Synthesis, Characterization, and Evaluation of Natural Rubber-*graft*-*N*-(4-Aminodiphenyl methane) Acrylamide as an Antioxidant

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ABSTRACT: The synthesis of *N*-(4-aminodiphenylmethane) acrylamide (ADPMA) was performed through the reaction of 4,4'-diaminodiphenyl methane and acryloyl chloride in the presence of triethyl amine. The grafting of ADPMA onto natural rubber was executed with UV radiation. Benzoyl peroxide was used to initiate the free-radical grafting copolymerization. Natural rubber-*graft*-*N*-(4-aminodiphenyl methane) acrylamide (NR-*g*-ADPMA) was characterized with an IR technique. We studied the effect of aging on the mechanical properties and the swelling and extraction phenomena for acrylonitrile–butadiene copolymer (NBR) vulcanizates, which contained the prepared NR-*g*-ADPMA and a commercial antioxidant, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine. The prepared antioxidant enhanced both the mechanical properties of the NBR vulcanizates and the permanence of the ingredients in these vulcanizates. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 843–849, 2006

Key words: copolymerization; mechanical properties; radiation; rubber; swelling
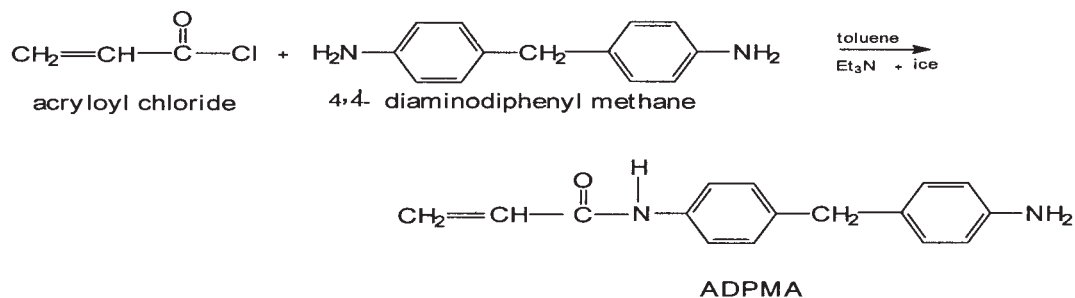
INTRODUCTION

Many industrial polymer products are exposed to various types of degradation by the subjection of polymer products to heat, various kinds of radiation, and mechanical stresses. Main-chain scission takes place, so their mechanical properties worsen. These degradation processes are considerably accelerated in the presence of oxygen. Degradation processes of polymers are influenced by the addition of various kinds of stabilizers, which should lower the rate of degradation via reactions with various radicals formed by polymer main-chain scission, isomerization, and free-radical transfer, as indicated by an inhibition of the oxidative degradation.

The reaction of a peroxy radical with an inhibitor plays the main role in the retardation of polymer oxidation by antioxidants. The activity of antioxidants depends not only on their ability to trap peroxy and hydroperoxy radicals and the catalytic action in hydroperoxide decomposition but also on their compatibility with the polymer.[1] Antioxidants may be added to polymers to minimize the effects of oxidative degradation during processing at elevated temperatures or to prolong the service life of the finished product.

In the selection or design of antioxidants for practical situations, problems with the loss of antioxidants by both chemical and physical processes may be encountered. The chemical loss of an antioxidant can occur during processing if the base polymer is to be crosslinked; the antioxidant may be consumed by interfering with the crosslinking reactions.[2] The net result is that the concentration of the antioxidant in the base polymer is reduced, and so the service life of the product is shortened. Physical losses of an antioxidant can occur during the processing of the polymer if the antioxidant is sufficiently volatile at the fabrication temperature. Antioxidants also may diffuse to the surface, or those that are soluble in molten polymers may become insoluble at service temperatures and may separate out preferentially on the surface. This phenomenon is known as blooming, and the subsequent loss of the antioxidant then occurs from the polymer surface by evaporation. Finally, if the polymer is in contact with appropriate solvents during service, these may lead to the loss of a soluble antioxidant via leaching.[3] To avoid the loss of antioxidants through extraction or volatilization; macromolecular, polymerizable, or grafting antioxidants may be used.[4] High-molecular-weight antioxidants and polymerizable antioxidants do not ensure the protection of the entire volume because they cannot diffuse through the rubber. Grafted antioxidants are high-molecular-weight compounds that bond by chemical treatments to the macromolecules or sometimes during the processing of the polymer, and the use of grafting antioxidants is

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Scheme 1

one of the best ways of protecting unsaturated rubbers.[5,6]

Irradiating the polymer in the presence of a solvent containing a monomer leads to photografting. UV radiation is well absorbed by UV initiators, so a photoinitiator (e.g., benzoyl peroxide and its derivatives) is used to initiate the reaction.[7] UV irradiation appears to be an excellent method for grafting copolymerization because of its simplicity and cleanliness and the lower cost of its energy source.

EXPERIMENTAL

Materials

4,4′-Diaminodiphenyl methane and benzoyl peroxide were supplied by Fluka Chemie AG (Postfach 260, CH-9471 Buchs, Switzerland) and Sigma–Aldrich Co. (Milwaukee, WI), respectively. Acryloyl chloride and triethylamine were obtained from Merck (Sarmstadt, Germany). All solvents were laboratory-grade and were supplied by Edwic (Cairo, Egypt).

Synthesis of *n*-(4-aminodiphenyl methane) acrylamide (ADPMA)

4,4′-Diaminodiphenyl methane (0.1 mol) in 100 mL of toluene was stirred with 0.1 mol of Et_3N in an ice bath. Acryloyl chloride (0.1 mol) was added dropwise. After the addition, the reaction mixture was stirred for 2 h, left overnight, and then filtered.[8] The filtrate was dried in vacuo, and the product, obtained as a solid, was then crystallized from tetrahydrofuran/heptane mixtures. The synthesis of ADPMA is graphically presented in Scheme 1.

Synthesis of natural rubber-*graft*-N-(4-aminodiphenyl methane) acrylamide (NR-*g*-ADPMA)

UV irradiation was performed with a low-pressure mercury lamp. The power supply model was SCT-1A/F (230 V, 0.15 A, 50 Hz). The UV pencil lamp

model was 11 SC-LOP (short-wave UV, 254 nm) (Westbury, NY).

Natural rubber (NR; 1,4-polyisoprene; 3 g) was dissolved in 300 mL of toluene, with constant stirring, at room temperature in a reaction bottle. The NR solution was irradiated for 24 h by a UV lamp. Mohr's salt (ferrous ammonium sulfate; 0.0588 g), 0.6 g of ADPMA, and 0.0015 g of benzoyl peroxide were added to the contents of the reaction bottle. The reaction was allowed to proceed for 12 h. After that, the reaction mixture was poured into ethanol to precipitate ungrafted NR. The grafted NR was isolated by the evaporation of the solution. The grafting percentage was taken as the ratio of the graft yield to NR multiplied by 100:[9]

$$\text{Degree of grafting} = (W_g/W_{NR}) \times 100$$

where W_{NR} is the weight of NR and W_g is the weight of the graft yield. The degree of grafting was calculated and is reported in Table I. The synthesis of NR-*g*-ADPMA is graphically presented in Scheme 2.
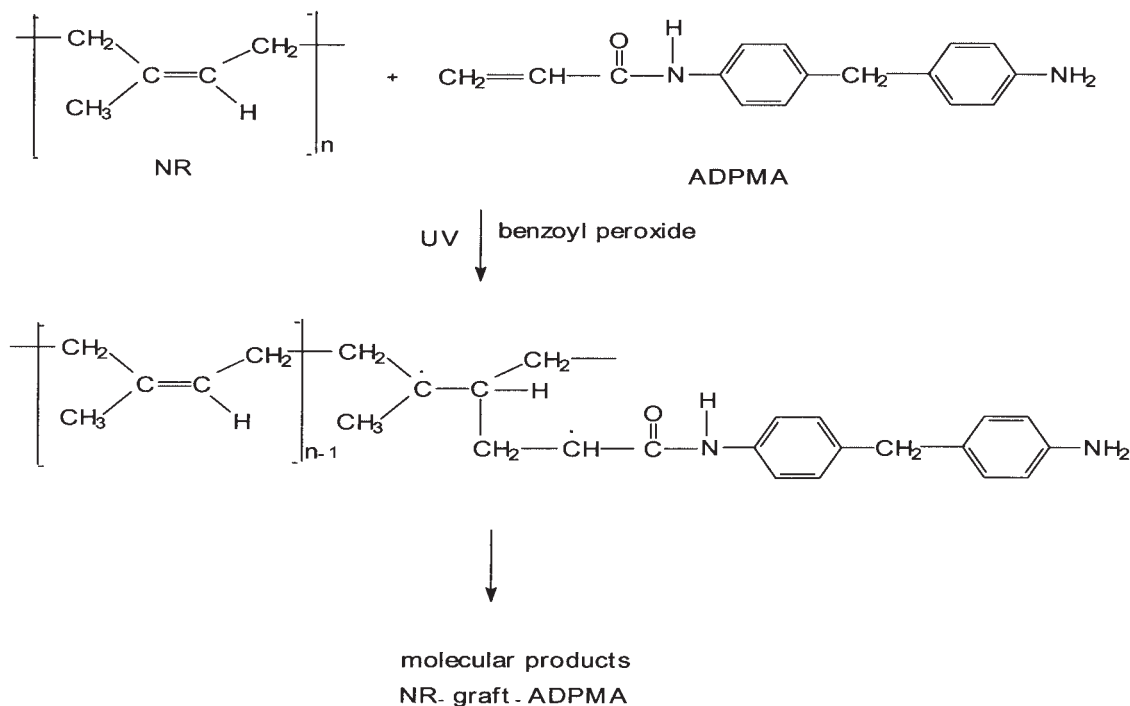
Characterization of ADPMA and NR-*g*-ADPMA

IR spectroscopy data were recorded on a PerkinElmer 11650 FTIR spectrometer (Wellesley, MA) to elucidate the structure and to ensure the purity of the products. The IR spectroscopy data for ADPMA and NR-*g*-ADPMA are summarized in Tables II and III. Figures 1–3 present the IR spectra of ADPMA, NR, and NR-*g*-ADPMA, respectively.

The IR spectrum of NR is shown in Figure 3. The spectrum shows the characteristic peaks of the —C=C— group at 1693.4 cm^{-1}, the —CH$_2$—

TABLE I
Degree of Grafting of NR-*g*-ADPMA

Prepared antioxidant	Degree of grafting (%)
NR-*g*-ADPMA	39.72

Scheme 2

C(CH$_3$)H— group at 2924.6 cm^{-1}, and the —CH$_2$ group at 1423.5 cm^{-1}.[9]

The IR spectra of Figures 1–3 were compared. In the spectrum of Figure 3, the intensity of the double-bond absorption peak for NR and ADPMA decreases, and a new absorption appears for NH, NH$_2$, and amide groups. The results prove that ADPMA was grafted onto NR.

Mixing and processing

The mixes examined in this study were based on an acrylonitrile–butadiene copolymer (NBR) with the trade name Humex N-34/47, which is produced by Polymer Corp. (Cosne sur Loire, France). NBR mix formulations containing NR-*g*-ADPMA and the mechanical properties of unaged samples are given in Table IV.

A semireinforcing furnace (SRF) was used as a carbon black filler in the NBR mixes, and the main properties of the SRF are given in Table V.

Zinc oxide as an inorganic accelerator activator and stearic acid as an organic acid accelerator activator were used to activate the accelerators used in the vulcanization process. The accelerators were mercaptobenzthiazole (MBT) and tetramethyl thiuram disulfide (TMTD). Elemental rhombic sulfur was used as a vulcanizing agent in all mixes.

All rubber mixes were prepared on a water-cooled, two-roll mill 150 mm in diameter and 300 mm wide. The roll temperature was kept at about 50°C during mixing. The rubber mixes were vulcanized at 152°C with an electric press for the optimum cure time, which was indicated by a Monosanto rheometer (Swindon, UK). A vulcanized sheet 20 cm long and 2 mm thick was obtained. Test pieces were cut from this sheet for the determination of the different properties of the prepared rubber mixes.

RESULTS AND DISCUSSION

The prepared NR-*g*-ADPMA was incorporated into an NBR vulcanizate, and we used a mechanical technique

TABLE II
Spectral Properties of ADPMA

Name	IR (KBr, ν, cm^{-1})
ADPMA	—CH$_2$=CH—, 1061.0
	Amide I, 1613.1
	Amide II, 1500.6
	NH, 3275.5
	NH$_2$, 1224.0

TABLE III
Spectral Properties of NR-*g*-ADPMA

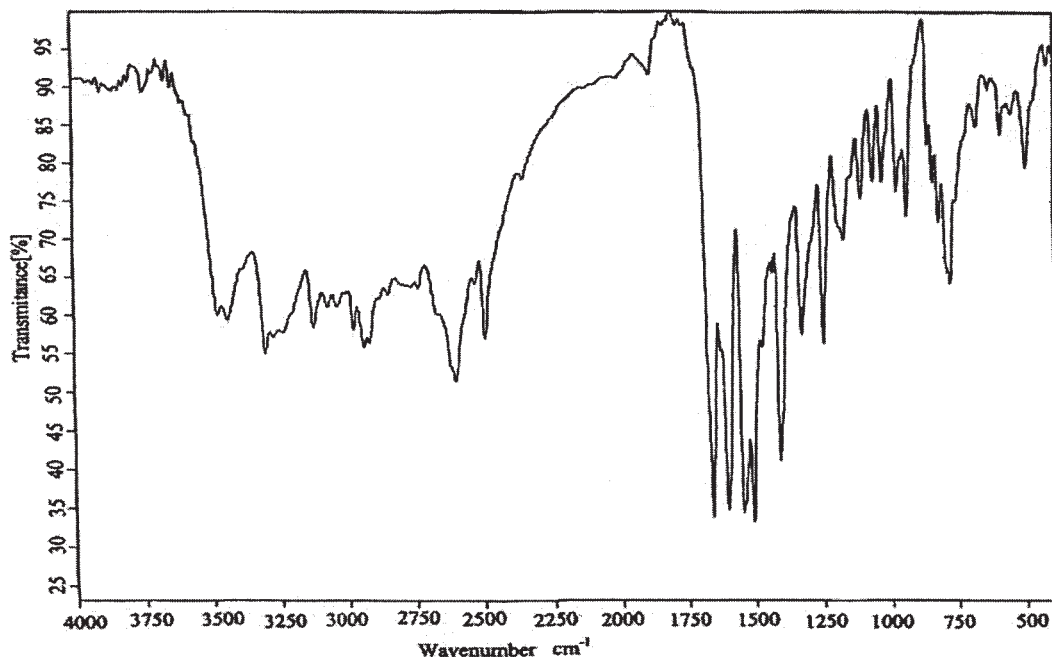| Prepared antioxidant	IR (KBr) ν (cm^{-1})	
NR-*g*-ADPMA	Amide	I,1599.4
	Amide	II,1577.9
	NH$_2$,	1277.2
	NH,	2959.0

Figure 1 IR spectrum of ADPMA.

and swelling and extraction phenomena to study the effect of the prepared antioxidant on the NBR vulcanizate properties. Because *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) is still the most widely used antioxidant for rubber, we used it to judge the ability of the prepared antioxidant to protect NBR vulcanizates.

Effect of aging on the mechanical properties of the NBR vulcanizates

NBR mixes (Table IV) were vulcanized at 152°C with an electric press for the cure time. Unaged, dumbbell-shaped samples were prepared, and their tensile strength, modulus at 200% strain, and elongation at
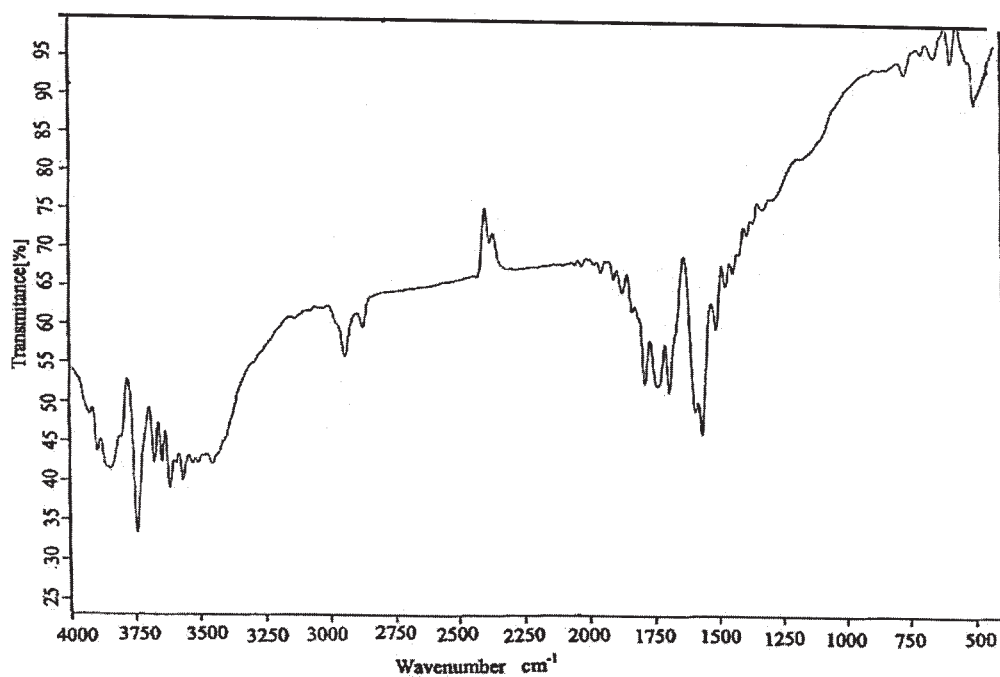

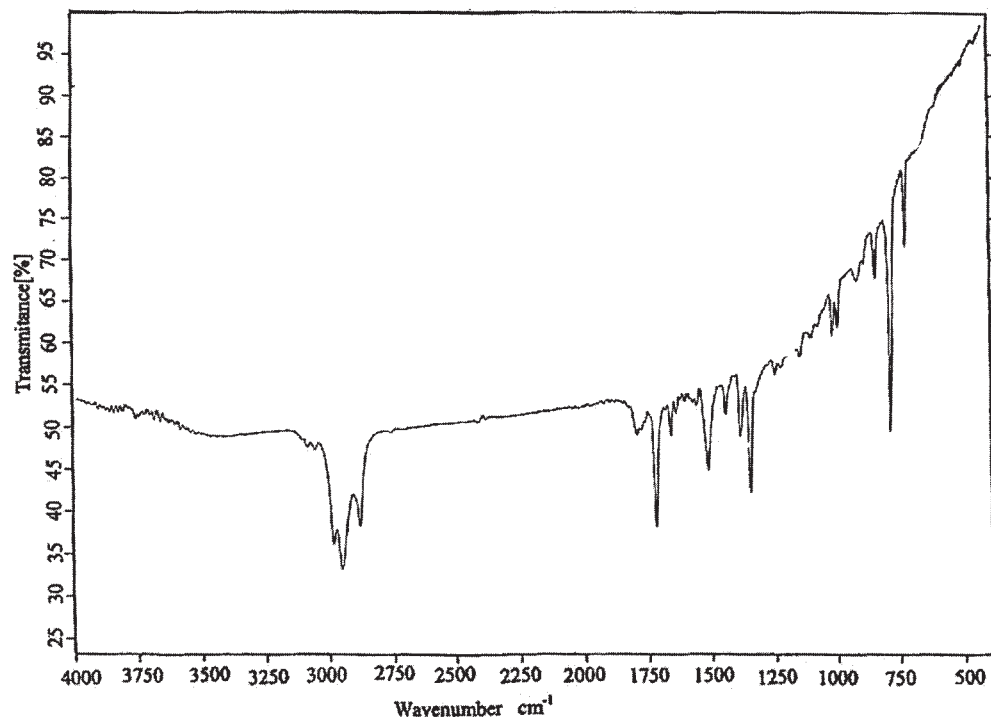**Figure 2** IR spectrum of NR.

Figure 3 IR spectrum of NR-*g*-ADPMA.

break were measured with a Zwick model Z010 tensile testing machine (Ulm, Germany); the values are reported in Table IV. Other NBR vulcanizates were aged in an oven fixed at 90°C for 2, 4, 6, and 7 days, and the values of the same properties were calculated with respect to the values of the unaged samples.

The results in Table IV indicate that the unaged mix containing 1 phr NR-*g*-ADPMA had different properties than the mix containing IPPD and the control mix. NR-*g*-ADPMA may have been affected by the cure

TABLE IV
NBR Mix Formulations Containing NR-*g*-ADPMA and Mechanical Properties of Unaged Samples

Mix ingredient	Sample		
	A1	A2	A3
NBR	100	100	100
ZnO (phr)	5	5	5
Stearic acid (phr)	2	2	2
Processing oil (phr)	5	5	5
SRF (phr)	30	30	30
Sulfur (phr)	1.5	1.5	1.5
MBT (phr)	0.75	0.75	0.75
TMTD (phr)	0.75	0.75	0.75
IPPD (phr)	—	1	—
NR-*g*-ADPMA (phr)	—	—	1
Cure time (min)	8.7	5.3	9.96
Scorch time (min)	2.48	1.96	1.23
Tensile strength (MPa)	7.32	5.96	8.99
Modulus at 200% (MPa)	1.95	1.87	2.41
Elongation at break (%)	367	341	308

rate, polymer–filler interaction parameters, and filler–filler interaction parameters in the NBR vulcanizate.

Figures 4–6 illustrate the relations between the retained values of the mechanical properties and the aging time. In each figure, curves representing the investigated antioxidant, IPPD, and a control mix are presented. Figure 4 shows the relationship between the retained values of the tensile strength and aging time; the NBR vulcanizate containing the prepared antioxidant had higher tensile strength than the mix containing IPPD and the control mix. Figure 5 shows the relationship between the retained values of the modulus at 200% strain and the aging time; NR-*g*-ADPMA reduced the modulus at 200% strain for the NBR vulcanizate in comparison with the mix containing the commercial antioxidant and the control mix.

Figures 4 and 5 indicate that the tensile strength and modulus at 200% strain of the NBR mix containing the prepared antioxidant increased with increasing aging time up to 4 and 6 days, respectively, and then decreased with increasing aging time because generally aging causes crosslinking and crosslink cleavage in NBR vulcanizates. When aging was initiated, the rate of crosslink formation was more than that of crosslink

TABLE V
Main Properties of SRF

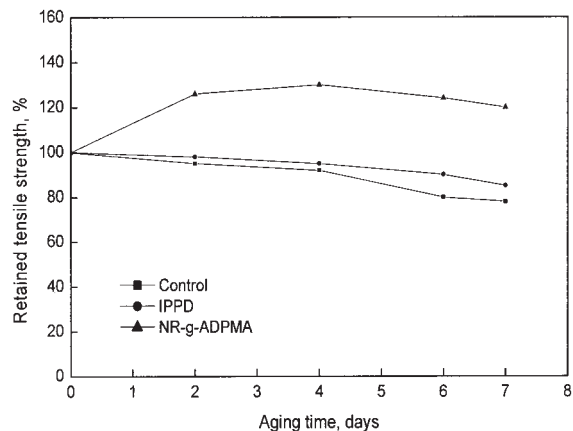| Name	Particle size (Å)	pH
SRF	800	9.9

Figure 4 Relationship between the retained tensile strength (%) and aging time (days) for NBR mixes containing IPPD and NR-*g*-ADPMA and a control mix.

cleavage. With increasing aging time, the rate of crosslink cleavage increased gradually.[10]

Figure 6 shows that the mix containing the prepared NR-*g*-ADPMA compound had high retained values of the elongation at break in comparison with the mix containing the commercial antioxidant and the control mix.

Finally, we can say that NR-*g*-ADPMA provided significant protection to NBR vulcanizates in comparison with the mix containing the commercial antioxidant and the control mix. This can be attributed to the following:

1. The ease of liberating the active hydrogen atom from the para position to deactivate peroxy radicals formed by aging.[11,12]
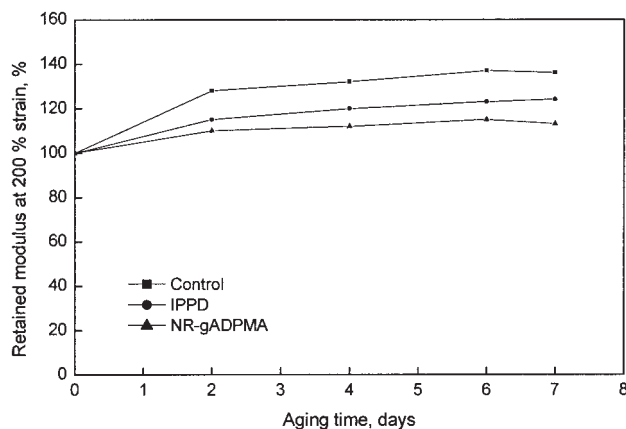2. The resonance stability of the resulting grafted antioxidant radical, which minimized the possi-

Figure 5 Relationship between the retained modulus at 200% strain and aging time (days) for NBR mixes containing IPPD and NR-*g*-ADPMA and a control mix.
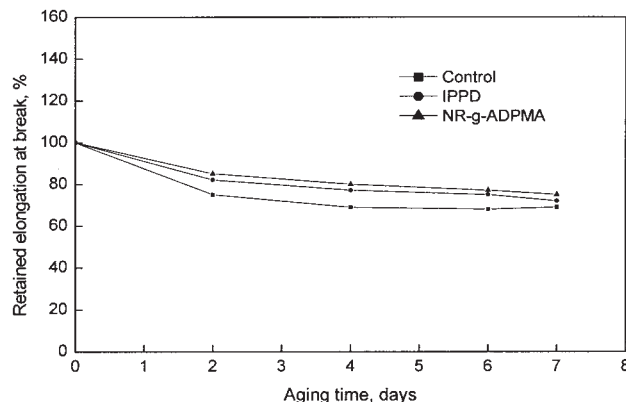

Figure 6 Relationship between the retained elongation at break (%) and aging time (days) for NBR mixes containing IPPD and NR-*g*-ADPMA and a control mix.

bility of chain-transfer reactions responsible for further rubber degradation by aging.[11,12]
3. The grafted antioxidants, which were high molecular antioxidants that partially bonded to the macromolecules during the processing of the polymers and had a good ability to diffuse through the unsaturated rubber.[5]

Effect of aging on the volume swelling percentage and volume extraction percentage of the NBR vulcanizates in toluene

The swelling of rubbers by solvents is an important aspect to be considered, especially for sealing applications.[11] When a certain rubber is in contact with a solvent, a swelling process happens. If the number of crosslinks increases, the distance between crosslinks shortens, and consequently swelling is reduced and vice versa. The properties of industrial polymer products depend on the volume swelling percentage and the volume extraction percentage. When the volume extraction percentage of polymer products decreases, polymer products retain the incorporated ingredient. Here we report the effect of the prepared NR-*g*-AD-PMA on the values of the volume swelling percentage and volume extraction percentage for aged samples. To achieve this, the samples were immersed in toluene until maximum swelling was reached. The effect of aging on the swelling behavior of the investigated samples containing the prepared antioxidant, IPPD, and the control mix is illustrated in Figure 7. All the samples possessed higher volume swelling percentage values before aging. These values markedly decreased after 2 days of aging and further decreased as the aging continued up to 7 days. Such a phenomenon could be attributed to the hindrance of the solvent uptake brought about by the additional crosslinks that were formed with the exposure of the rubber samples to aging.[10] The prepared antioxidant showed lower

swelling values than the mix containing the commercial antioxidant and the control mix.

The volume extraction percentage of the swelled samples was calculated and plotted against the aging time, as shown in Figure 8. The results clearly indicate that the antioxidant NR-*g*-ADPMA significantly lowered the percentage of extractable ingredients with the aging time in comparison with the control mix and the mix containing the commercial antioxidant. This means that the grafted antioxidant was a high molecular antioxidant that partially bonded to the macromolecules during the processing of the polymers and hindered the reaction of the swelling solvent with the ingredients inside the rubber matrix. The results obtained for the volume swelling percentage and volume extraction percentage constitute very significant evidence for the NR-*g*-ADPMA antioxidant being of great value for rubber industry applications.

CONCLUSIONS

UV irradiation is an excellent approach for grafting ADPMA onto NR.

NR-*g*-ADPMA provided significant protection to NBR vulcanizates in comparison with a mix containing a commercial antioxidant (IPPD) and a control mix because the grafted antioxidants were high molecular
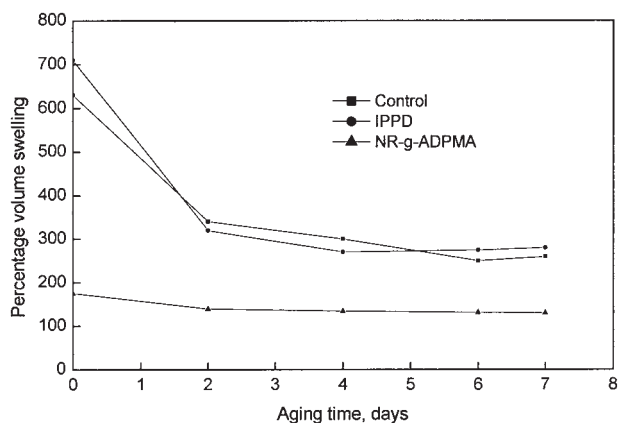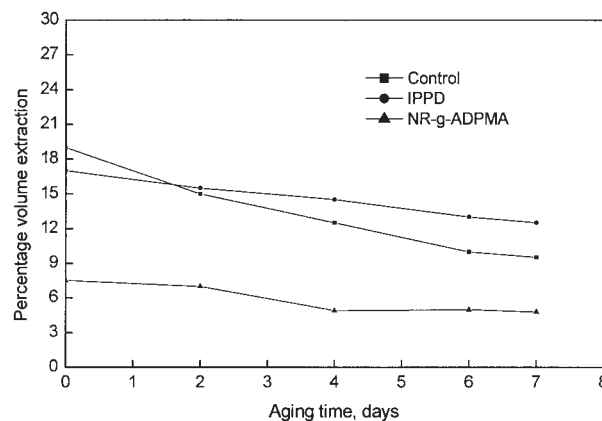

Figure 8 Relationship between the volume extraction (%) and aging time (days) for an NBR control mix and NBR mixes containing IPPD and NR-*g*-ADPMA.

antioxidants that partially bonded to the macromolecules during the processing of the polymers.

The results obtained for the volume swelling percentage and volume extraction percentage constitute very significant evidence for the NR-*g*-ADPMA antioxidant being of great value for rubber industry applications. Therefore, NR-*g*-ADPMA could improve the economic value of polymer products.

Figure 7 Relationship between the volume swelling (%) and aging time (days) for NBR mixes containing IPPD and NR-*g*-ADPMA and a control mix.

References

1. Hrabac, F.; Posta, A. Czech. Pat. CS249,095 (1988); Chem Abstr 1989, 11, 39517.
2. Haddadi-Asl, V.; Burford, R. P.; Garnett, J. L. Radiat Phys Chem 1995, 45, 191.
3. Al-Malaika, S.; Ibrahim, A. Q.; Rao, M. J.; Scott, G. J Appl Polym Sci 1992, 44, 1287.
4. Herdan, J. M.; Giurginca, M. Polym Degrad Stab 1993, 41, 159.
5. Giurginca, M.; Herdan, J. M.; Cira, L.; Valeanu, G.; Ivan, G. Polym Degrad Stab 1992, 36, 53.
6. Flory, P. J. Ind Eng Chem 1946, 38, 417.
7. Yu, J. J.; Ryu, S. H. J Appl Polym Sci 1999, 73, 1733.
8. Shehata, A. B.; Lawandy, S. N.; El-Wakeel, A. A. Polym Plast Technol Eng 2000, 39, 1.
9. Avirah, S. A.; Joseph, R. J Appl Polym Sci 1995, 57, 1511.
10. Claramma, N. M.; Mathew, N. M.; Thomas, E. V. Radiat Phys Chem 1989, 33, 87.
11. Lawandy, S. N.; Younan, A. F.; Shehata, A. B. Polym Plast Technol Eng 1996, 35, 207.
12. Lawandy, S. N.; Younan, A. F.; Shehata, A. B. Kautsch Gummi Kunstst 1997, 6, 452.