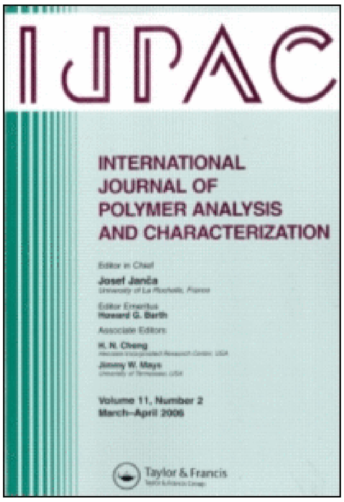

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Evaluation of Some Polyaromatic Amines as Antirads and Antifatigue Agents in SBR Vulcanizates

A. A. Wazzan[a]; M. N. Ismail[b]; M. A. Abd El Ghaffar[b]
[a] Department of Chemical and Materials Engineering, King AbdulAziz University, Jeddah, Saudi Arabia [b] Department of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

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A. A. Wazzan
Department of Chemical and Materials Engineering,
King AbdulAziz University, Jeddah, Saudi Arabia

M. N. Ismail and M. A. Abd El Ghaffar
Department of Polymers and Pigments, National Research Centre,
Dokki, Cairo, Egypt

Abstract: Six polyaromatic amines, polyaniline, poly(o-toluidine), poly(*m*-toluidine), poly(*m*-anisidine), poly(2-aminopyridine), and poly(2-amino-6-methylpyridine), have been prepared by the chemical oxidation of their monomers using potassium persulphate. These polymers were incorporated into styrene-butadiene rubber (SBR) mixes. The rheometric characteristics of the green rubber mixes were determined using an oscillating disc rheometer. The compounds were evaluated as antirads and antifatigue agents in SBR vulcanizates. The efficiency of the polymers was correlated with their chemical structures. It was found that the polymers investigated show good antirad and antifatigue behavior compared with the conventional, industrially used agent, phenyl-β-naphthyl amine (PβN).

Keywords: SBR vulcanizates; Polyaromatic amines; Rheometric characteristics; Physico-mechanical properties; Antirad; Antifatigue

Address correspondence to A. A. Wazzan, Department of Chemical and Materials Engineering, King AbdulAziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia. E-mail: awazzan@kau.edu.sa

INTRODUCTION

All elastomeric materials undergo different types of degradation. Depending on their structure the deterioration leads to chain scission, cross-linking, or formation of oxygen-containing functional groups in the polymer chain or as degradation products.[1,2]

The exposure of polymers to air during aging (radiation, thermal, UV) causes fast oxidative degradation. The degradation rate can be lowered by the addition of suitable chain-breaking antioxidants.[3]

In spite of the fact that compounds that can be used as antioxidants, antiradiation agents, and antifatigue agents are added in small amounts (1–2 phr), they play a very important role in determining the service characteristics of the rubber vulcanizates.[4,5] The influence of the chemical structure of antioxidants on the development of oxidation has attracted much interest due to the importance of the service life of polymer products.[6–10]

Phenolics, amines, organosulfur, and organophosphonate compounds are well known as antioxidants and antiradiation agents (antirads) for natural and synthetic rubbers. The molecular weights of these compounds are relatively low, often leading to surface bloom and volatilization. One method to increase the persistence of the antioxidant in the polymer is to use high molecular weight compounds that cannot migrate to the rubber surface and hence are less readily lost by volatilization.[11–16]

Polyanilines are compounds with wide applications as conducting polymers[17,18] and as efficient corrosion inhibitors for steel protection.[19] Recent studies,[20–23] reported that polyaniline and some polyaniline derivatives showed high efficiency as novel antioxidants for NR and SBR vulcanizates.

The present work aims to confirm and evaluate the effects of some of polyaromatic amines as antirads and antifatigue agents in styrene-butadiene (SBR) vulcanizates. The role of the chemical structure of the polymers being investigated was also examined.

MATERIALS AND TECHNIQUES

Materials

- Rubber: Styrene butadiene rubber (SBR-1502).
- Accelerators: *N*-cyclohexyl-2-benzothiazole sulphen-amide (CBS).
- Antioxidants: Phenyl-β-naphthyl amine (PβN), commercial grade.
- Activators: Stearic acid and zinc oxide.
- Curing agent: Sulfur.
- Fillers: High-abrasion furnace carbon black (HAF).
- Plasticizer: Naphthenic processing oil.

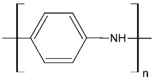
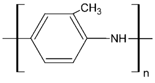
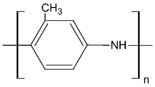
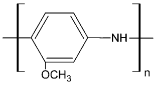
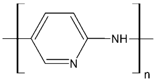
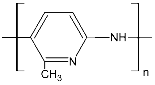
Techniques

Preparation of Polymeric Samples

First, 0.1 M of the monomer involved was dissolved in 100 mL of absolute ethyl alcohol and placed in an ice bath (0–5°C) with continuous magnetic stirring. Another solution of 0.025 M of potassium persulphate in 25 mL of distilled water was rapidly added to the monomer solution. After strong stirring for 20 min, the reaction medium was allowed to stand overnight. The precipitate was separated by filtration through a sintered glass funnel (G3) and washed with 250 mL of distilled water, 50 mL of absolute ethyl alcohol and ethyl acetate, and then dried overnight in a vacuum oven at 100°C. The six resulting polymers: polyaniline, poly(*o*-toluidine), poly(*m*-toluidine), poly(*m*-anisidine), poly(2-aminopyridine), and poly(2-amino-6-methylpyridine) are listed in Table I. These polymers were characterized using various spectrophotometric measurements like UV-vis, IR, and thermal analysis.[21]

The viscosity measurements of these polymers were carried out using an Ostwald viscometer. The intrinsic viscosity was calculated and the relative molecular mass of each polymer were estimated using the method

Table I. The polyaromatic amine polymers prepared in this work

No.	Polymer	Relative molecular mass	Formula	Abbrev.
1.	Polyaniline	4748		PA
2.	Poly(*o*-toluidine)	5042		PoT
3.	Poly(*m*-toluidine)	5141		PmT
4.	Poly(*m*-anisidine)	5342		PmAs
5.	Poly(2-amino-pyridine)	4845		PAPy
6.	Poly(2-amino-6-methylpyridine)	4943		PMAPy

outlined by Atkins.[24] The results are given in Table I from the following equation.[24]

$$[\eta] = KM_r^a \qquad (1)$$

where K and a are the Mark-Houwink constants.

Preparation of Rubber Mix Vulcanizates

All rubber mixes were prepared on a two-roll mill (diameter 470 mm, width 300 mm, speed of slow roll 24 rpm, gear ratio 1:1.4). The roll temperature was kept at about 50°C during mixing. The compounded rubber was left overnight before vulcanization. The vulcanization press was operated at 152 ± 1°C under a pressure of about 4 MPa.

Tests of Rubber Mixes and Vulcanizates

The following standard methods were employed for the characterization of the prepared samples:

(a) ASTM D 1646 (1994) for the determination of the rheometric characteristics using a Monsanto oscillating disc rheometer 100.
(b) ASTM D 412-98a (1998) for the determination of physico-mechanical properties using a fully computerized Instron tensile testing machine 5586.
(c) ASTM D 471-97 (1998) for equilibrium swelling, Q.
(d) ASTM D430-73 (1973) for the determination of fatigue property using Monsanto fatigue tester 1425.

Irradiation Procedure

A cobalt-60 source (Gamma cell-40GS 6500), manufactured by the Atomic Energy Agency of Canada, was used as a source of radiation. The dose rate used was about 30 k Gray/h. The SBR mix specimens were subjected to irradiation from 30 to 150 k Gray.

In addition, a UV lamp of 254 nm wavelength and 7 MW/cm^3 intensity was used as a source of irradiation.

RESULTS AND DISCUSSION

Effect of Polyaromatic Amines on the Properties of SBR Mixes

The polyaromatic amines were incorporated into SBR formulations according to the usual regime. The rubber formulations, rheometric characteristics, and the physico-mechanical properties are shown in

Table II. Rubber formulations containing the investigated polymers

	Formula number							
Ingredient, phr[a]	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
SBR	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Processing oil	5	5	5	5	5	5	5	5
HAF	20	20	20	20	20	20	20	20
S	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
PβN	—	1	—	—	—	—	—	—
PA	—	—	1	—	—	—	—	—
PoT	—	—	—	1	—	—	—	—
PmT	—	—	—	—	1	—	—	—
PmAs	—	—	—	—	—	1	—	—
PAPy	—	—	—	—	—	—	1	—
PMAPy	—	—	—	—	—	—	—	1

[a] phr: part per hundred parts of rubber.

Tables II and III for the eight formulations tested during this research work.

From the results given, it can be seen that the polymers investigated have a slight effect on the maximum torque and cure rate index. Such a behavior is very important for compounds usually used as age resistors. It

Table III. Rheometric characteristics and physico-mechanical properties of the investigated vulcanizates

	Formula number							
Properties, phr	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
ML (dN m)	7.5	7.5	7.5	6.5	7.5	7.5	7.5	6.5
MH (dN m)	82	78	79.5	77.5	78	80	79.5	79
tc_{90} (min)	16	15.5	16	16	15.5	16.5	16	16
ts_2 (min)	5	5	5.5	5.5	5	5.5	5.5	5.5
CRI $(min)^{-1}$	9.1	9.5	9.5	9.5	9.5	9.5	9.5	9.5
TS, MPa	6.9	7.2	7.4	7.5	7.8	7.9	7.6	7.8
E, %	341	393	450	534	470	466	504	486
Q, %	490	460	415	390	400	405	400	410

phr: part per hundred parts of rubber; ML: minimum torque; MH: maximum torque; tc_{90}: optimum cure time; ts_2: scorch time; CRI: cure rate index; TS: tensile strength; E: elongation at break; Q: equilibrium swelling.

is also observed that the prepared compounds increase tensile strength and elongation at break while they decrease equilibrium swelling.

Evaluation of the Polymers as Antiradiation Agents of SBR Mixes

The SBR mixes containing the aforementioned polymers were vulcanized at 152 ± 1°C up to their optimum cure time. The rubber vulcanizates were then subjected to gamma irradiation at different doses up to 150 k Gray. The percent retained values of tensile strength, elongation at break, and equilibrium swelling were calculated and are illustrated in Figures 1–6.

From Figures 1–3, it is clear that Pm As, PmT, PoT, and PA can protect SBR vulcanizates against gamma radiation to higher levels than PβN, the antirad widely used in the rubber industry. The SBR vulcanizates, for example, after exposure to gamma radiation up to 150 k Gray can retain at least 74, 72, 71, and 69% of their tensile strength, 70, 68, 66, and 63% of the elongation at break, and 83, 82, 97, and 69% of the equilibrium swelling, respectively. The high efficiency of poly(*m*-anisidine) is attributed to the linear structure, which exhibits a high degree of conjugation in the extended aromatic amine system and the presence of methoxy groups in the polymer backbone, which increases the basicity of the amino groups.

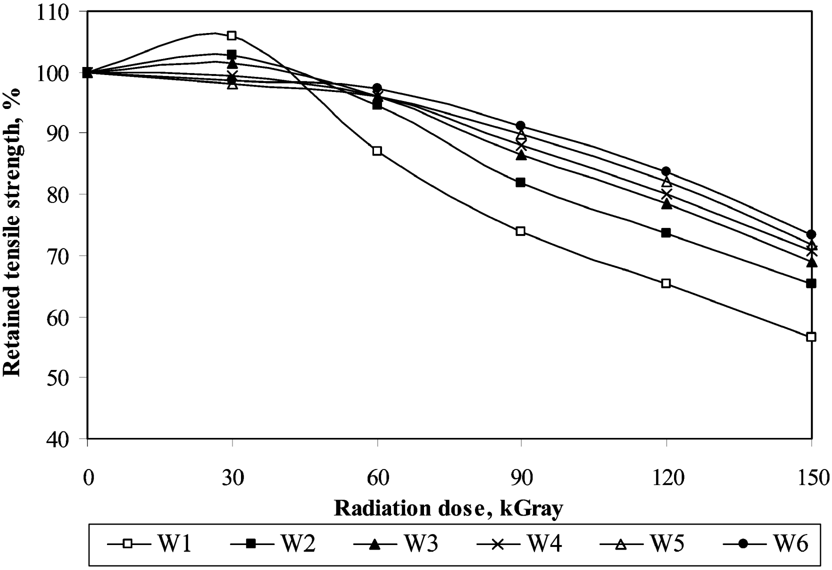


Figure 1. Retained tensile strength vs. radiation dose for SBR vulcanizates containing polyaniline derivatives.

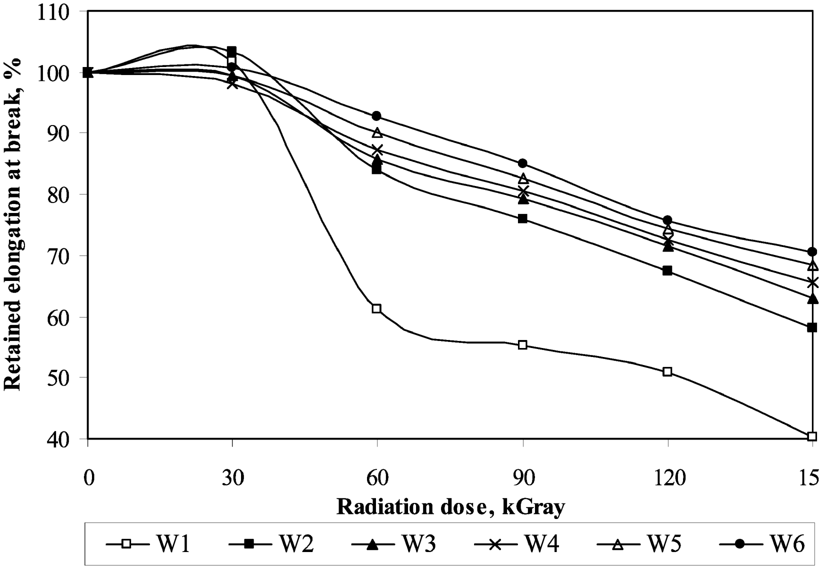


Figure 2. Retained elongation at break vs. radiation dose for SBR vulcanizates containing polyaniline derivatives.

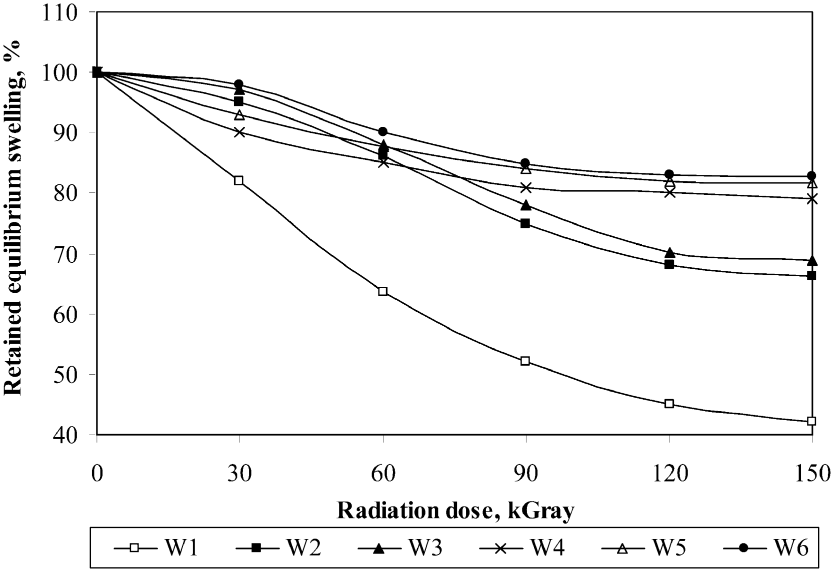


Figure 3. Retained equilibrium swelling vs. radiation dose for SBR vulcanizates containing polyaniline derivatives.

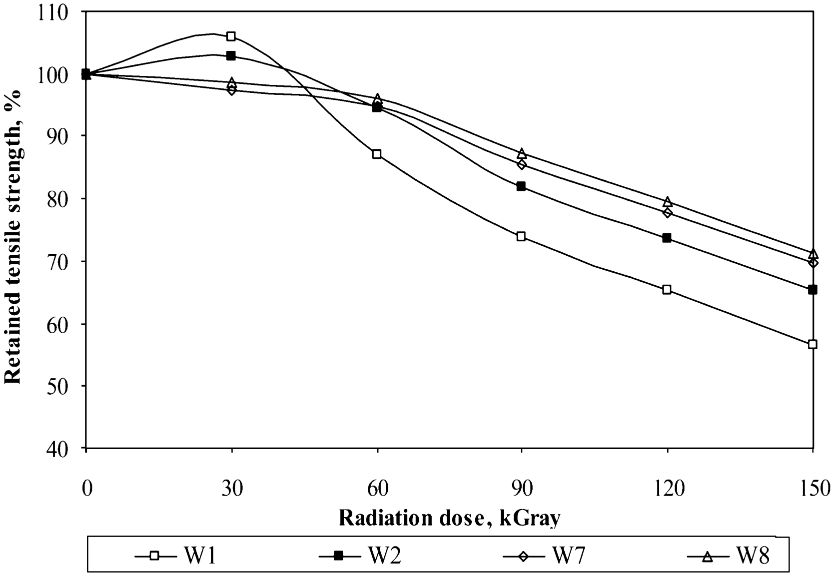


Figure 4. Retained tensile strength vs. radiation dose for SBR vulcanizates containing PAPy and PMAPy.

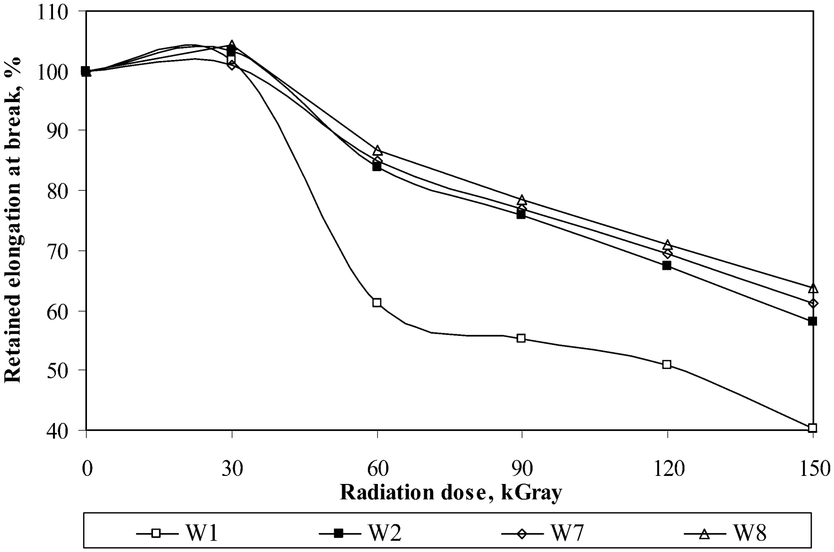


Figure 5. Retained elongation at break vs. radiation dose for SBR vulcanizates containing PAPy and PMAPy.

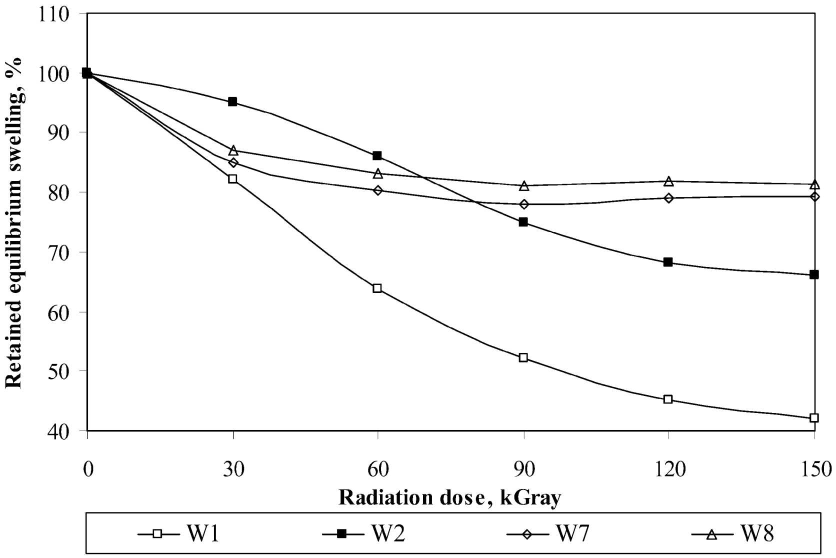


Figure 6. Retained equilibrium swelling vs. radiation dose for SBR vulcanizates containing PAPy and PMAPy.

On the other hand, the polytoluidines can be considered as efficient antirad agents compared to PβN due to the linear structure and the highly conjugated polyamine systems, in addition to the presence of the methyl group, which has a positive inductive effect. In addition, the methyl group in the meta position with respect to the –NH– group reduces the degree of degradation in the rubber vulcanizates and facilitates removing the proton of the –NH– group. However, the methyl group in the ortho position to the –NH– group deactivates the removal of the proton via steric hindrance.

From the results of the physico-mechanical properties under investigation for the rubber vulcanizates, polyaniline retards the degradation process due to gamma radiation. This can be interpreted as a result of the resonance effect of the benzene ring, which stabilizes the radicals formed. The results show that the PA compound can protect SBR vulcanizates against radiation damage in competition with the commercial compound PβN. It can be concluded that the polyaromatic amines studied may be used as antirads for SBR vulcanizates, and their efficiencies can be arranged as follows:

$$\text{PmAs} > \text{PmT} > \text{PoT} > \text{PA} > \text{P}\beta\text{N} > \text{Without}$$

From Figures 4–6, it can be observed that poly(2-aminopyridine) and poly(2-amino-6-methylpyridine) can also protect SBR vulcanizates against gamma radiation better than PβN. The SBR vulcanizates containing PAPy and PMAPy after exposure to gamma radiation up to 150 k Gray can retain at least 71 and 69% of their tensile strength, 64 and 61% of the elongation at break, and 81 and 79% of the equilibrium swelling, respectively, whereas the vulcanizates containing PβN retain 65%, 58%, and 66% of their tensile strength, elongation at break, and equilibrium swelling values respectively. This can be attributed to the presence of the nitrogen atom in the pyridine ring in the ortho position to the –NH– group, which consequently deactivates more and more of deprotonation, and hence the degree of degradation of the rubber chains will be reduced less. It can be concluded that the compounds studied may be used as antirads for SBR vulcanizates, and the efficiencies can be arranged as follows:

$$\text{PMAPy} > \text{PAPy} > \text{P}\beta\text{N} > \text{Without}$$

The SBR vulcanizates of all formulations (W_1–W_8) under investigation were also subjected to UV irradiation for 200 h. The physico-mechanical properties were determined and the retained values are presented in Figure 7. As shown from these data, the prepared polymers retard the degradation process and protect SBR vulcanizates against UV radiation damage. The efficiency of protection and the effect of chemical structure show the same trend as observed previously with gamma radiation.

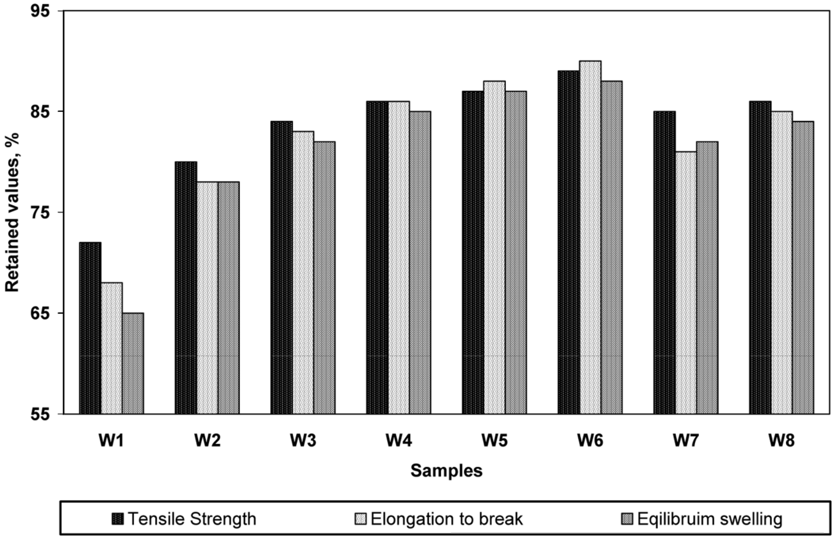


Figure 7. Retained tensile strength, elongation at break, and equilibrium swelling after exposure to 200 h UV radiation.

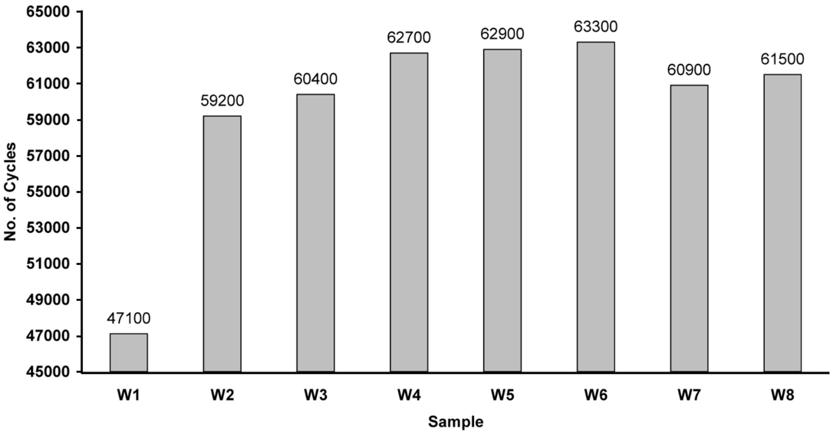


Figure 8. Fatigue to failure test for SBR vulcanizates.

Evaluation of the Polymers as Antifatigue Agents for SBR Mixes

Fatigue crack resistance of rubber is an important property in tire service as well as for other rubber products. Therefore, it is necessary to add some ingredients in rubber mixes to protect the resulting rubber products from fatigue failure under the service conditions. The synthesized compounds polyaniline, poly(*o*-toluidine), poly(*m*-toluidine), poly(*m*-anisidine), poly(2-aminopyridine), and poly(2-amino-6-methylpyridine) were incorporated in SBR mixes. The vulcanizates were tested according to standard methods, and the number of cycles was taken as a measure of the service life of the rubber vulcanizates. The data obtained are presented in Figure 8. It is worth noting that the prepared polymers are highly efficient antifatigue agents in SBR vulcanizates. The differences in efficiency among the six polyaromatic amine compounds can be attributed to the differences in their chemical structure and can be arranged as follows:

$$\mathrm{P_mAs > PmT > PoT > PMAPy > PAPy > PA > P\beta N > Without}$$

CONCLUSIONS

All six polyaromatic amines prepared, polyaniline, poly(*o*-toluidine), poly(*m*-toluidine), poly(*m*-anisidine), poly(2-aminopyridine), and poly(2-amino-6-methylpyridine), serve as excellent antirad and antifatigue agents in protecting SBR vulcanizates, as has been observed during the course of this research work.

The chemical structure of the prepared polymers has a major effect on their efficiency as antirads and antifatigue agents for SBR valcanizates.

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