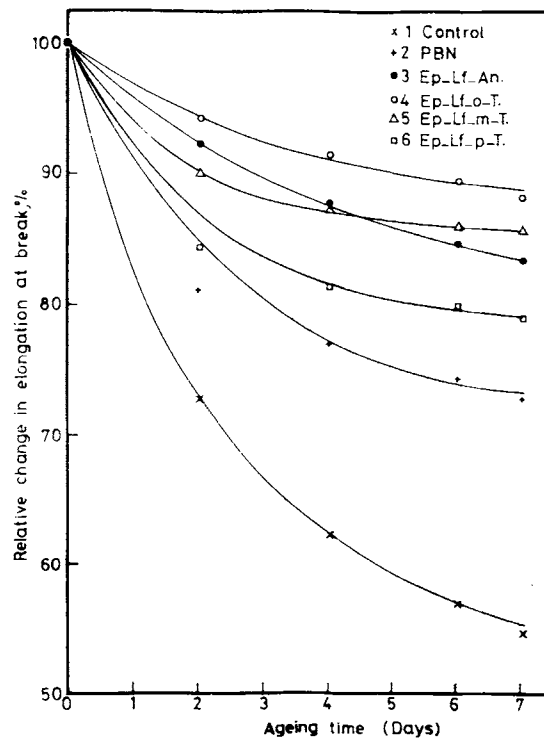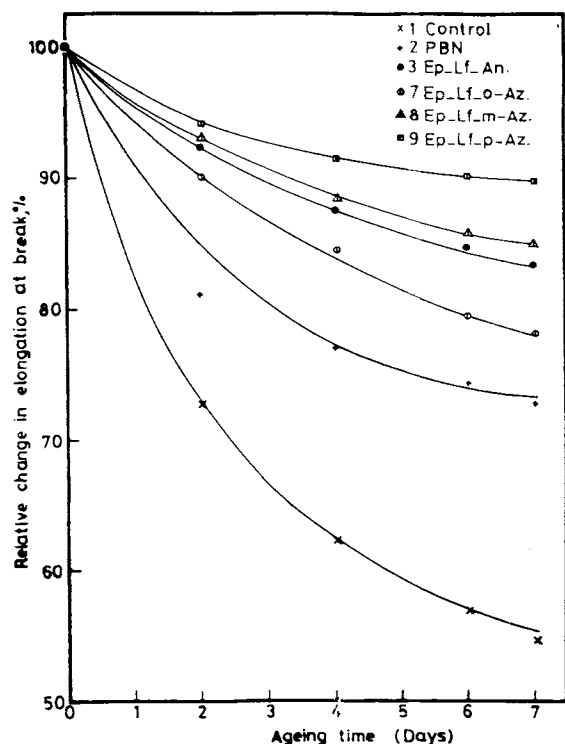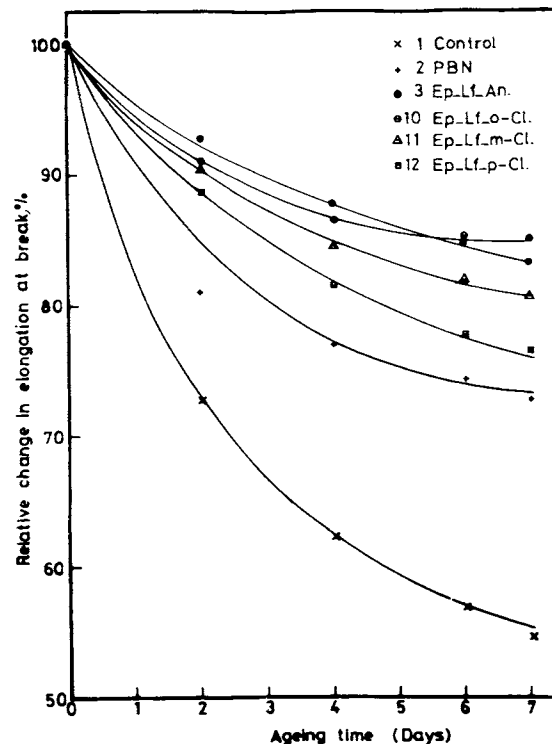**Figure 2**   Relative change in tensile strength vs. aging time.

Figure 4   Relative change in elongation at break vs. aging time.

Figure 5 Relative change in elongation at break vs. ageing time.

Figure 6 Relative change in elongation at break vs. ageing time.
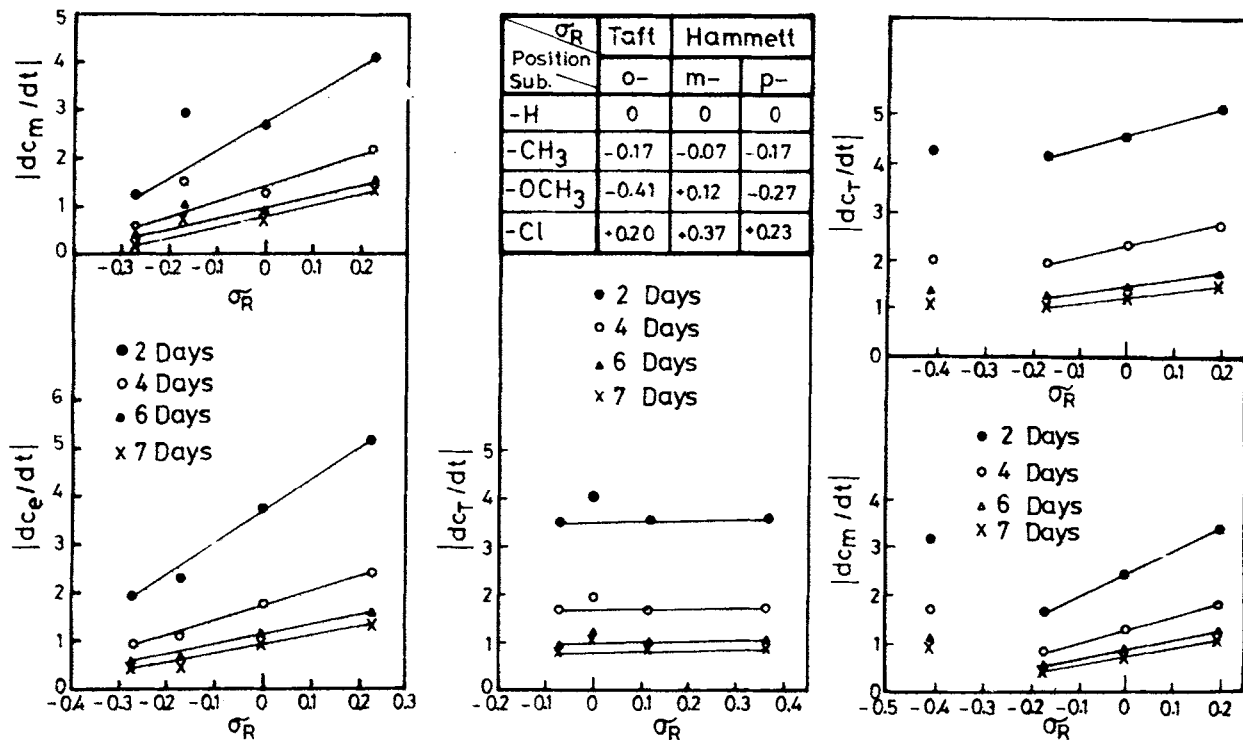
of the prepared compounds, and their efficiencies as antioxidants, was studied as a function of the rate of change of the relative changes of the physico-mechanical properties, during thermal oxidative aging. Thus, the lower the absolute value of the rate

of change, the higher the efficiency of the compound as antioxidant. The differentiation:

$$\frac{dc}{dt} = abt^{b-1}, \quad 2 \le t \le 7$$

**Table III The Constants a and b of the Relative Changes of the Samples Containing the Prepared Adducts**

Rel. Chan. Const. Samp. No.	Tensile Strength		Modulus 300%		Elongation %		Swelling %		M_C	
	a	b	a	b	a	b	a	b	a	b
1	91.927	−0.1046	106.299	0.0715	84.860	−0.2248	97.713	−0.1153	96.106	−0.1845
2	102.986	−0.0889	103.932	0.0724	86.161	−0.0861	99.704	−0.0805	99.477	−0.1294
3	113.081	−0.0908	103.788	0.0443	97.717	−0.0804	99.065	−0.0529	98.453	−0.0848
4	109.215	−0.0790	105.941	0.0296	98.040	−0.0511	100.266	−0.0452	100.192	−0.0731
5	104.551	−0.0697	102.289	0.0717	92.146	−0.0372	98.231	−0.0414	97.060	−0.0664
6	109.839	−0.1117	104.954	0.0536	87.826	−0.0533	98.569	−0.0586	97.738	−0.0946
7	108.052	−0.0850	103.211	0.0585	101.080	−0.1335	98.019	−0.0508	96.862	−0.0814
8	113.089	−0.0647	101.464	0.0463	98.099	−0.0750	99.631	−0.0496	99.335	−0.0794
9	116.713	−0.0547	101.413	0.0232	96.853	−0.0402	100.246	−0.0442	100.427	−0.0710
10	111.310	−0.0754	101.092	0.0633	94.413	−0.0556	102.447	−0.0752	103.905	−0.1210
11	106.637	−0.0696	103.808	0.0578	96.404	−0.0915	104.191	−0.0902	106.754	−0.1451
12	103.816	−0.0714	102.240	0.0766	95.798	−0.1160	102.482	−0.0871	103.943	−0.1398

σ_R Position Sub.	Taft	Hammett	
	o-	m-	p-
-H	0	0	0
-CH$_3$	-0.17	-0.07	-0.17
-OCH$_3$	-0.41	+0.12	-0.27
-Cl	+0.20	+0.37	+0.23

Figure 7 (a) The relation between $|dc_e/dt|$ and $|dc_m/dt|$ vs. Hammett constants (δ_R) for the parasubstituted An adducts. (b) The relation between $|dc_T/dt|$ vs. Hammett constants (δ_R) for the metasubstituted An adducts. (c) The relation between $|dc_m/dt|$ and $|dc_T/dt|$ vs. Taft constants (δ_R) for the ortho-substituted An adducts.
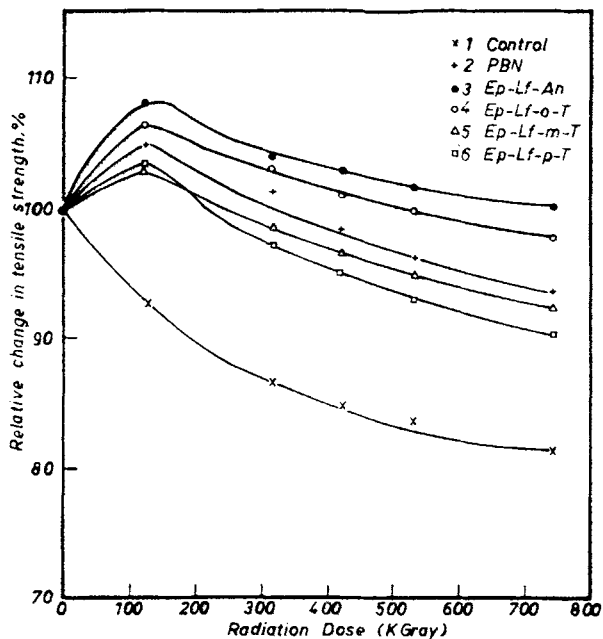
Figure 8 Relative change in tensile strength vs. radiation dose.
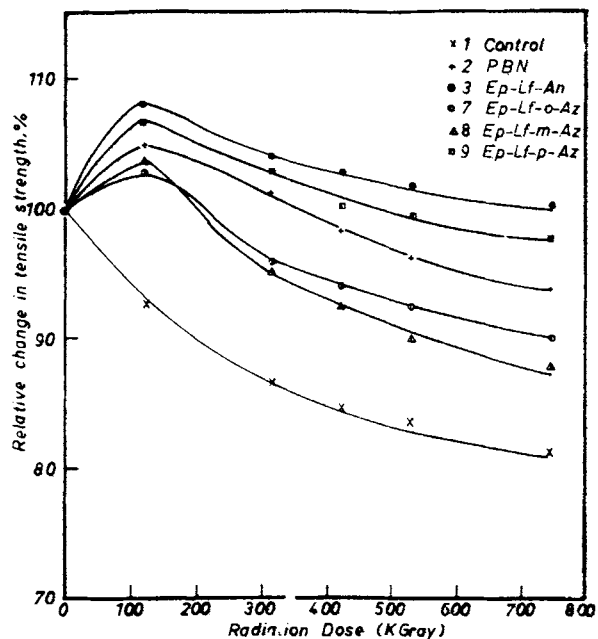
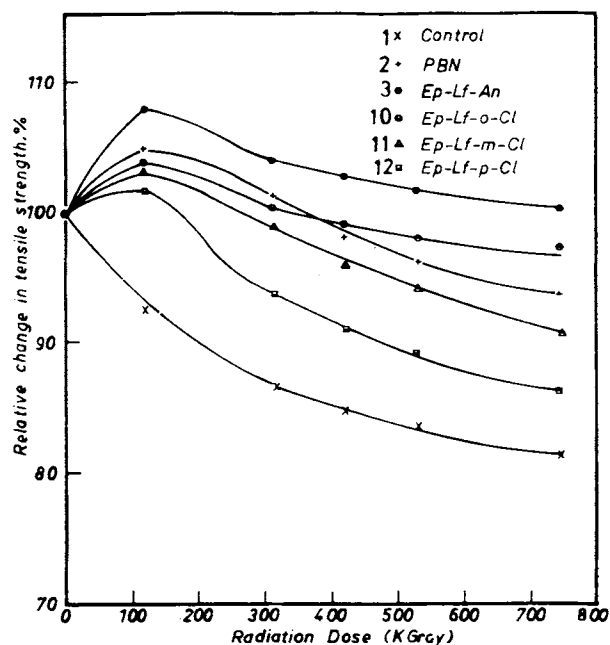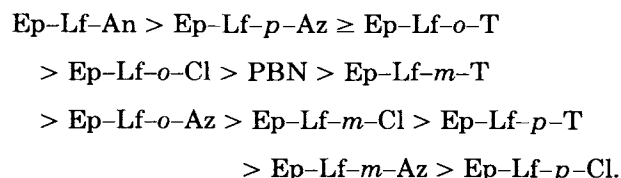**Figure 9** Relative change in tensile strength vs. radiation dose.

Figure 10 Relative change in tensile strength vs. radiation dose.

745 K. Gray. The relative changes in the tensile strength curves were taken as an example for the physicomechanical properties. Figures 8, 9, and 10 show the relative changes in tensile strength vs. radiation dose in K. Gray. The results show that crosslinking is the predominating process and the laboratory compounds can protect SBR vulcanizates against radiation damage in descending order:

Ep–Lf–An > Ep–Lf–p–Az $\geq$ Ep–Lf–o–T

> Ep–Lf–o–Cl > PBN > Ep–Lf–m–T

> Ep–Lf–o–Az > Ep–Lf–m–Cl > Ep–Lf–p–T

> Ep–Lf–m–Az > Ep–Lf–p–Cl.

CONCLUSIONS

1. The modified epoxidized linseed oil-free fatty acids with amines are useful as antioxidants and antirads in SBR formulations.
2. The chemical structure of the adducts plays an important role in the adducts efficiencies.

gives the rate of change, C, with respect to aging time. Figure 7(a) represents the dependence of the rate of change of modulus 300% $|dC_m/dt|$ and elongation at break $|dc_o/dt|$ against Hammett Constants (δ_R) for the parasubstituted aniline adducts. Both relations are found to be straightforward, where all these relations are linear and the rates of change, in each property, decrease with the increase of the electronegativity of the adducts, especially after 2 days of aging. On the other hand, the rate of change decreases with aging time and the lines become close together after 4 days and the lines for 6 and 7 days of aging are nearly parallel. Figure 7(b) represents the relation between the rate of change of tensile strength $|dc_T/dt|$ and the Hammett Constants (δ_R) for the meta-substituted aniline adducts. These relations are linear, but the effect of the substituent in the meta-position can be neglected. Figure 7(c) shows the dependence of $|dc_T/dt|$ and $|dc_m/dt|$ on Taft Constants (δ_R) for the ortho-substituted adducts. The lines of both relations lead to the same conclusion as above, except for the behavior of O-anisidine, which is always odd, and its efficiency is less than predicted.

Evaluation of the Laboratory Compounds as Antirads

The vulcanizates of all formulations in Table II were subjected to gamma rays for different doses up to

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