

Amelioration of Acrylonitrile–Butadiene Copolymer Properties Using Natural Rubber Graft *p*-Aminophenol

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ABSTRACT: A two-roll mill machine was used for the grafting of *p*-aminophenol (pAP) onto natural rubber (NR). The prepared NR graft *p*-aminophenol (NR-g-pAP) was characterized by ¹H NMR and IR spectroscopy techniques. The goal of this article is to study the effect of commercial antioxidants, *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (6PPD) and *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), and the prepared NR-g-pAP, on the mechanical properties of acrylonitrile–butadiene (NBR) vulcanizates, the fluid compatibility of NBR vulcanizates, the hydraulic brake and clutch fluid dot, the diffusion out for NBR vulcanizate components, and the compression recovery of NBR vulcanizates. This study indicates that the

NBR copolymer vulcanizate which contains the prepared NR-g-pAP has good protection against mechanical stress and the diffusion out of NBR vulcanizate components. The 6PPD and the prepared NR-g-pAP ameliorates the fluid compatibility of the oil seals, which is based on NBR as elastomer, and the hydraulic brake and clutch fluid dot. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 27–34, 2007

Key words: graft copolymerization; two-roll mill machine; acrylonitrile–butadiene copolymer; natural rubber; mechanical properties; fluid compatibility; diffusion out; compression recovery phenomena

INTRODUCTION

Acrylonitrile–butadiene (NBR) copolymer is used most widely to fabricate the industrial seal elastomers. The nitrile rubber is used for seals more than all of the others elastomers combined. It is the most versatile rubber material for oil seals because of its resistance to wide varieties of the fluids and its unique combination of physical properties, which are so well suited for oil seal applications, within its temperature and fluid compatibility limits.

For engineering applications, the stability of these seals and their long-term service is required. Degradation processes of polymers are influenced by the addition of various kinds of stabilizers, which lower the rate of degradation via reactions with various radicals formed by main-chain scission, isomerization, and free radical transfer as indicated by an inhibition of its oxidative degradation.¹

Antioxidants may be lost from polymers in the presence of extractive media which they contact in the course of their service life. This is particularly significant in the case of packing plastics and elastomeric seals that come into contact with solvents, oils, and fats, in which incompatible additives migrating into the surface may cause severe toxicity problems. The second

reason for migration of antioxidants, which is important to their performance in polymers and which may substantially reduce its effectiveness, is the physical loss of the antioxidants from the elastomers.² This is a cause of considerable concern in rubbers that are used in engineering components in which extraction of the antioxidants by solvents, mineral oils, and synthetic fluids may reduce the lifetime of the article. Besides the ability of the antioxidants to trap peroxy and hydroperoxy radicals and its catalytic action in hydroperoxide decomposition, the antioxidants should be compatible with the host polymers. Thus, it is very important to limit antioxidant loss by extraction or volatilization. This is the reason for the increasing interest in the synthesis of grafting antioxidants.² Grafted antioxidants are low molecular antioxidants that partially bond to the macromolecules during the processing of polymers, and the use of grafting antioxidants is one of the best ways to protect unsaturated rubbers.³

EXPERIMENTAL

Materials

p-Aminophenol (pAP) was got from Merk (Sarmstadt, Germany). All solvents were of laboratory grade and were supplied by Adwic (Cairo, Egypt).

Synthesis of NR-graft-pAP

Mastication of natural rubber

Mastication of NR was carried out using a two-roll mill machine, with 150 mm diameter and 300 mm

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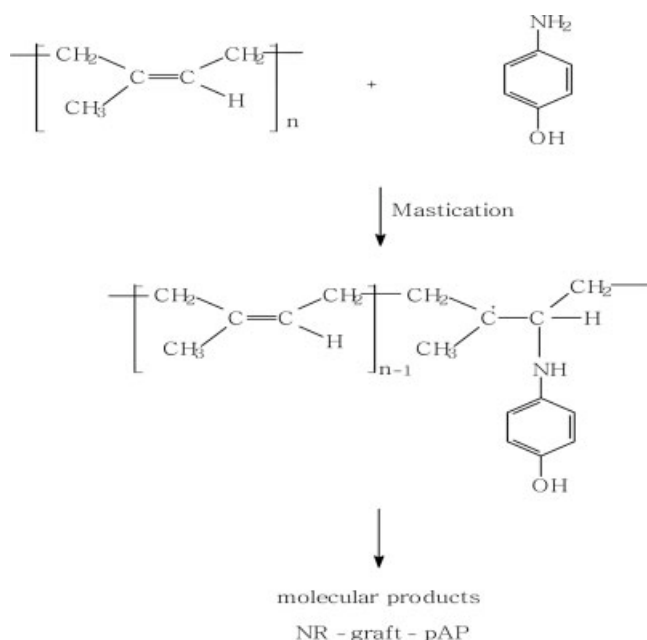
width, to prepare the NR that has a molecular weight less than that of original NR. Each batch of 100 g of NR was loaded onto the water-cooled mill. The nip gap was gradually reduced at the same time as the rubber was quartered.⁴

Grafting of *p*-aminophenol onto natural rubber

Mastication was continued for 8 min before treatment with the pAP. Then the masticated NR after treatment with pAP was dissolved in toluene, and the mixture solution was filtrated. The ungrafted NR was precipitated by boiling in ethanol. A rotating evaporator isolated the grafted NR. The product was dried in an oven at 40°C to constant weight within 24 h. The percent graft (*G*%) was taken as the ratio of the graft yield to the NR multiplied by 100.^{5,6}

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

where, W_{NR} is the weight of NR and W_g is the weight of graft yield. The degree of grafting was calculated as the ratio of the amount of the graft copolymer to the amount of the rubber. The degree of grafting (*G*%) of the prepared NR graft pAP was 26.5%. The following mechanism can be suggested for the attachment of pAP onto NR.



Characterization of NR-*g*-pAP

IR and ^1H NMR spectroscopic data were recorded by Bruker, Vector 22, FTIR Spectrometer and Jeol-EX-270, respectively, to elucidate the structure and to ensure the purity of the products. Figures 1–3 show

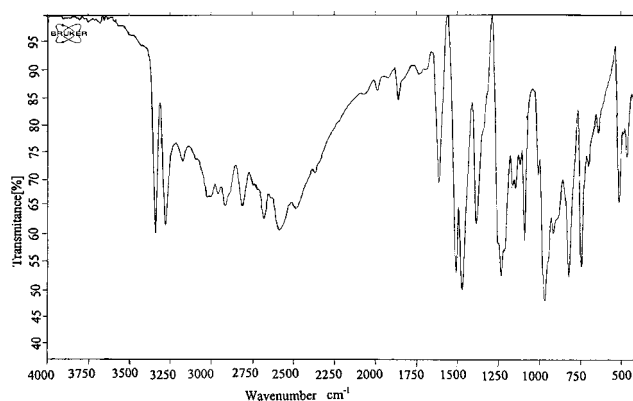


Figure 1 IR spectrum of *p*-aminophenol.

the IR spectra of pAP, original (ungrafted) NR, and the grafted NR. The samples were scanned from 400 to 4000 cm^{-1} .

Figures 1–3 indicate that the new absorption peak at 3432 cm^{-1} , which corresponded to the OH group of pAP, and the intensity of the C=C in NR is decreased in the IR spectrum of NR-*g*-pAP. Therefore, pAP was grafted onto the NR.

Figures 4 and 5 show the ^1H NMR spectra of original (ungrafted) NR and the grafted NR.

Figure 4 shows the ^1H NMR spectrum of NR. There are peaks at $\delta = 4.6$ ppm ($-\text{C}=\text{C}$), $\delta = 1.25$ ppm ($-\text{CH}_2$), and $\delta = 1.45$ ppm ($-\text{CH}_3$). Figure 5 shows the ^1H NMR spectrum of NR-*g*-pAP, which shows an additional peak at 7.4 ppm, corresponding to the aromatic ring present in pAP. This again indicates that the pAP was grafted onto the NR.

Rubber mix formulation

The mixes examined in this study were based on acrylonitrile–butadiene copolymer produced by Polymer Corp., France. The grade used in this investigation is Humex N-34/47. The basic formulation is given in Table I.

Zinc oxide and stearic acid were used in the mixes as an inorganic accelerator activator and organic acid

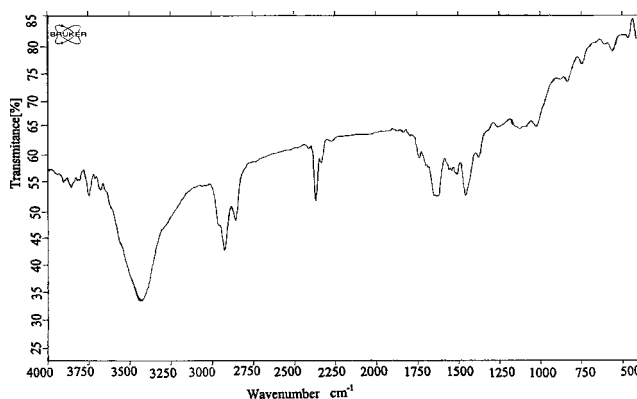


Figure 2 IR spectrum of natural rubber.

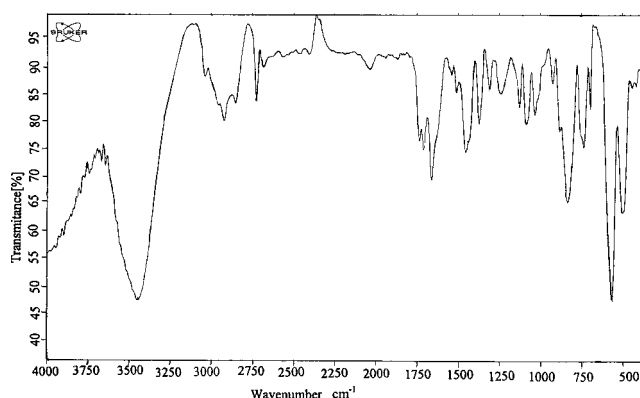


Figure 3 IR spectrum of NR-g-pAP.

accelerator activator, respectively. Naphthanic oil was used as a processing oil in the mixes. Semireinforcing furnace (SRF) was used as carbon black in the mixes at one concentration 30 phr (part per hundred). Sulfur was used as a vulcanizing agent in all mixes. The accelerators used were mercaptobenzthiazole (MBT) and tetramethylthiuram disulphide (TMTD). *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (6PPD) and *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD) were used as commercial antioxidants.

Mastication and mixing were carried out using a water cooled two-roll mill ($300 \times 150 \text{ mm}^2$) operating at friction ratio 1.25:1. Vulcanized sheets, from which the test pieces were cut, were produced by molding in an electrically heated platen press at 152°C . Rheometer tests at 152°C indicated that 90% crosslinking occurs at the corresponding cure time for each NR mix as indicated in Table I. All samples were cured at this temperature and the specific cure time.

Free swelling measurements in the hydraulic brake and clutch fluid dot

Rectangular specimens of dimensions $10 \times 10 \times 2 \text{ mm}^3$ were weighted accurately in air (W_1), and in hydraulic brake and clutch fluid dot (W_2) and were allowed to swell at room temperature for 48 h in stoppered glass bottles containing 20 mL of hydraulic brake and clutch fluid dot. The sample was weighted in hydraulic brake and clutch fluid dot to determine W_4 , and the sample was weighted in air to determine W_3 . The sample used for swelling measurements was first dried at room temperature for 24 h, then in an oven at 70°C until constant weight in air (W_5), and then in hydraulic brake and clutch fluid dot (W_6).⁷

The percentage volume swelling (ΔV) was calculated as

$$\Delta V(\%) = [((W_3 - W_4) - (W_1 - W_2)) / (W_1 - W_2)] \times 100$$

The percentage volume extraction (ΔE) was calculated as

$$\Delta E(\%) = [((W_1 - W_2) - (W_5 - W_6)) / (W_5 - W_6)] \times 100$$

Compression recovery measurements

To study the effect of compression stress on the percentage of compression recovery, cylindrical samples, 10 mm diameter and 5 mm height, were molded.⁷ The samples were vulcanized at the same conditions of pressure, temperature, and time as estimated by a Monosanto rheometer. A compression set clamp device was used to accommodate samples of four mixes at the same time. The clamp consists of four circular,

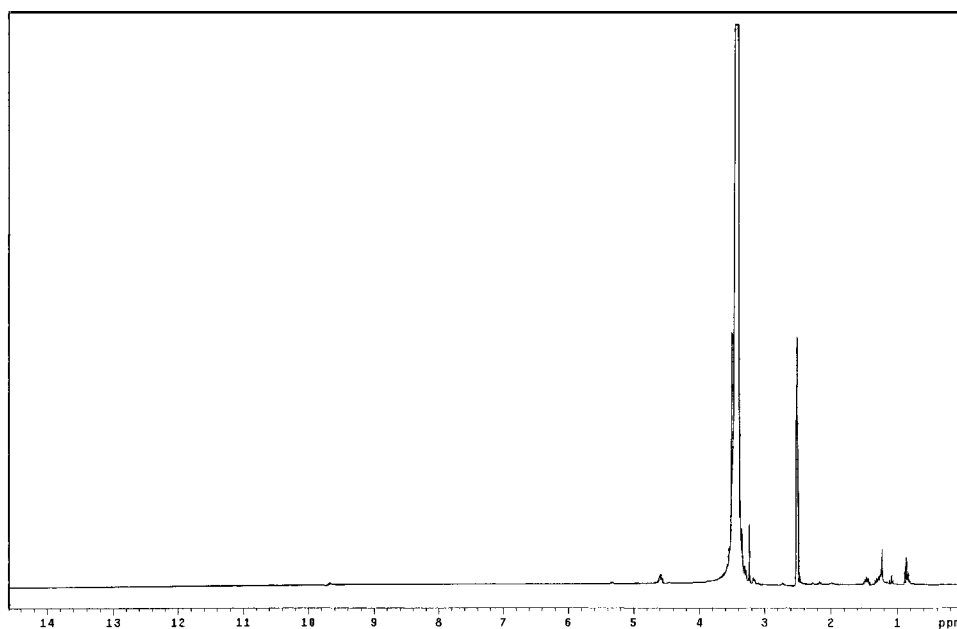


Figure 4 ^1H NMR spectrum of natural rubber.

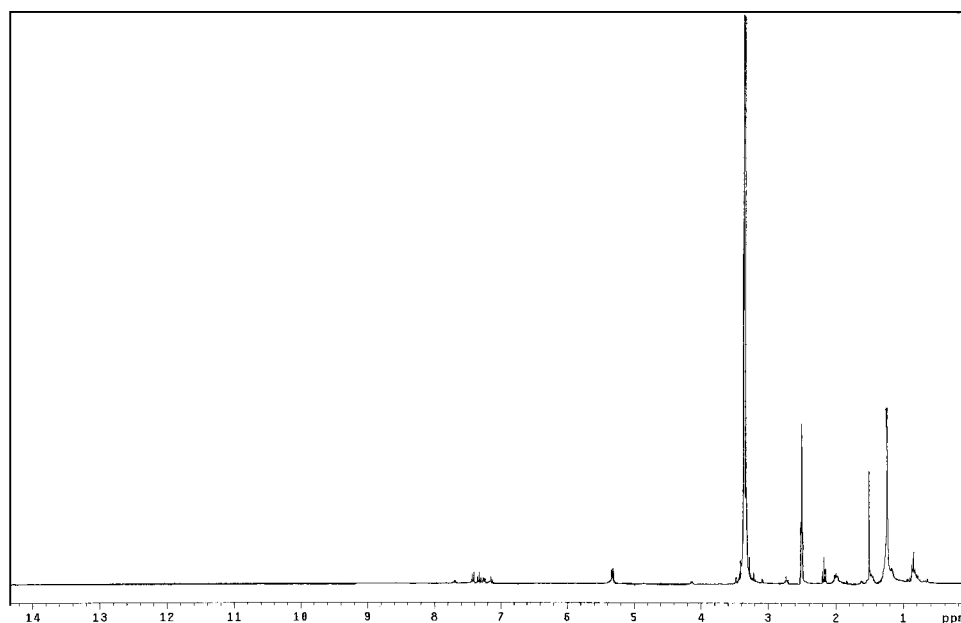


Figure 5 ^1H NMR spectrum of NR-g-pAP.

highly polished steel plates between which the test pieces were compressed. The plates were held together by a bolt. Spacers in the form of rings were placed around the axial bolt and between the plates to limit the degree of compression of the test pieces. The spacers used were of different thickness (h_s). The procedure used in these measurements can be summarized as follows: (i) The test pieces were marked and placed symmetrically between the plates of the compression device, after measuring accurately their exact thickness; the thickness was measured by using a rubber thickness gauge to the nearest 0.1 mm. (ii) The bolt was tightened uniformly until the plates were in contact with the spacers; the compression set device was then immersed completely in the hydraulic brake and clutch fluid dot 4 manufactured by Shell Company. The oil container was then transferred to an air circulating oven fixed at 90°C. (iii) After each time interval, the clamp device was parted and the excess oil on the surface of the test piece was removed by blotting with filter paper; then the test pieces were allowed to recover for 30 min.⁸ (iv) Their thickness was measured accurately and then immersed in the oil. This procedure was repeated at each time interval.

The recovery percentage was calculated as

$$\text{Recovery percentage} = [(h - h_o)/(h_o - h_s)] \times 100$$

The compression percentage was calculated as

$$\text{Compression percentage} = [(h_o - h_s)/h_o] \times 100$$

RESULTS AND DISCUSSION

The objectives concerning this study are as follows: first, to synthesize and characterize NR-g-pAP; sec-

ond, to study the effect of the commercial antioxidants IPPD and 6PPD, and the prepared antioxidant NR-g-pAP on the mechanical properties of NBR vulcanizates, fluid compatibility of NBR vulcanizates and hydraulic brake and clutch fluid dot, the diffusion out of NBR vulcanizate components, and the compression recovery of NBR vulcanizates to evaluate the properties of oil seals, which are based on NBR as elastomer base.

Effect of 6PPD, IPPD, and NR-g-pAP on the mechanical properties of NBR vulcanizates

Tensile tests were performed according to ASTM D 412-98, a test method by using a Zwick universal test-

TABLE I
NBR Mix Formulations Containing NR-g-pAP
and the Mechanical Properties of Unaged Samples

Samples	A1	A2	A3	A4
Mix ingredients				
NBR (33/45)	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	2	2	2
Processing oil	5	5	5	5
SRF	30	30	30	30
S	1.5	1.5	1.5	1.5
MBT	0.75	0.75	0.75	0.75
TMTD	0.75	0.75	0.75	0.75
6PPD	–	1	–	–
IPPD	–	–	1	–
NRGPAP	–	–	–	1
Cure time (min)	4.61	3.74	3.83	4.95
Scorch time (min)	1.38	1.06	1.23	1.52
Tensile strength (Mpa)	10.05	9.80	10.14	10.52
Elongation at break (%)	1043	992	1005	1055

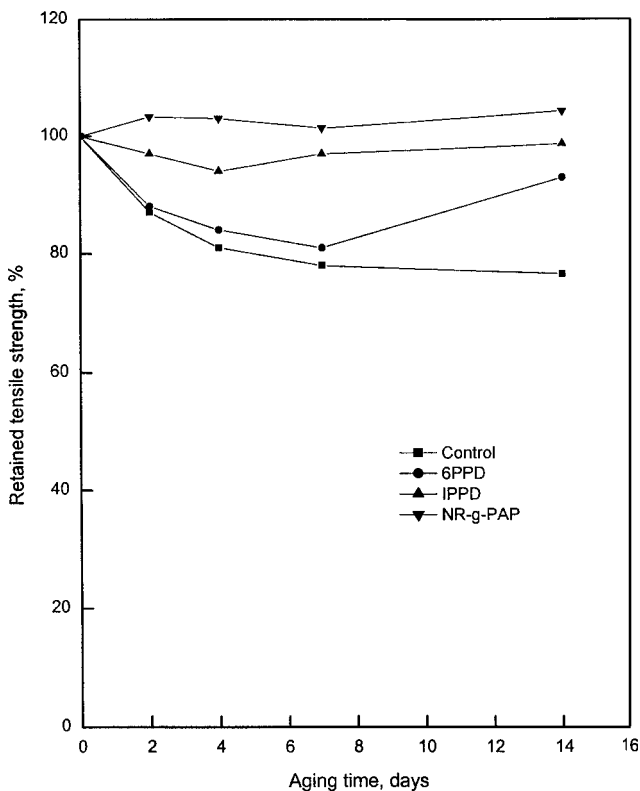


Figure 6 Relation between retained tensile strength (%) and aging time (days) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix.

ing machine (model Z010). Figure 6 shows the relation between the retained tensile strength and the aging time. It indicates that the prepared NR-g-pAP improves the tensile strength of the NBR vulcanizate, and the commercial antioxidant (IPPD) maintains the tensile strength of the NBR vulcanizate with increases in the aging time.

The tensile strength of the NBR vulcanizate, which contains 6PPD decreased with the increasing of aging time up to 7 days and it improved at 14 days aging time. The mechanical properties of the NBR vulcanizate which did not contain any type of antioxidants were decreased with increasing the aging time. The tensile strength of the NBR vulcanizate which contained the prepared NR-g-pAP was enhanced with the increasing of the aging time up to 14 days. Because the antioxidant radicals of the prepared NR-g-pAP compound minimize the possibility of the chain transfer reactions because of the high resonance stability,^{9,10} The commercial antioxidants were lost during processing, curing, and usage of the rubber article under severe operating conditions. The IPPD can provide adequate protection to NBR vulcanizates against all degradative forces and exhibits superior performance in all respects when compared with 6PPD. The IPPD has lower molecular weight and higher volatility.

Figure 7 shows the relation between the retained elongation at break and the aging time. It indicates that the retained elongation at break of the NBR vulcanizates, which contain the commercial antioxidants 6PPD, IPPD, the prepared antioxidant NR-g-pAP, and the control mix, were significantly decreased with increasing aging time up to 2 days, and then slightly decreased with increasing aging time from 2 days to 14 days. Because aging causes crosslinks' cleavage in the NBR vulcanizates, in initial aging the rate of crosslinks' cleavage was higher. With increasing aging time, different types of antioxidants played an important role to decrease the rate of crosslinks' cleavage within the NBR vulcanizates.⁵

Figures 6 and 7 indicate that after the NBR vulcanizates were exposed to aging for 14 days, the prepared NR-g-pAP improves the mechanical properties of NBR vulcanizates more than the commercial antioxidants IPPD and 6PPD, respectively. Because the rubber part of the grafted antioxidant gets attached to nitrile rubber during sulfur vulcanization and the antioxidant becomes nonvolatile and nonextractable,¹¹ the commercial antioxidants IPPD and 6PPD have high thermal sensitivity. This high thermal sensitivity is due to the presence of isopropyl chain and 1,3-dimethylbutyl chain, respectively, in the molecular skeleton, and they produce the electron-donor effect on the benzene ring.¹²

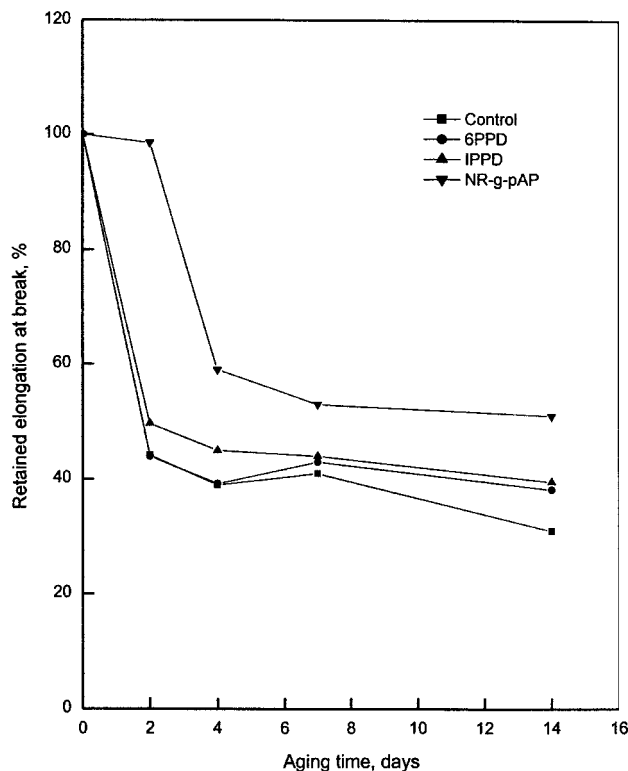


Figure 7 Relation between retained elongation at break (%) and aging time (days) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix.

Therefore, the NBR vulcanizate which contains the prepared NR-g-pAP has higher mechanical properties than that of the NBR vulcanizates which contain IPPD, 6PPD, and the control mix.

Effect of 6PPD, IPPD, and NR-g-pAP on the fluid compatibility of NBR vulcanizates and the hydraulic brake and clutch fluid dot

Volume swell of the polymer after exposure to the fluids is the most usual compatibility criteria. Figure 8 shows the relation between the percentage of volume swelling and the aging time (days).

It indicates that the percentage of volume swelling of the NBR vulcanizate that contains 6PPD, IPPD, and NR-g-pAP decrease with thermal aging at 2 days, and then increase with increasing aging time up to 14 days. The percentage volume swelling of the NBR vulcanizate which contains the control mix increases with thermal aging up to 14 days. This result indicates that at 2 days thermal aging the permanent action is the creation of new crosslinks and with increase in the thermal aging time up to 14 days the permanent action is breaking down of the crosslinks between the NBR chains.

The percentage volume swelling values of NBR vulcanizates that contain 6PPD, NR-g-pAP, IPPD, and the control mix after 14 days thermal aging are 9%,

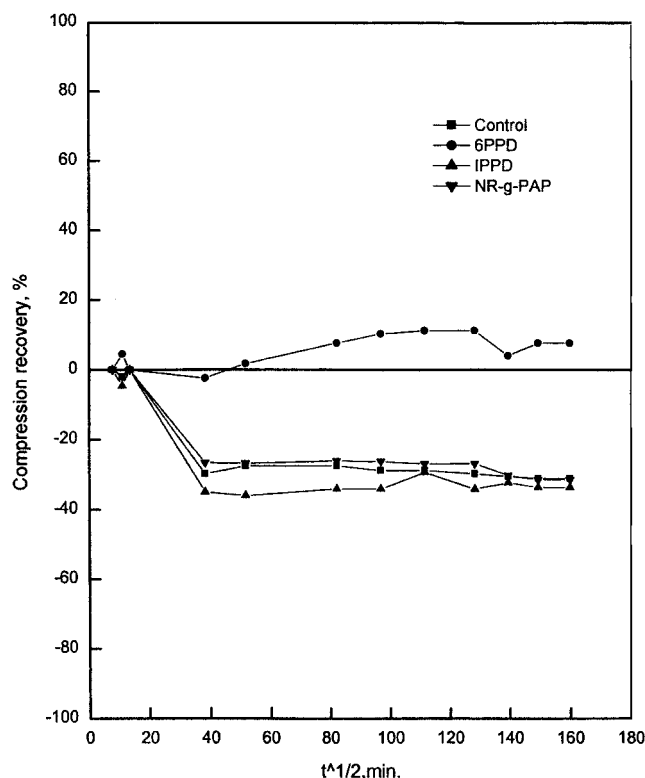


Figure 8 Relation between percentage of volume swelling and aging time (days) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix.

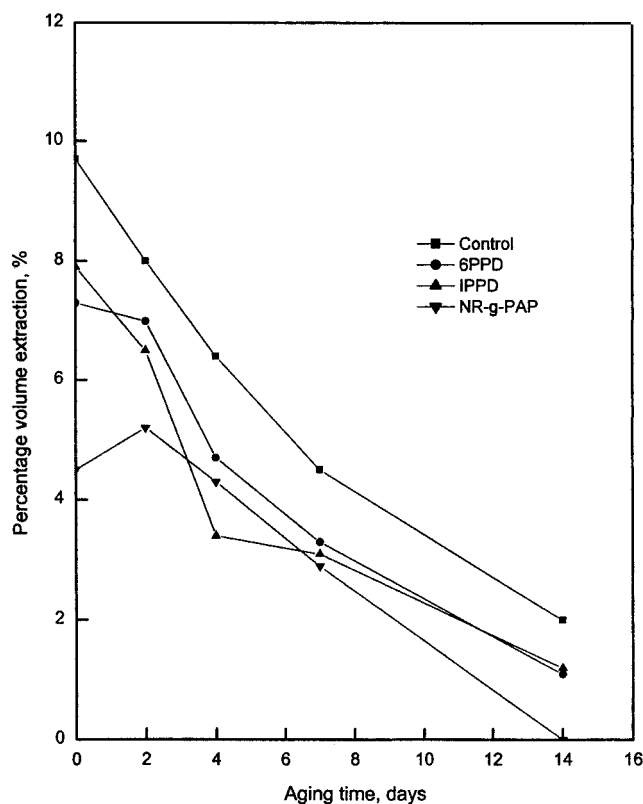


Figure 9 Relation between percentage volume extraction and aging time (days) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix.

10.5%, 11.3%, and 11.8%, respectively. The increase in volume swelling is an indication of a decrease in crosslink density. Therefore, the NBR vulcanizates, which contain 6PPD and the prepared NR-g-pAP, are more fluid compatibility with the hydraulic brake and clutch fluid dot 4.

Effect of 6PPD, IPPD, and NR-g-pAP on the diffusion out of NBR vulcanizates components

Figure 9 shows the plot of the percentage volume extraction and the aging time expressed as number of days.

There are three important aspects that can be seen in Figure 7. First, the percentage volume extraction of the NBR vulcanizates decreases with increasing of the aging time. Second, the NBR vulcanizate that contains the prepared NR-g-pAP has less percentage extraction value. Third, there are no extractable materials from NBR vulcanizate that contain the NR-g-pAP at 14 days aging time. The reason for this improvement of diffusion out for the NBR vulcanizate components can be mainly owed to the fact that the prepared anti-oxidants are bonded to the macromolecules, which prevents these compounds from diffusion out of the rubber mixes.⁵

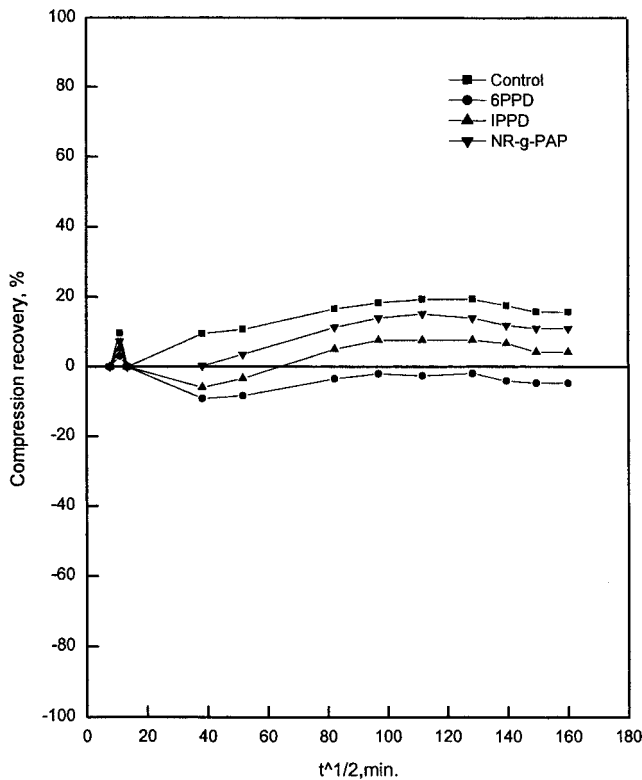


Figure 10 Relation between compression recovery (%) and $t_{1/2}$ (min) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix at 16% compression.

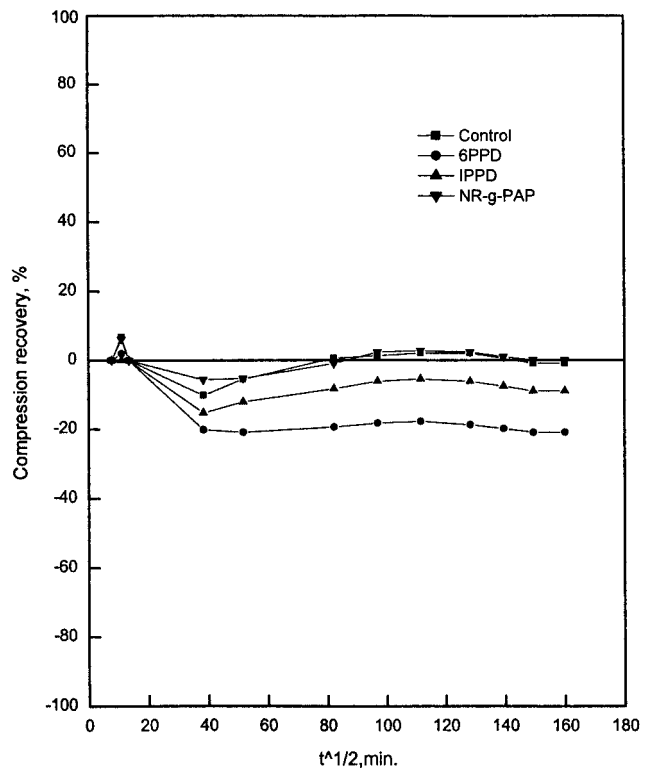


Figure 11 Relation between compression recovery (%) and $t_{1/2}$ (min) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix at 20% compression.

Effect of 6PPD, IPPD, and NR-g-pAP on the compression recovery of NBR vulcanizates

Figures 10–13 show the relation between the compression recovery of the NBR vulcanizates which contain the 6PPD, IPPD, the prepared NR-g-pAP, and the control mix and the square root time at different applied compression.

Figures 10–13 indicate the ability of NBR vulcanizates, which contain 6PPD, IPPD, the prepared NR-g-pAP, and the control mix to return to its original dimensions with increment of the applied compression percentage. This result indicates that the NBR vulcanizates at low compression possess a certain chain arrangement. At higher compression percentage, the NBR vulcanizate crosslinks are damaged, and some new physical crosslinks are formed.

At compression percentage 16%, the NBR vulcanizates which contain 6PPD and IPPD have good ability to return to the original dimension after removal of the applied compression. At compression percentage 20%, the prepared NR-g-pAP increases the ability of the NBR vulcanizate to return to the original dimension after removal of the applied compression. The NBR vulcanizates which contain NR-g-pAP return to about 88% of its original dimension at 26% compression percentage.

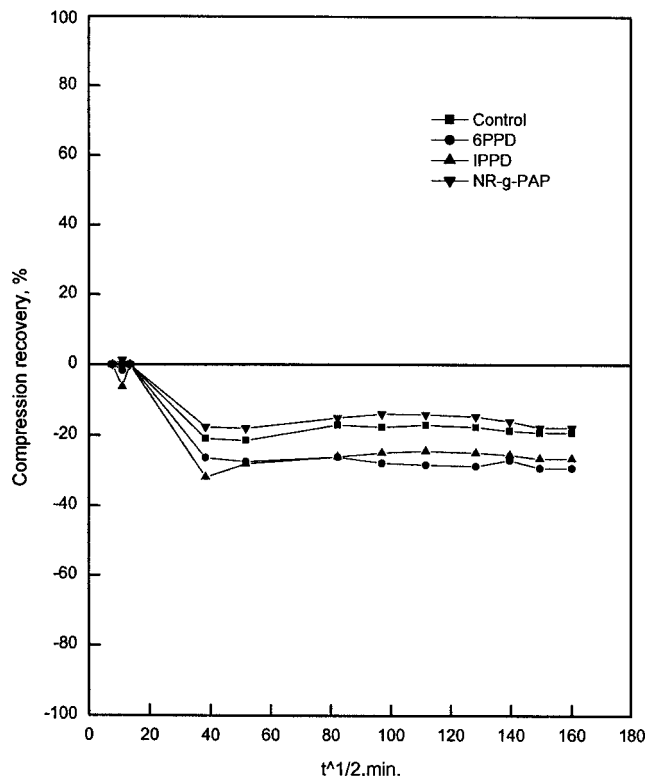


Figure 12 Relation between compression recovery (%) and $t_{1/2}$ (min) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix at 26% compression.

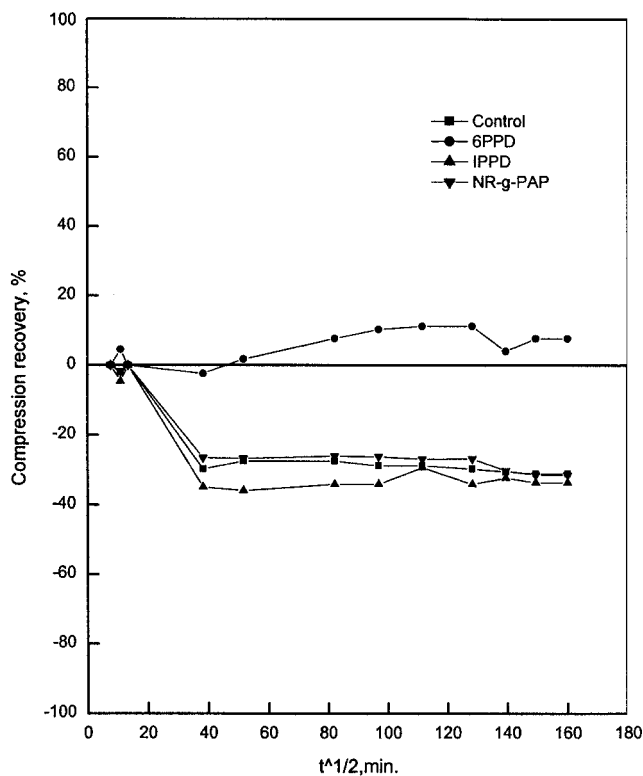


Figure 13 Relation between compression recovery (%) and $t_{1/2}$ (min) for NBR mixes containing 6PPD, IPPD, NR-g-pAP, and the control mix at 33% compression.

CONCLUSIONS

1. A two roll-mill machine was used to achieve the grafting of the pAP onto the NR.

2. The commercial antioxidant IPPD and the prepared NR-g-pAP maintain and ameliorate, respectively, the tensile strength of the oil seals, which are based on NBR as elastomer, with increasing aging time from 2 to 14 days.
3. The commercial antioxidants 6PPD and IPPD and the prepared NR-g-pAP increment the fluid compatibility of NBR vulcanizates and the hydraulic brake and clutch fluid dot, and 6PPD is the best.
4. The prepared NR-g-pAP prevents extractable materials from NBR vulcanizate at 14-days aging time.
5. At 20% compression percentage, the NBR vulcanizate that contains the NR-g-pAP has good ability to recover to the original dimension after removal of the applied compression.

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