

# Study of the Effect of Natural Rubber-Graft-*o*-Aminophenol on the Thermal Stability and Mechanical Properties of Nitrile Rubber

Abd El-Aziz El-Wakil,<sup>1</sup> Mirham A. Barakat<sup>2</sup>

<sup>1</sup>Polymer Metrology and Technology Department, National Institute of Standards, El-Harm, Giza 12211, Egypt

<sup>2</sup>Ultrasonic Department, National Institute of Standards, El-Harm, Giza 12211, Egypt

Received 24 March 2010; accepted 9 June 2010

DOI 10.1002/app.32934

Published online 1 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The grafting copolymerization of natural rubber and *o*-aminophenol was carried out by using two-roll mill machine. The prepared grafted antioxidant, NR-graft-*o*-AP, analyzed by using Infrared and <sup>1</sup>H-NMR Spectroscopy techniques. The thermal stability, mechanical properties, and ultrasonic attenuation coefficient were evaluated for NBR vulcanizates containing the commercial antioxidant, PBN, and the prepared grafted antioxidant, NR-graft-*o*-AP, and the control vulcanizate. Results of the thermal stability indicate that the prepared NR-graft-*o*-AP

can protect NBR vulcanizate against thermal treatment much better than the commercial antioxidant, PBN, and control mix, respectively. The prepared grafted antioxidant improves the mechanical properties of NBR vulcanizate. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2461–2467, 2011

**Key words:** graft copolymerization; mechanical properties; ultrasonic attenuation coefficient; natural rubber; thermal stability; two-roll mill machine

## INTRODUCTION

All polymers will degrade when exposed to certain environmental conditions such as high temperatures, mechanical shear, and high energy radiation (e.g., UV exposure). The presence of oxygen will often accelerate this degradation. The first step in the degradation process is usually the loss of hydrogen atom from the polymer chain due to this energy input. This polymer “free radical,” [R\*], can then react with an oxygen (O<sub>2</sub>) molecule to form peroxy radical [ROO\*], which will in turn abstract hydrogen atom from another polymer chain to form hydroperoxide [ROOH]. The hydroperoxide can split into two new free radicals, [RO\*] + [\*OH], which continue to propagate the reaction to other polymer molecules. For certain polymers, such as acrylonitrile–butadiene copolymer, a polymer chain containing free radical is likely to split into two smaller chains.<sup>1–3</sup>

One way to interrupt this process is to incorporate an antioxidant into the acrylonitrile–butadiene copolymer. There are different types of antioxidants that interrupt the degradation cycle: primary antioxidants, secondary antioxidants, multi-functional antioxidants,

hydroxylamines, carbon centered radical scavengers, and grafted antioxidants. Higher molecular weight compounds, such as grafted antioxidant, are less volatile and more effective at higher temperatures and at longer exposure times. The estimation of stabilizers efficiency is necessary for the correct choice of the most active stabilizers for practical use.<sup>4–7</sup> Therefore, we synthesized Natural rubber-graft-*o*-Aminophenol and tested as grafted antioxidants.

## EXPERIMENTAL

### Materials

*o*-Aminophenol was supplied by Sigma-Aldrich Co. (Steinheim, Germany). Acrylonitrile–butadiene copolymer, with the trade name Humex N-34/47, was obtained from Polymer Corp., France. Natural rubber was supplied by (Ningbo Yonggang Industry Development Co., China). All laboratory grade solvents were obtained from Edwic (Cairo, Egypt).

### Synthesis of NR-graft-*o*-AP

NR-graft-*o*-AP was synthesized by the reaction of natural rubber and *o*-Aminophenol by using two-roll mill machine. The masticated NR after treatment with *o*-AP was dissolved in toluene, and the mixture solution was filtrated. The ungrafted NR was precipitated by boiling in ethanol. A rotating evaporator used to isolate the grafted NR. The product was dried in an oven at 40°C to constant weight within

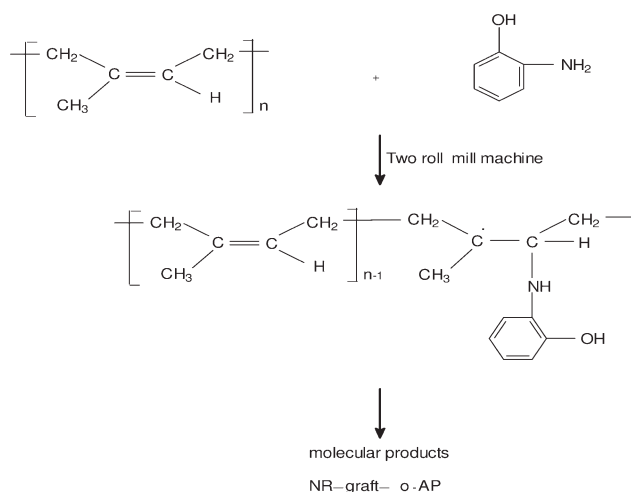
Correspondence to: A. A. El-Wakil (abdelaiz\_elwakil@yahoo.com) or Mirham A. Barakat (mirham75@yahoo.com).

24 h. The percent graft was taken as the ratio of the graft yield to the natural rubber multiplied by 100.<sup>8</sup>

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

Where  $W_g$  is the weight of graft yield and WNR is the weight of natural rubber.

The degree of grafting of the prepared natural rubber-graft-*o*-aminophenol is 18.32%. The synthesis of NR-graft-*o*-AP is shown in the following mechanism.<sup>8,9</sup>



### Formulation and mixing of NBR vulcanizates

The NBR rubber vulcanizates were compounded according to the recipe shown in Table I. The ingredients were added in the same order as listed.

All NBR vulcanizates masterbatch was mixed on two roll mill at 45°C to 55°C. The rubber mixes were vulcanized at 152°C with an electric press for the optimum cure time, which was indicated by a Monsanto rheometer (Swindon, UK).

Activators are zinc oxides and stearic acid. These materials were added to “activate” the accelerators to act fast in vulcanizing rubber. When elemental sulfur is used as the vulcanizing agent, certain auxiliary materials must also be added to obtain desirable properties. The most important of these materials is the organic accelerator.

The main applications of NBR require that the NBR chains be cross-linked after being formed into desired shape. After cross-linking of the NBR chains, which is called curing or vulcanization, the article become elastic. It deforms under stress but returns to its shape when vulcanization occurs and the stress is removed. The most common method of cross-linking NBR is using sulfur. The sulfur forms bridge between large chains of NBR, linking them together in fixed pattern.

Antioxidants are substances that retard oxidation by atmospheric oxygen at moderate temperatures (autoxidation). Autoxidation is a free radical chain

**TABLE I**  
Formulation of NBR Vulcanizates Containing PBN, and NR-g-*o*-AP and Control Vulcanizate Together with Mechanical Properties of the Unaged Samples

Ingredients (phr)	Mix name		
	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>
NBR	100	100	100
ZnO	5	5	5
Stearic acid	2	2	2
Processing oil	5	5	5
Semireinforcing furnace (SRF)	30	30	30
Sulfur	1.5	1.5	1.5
Mercaptobenzthiazole (MBT)	0.75	0.75	0.75
Tetramethylthiuram disulphide (TMTD)	0.75	0.75	0.75
N-phenyl-β-naphthylamine (PBN)	–	1	–
NR-graft- <i>o</i> -AP	–	–	5
Cure time (min)	8	6	9.5
Tensile strength (MPa)	8.95	9.45	9.85
Elongation at break (%)	695	704	714

reaction that can be inhibited at the initiation and propagation steps.

### Infrared and <sup>1</sup>H-NMR spectroscopy

IR spectra and <sup>1</sup>H-NMR spectra were registered on Bruker, Vector22, FTIR Spectrometer, and Jeol-EX-270, respectively.

### Mechanical measurements

Mechanical tests were performed according to the ASTM D 412 test method and were carried out using a Zwick tensile testing machine (model Z010, August-Nagel-Strassell, D-89079, Ulm, Germany) at 23°C ± 2°C and a crosshead speed was 500 mm/min. Five samples per each NBR vulcanizate were tested.<sup>10</sup>

### Ultrasonic testing method

Ultrasonic waves are a kind of mechanical waves with frequency more than 20 kHz. Ultrasonic waves can be generated from a piezoelectric transducer, and then they propagate in the tested samples. In this study, the ultrasound measurements were performed using an ultrasound flaw detector (USIP 20, Krautkramer, Germany), an oscilloscope (54615B, hp, USA), a longitudinal transducer (4 MHz, Krautkramer, Germany).

The incident waves were transmitted in a sample of thickness  $X$  and reflected back and forth at the two surfaces. When the reflected waves reached the upper surface and were received by the transducer, multiple echo signals appeared on the screen of the Flaw detector. However, the amplitudes of the echo signals are gradually decreased with time due to ultrasonic attenuation.

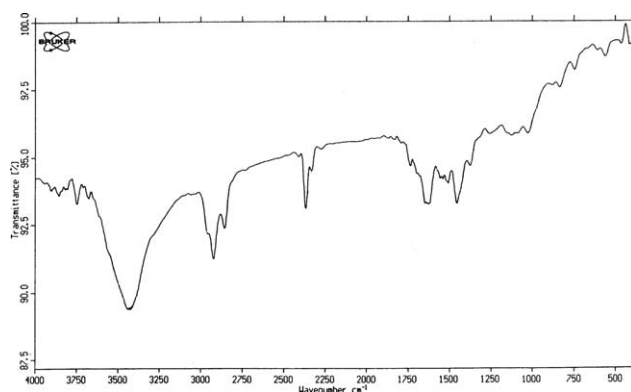


Figure 1 IR spectrum of *o*-aminophenol (*o*-AP).

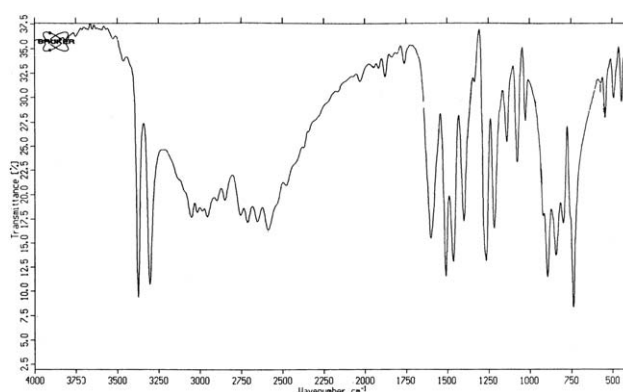
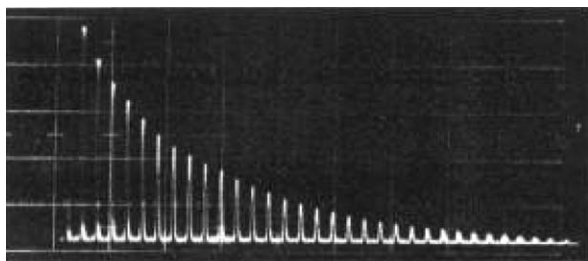


Figure 2 IR spectrum of natural rubber.



### Typical pulse-echo decay pattern

The first two echo signals, of amplitudes ( $A_1$ ,  $A_2$ ) and corresponding time ( $t_1$ ,  $t_2$ ), can be read and chosen to calculate the ultrasonic attenuation  $\alpha$ .<sup>11</sup>

$$\alpha = \frac{20 \log_{10}(A_1/A_2)}{2X}$$

The measurements of ultrasonic attenuation were repeated three times to check the reproducibility of the data. The estimated accuracies were 0.04, 0.05, and 0.07%, respectively.

### Thermal analysis

Thermogravimetric analysis (Shimatzu, Japan) measures the amount and rate of change in the mass of sample as function of temperature or time in controlled atmosphere. The measurements are used primarily to determine the thermal stability of materials. The technique is especially useful for the study of polymeric materials.

Thermogravimetric analysis (TGA) used to study the thermal degradation of the acrylonitrile-butadiene rubber vulcanizates which contain the commercial antioxidant (PBN) and the prepared grafted antioxidant (natural rubber-graft-*o*-aminophenol) as well as the control vulcanizate. The measurements were carried out at temperatures ranged from 23°C to 750°C with heating rate of 10°C/min.<sup>12</sup>

## RESULTS AND DISCUSSION

Thermal and mechanical degradation processes proceeding in the presence of oxygen have free radical character. Independent of the manner of the initiations generating the primary free-radical species, oxygen-centered radicals and hydro peroxides are formed in the chain propagation steps and carbon-centered radicals are regenerated. In the absence of oxygen, alkyl radicals are consumed in self-termination reactions. In the presence of oxygen, they are quickly oxidized to ROO $\cdot$ , and the free radical chain oxidation governs the degradation of the NBR chains. Therefore the studying of the effect of the prepared grafted antioxidant, NR-graft-*o*-AP on the thermal stability and the mechanical properties of the NBR vulcanizates became obligatory.

### Analysis of NR-graft-*o*-AP

Figures 1–3 show the IR spectra of *o*-AP, original (ungrafted) NR, and the natural rubber-graft-*o*-aminophenol.

Figures 4 and 5 show the  $^1\text{H}$  NMR spectra of original (ungrafted) NR and the natural rubber – graft – *o*-aminophenol.

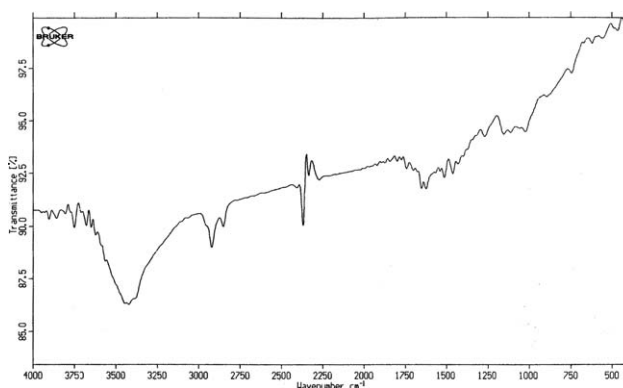


Figure 3 IR spectrum of natural rubber-g-*o*-aminophenol (NR-g-*o*-AP).

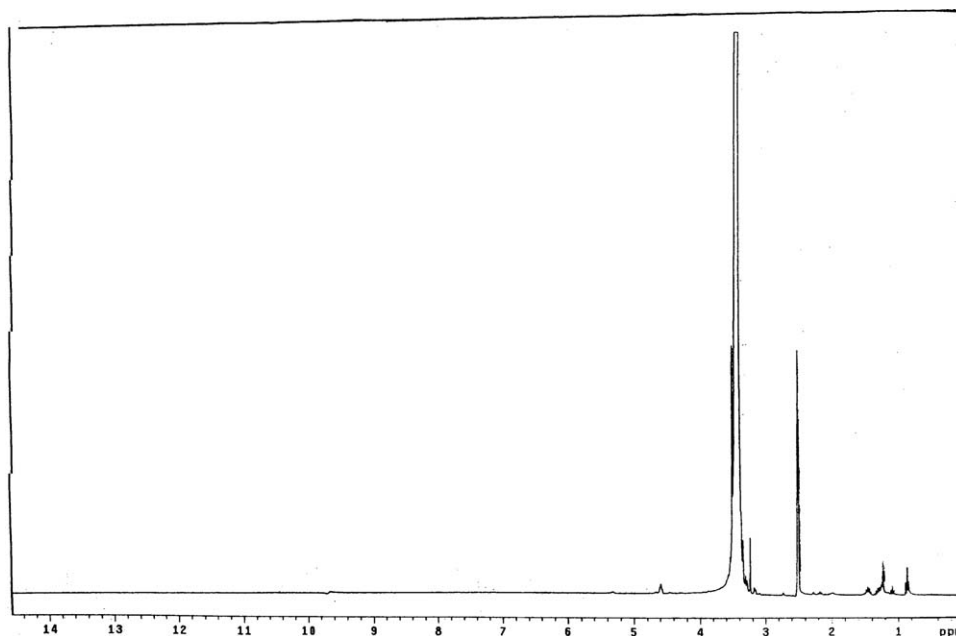


Figure 4  $^1\text{H-NMR}$  spectrum of natural rubber.

The assignments of various peaks found in Figures 1–3 show significant changes in the spectral behavior of the natural rubber, and *o*-aminophenol. The new absorption peak at  $3375\text{ cm}^{-1}$ , which corresponded to the OH group of *o*-AP, and the intensity of the C=C in NR is decreased in the IR spectrum of NR-g-*o*-AP. Figures 4 and 5 show the  $^1\text{H-NMR}$  spectra of the natural rubber and natural rubber-graft-*o*-aminophenol. Figure 5 shows additional peaks at 6.5 ppm and at 8.9 ppm, corresponding to the aromatic ring present in *o*-AP and the proton of

OH group is at 8.9 ppm. These indicate the *o*-aminophenol was grafted onto the natural rubber.

#### Effect of the prepared grafted antioxidant, NR-graft-*o*-AP, on the mechanical properties of nitrile rubber

Figure 6 shows the retained tensile strength, % as function of the aging time, days, and Figure 7 shows the relation between the retained elongation at break, % and the aging time. The NBR tested

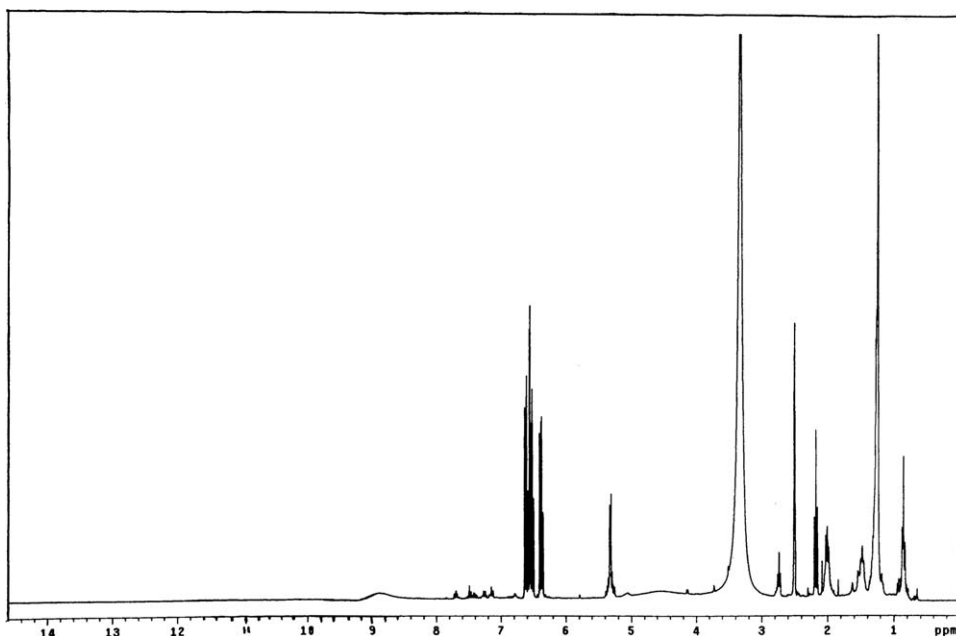
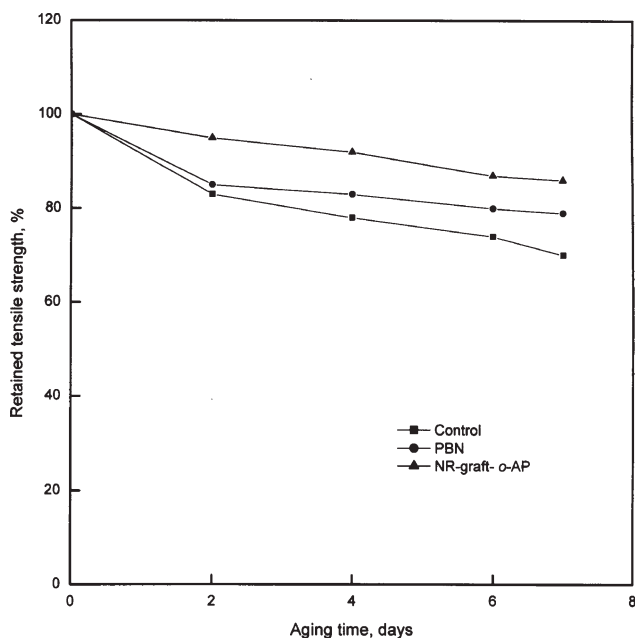
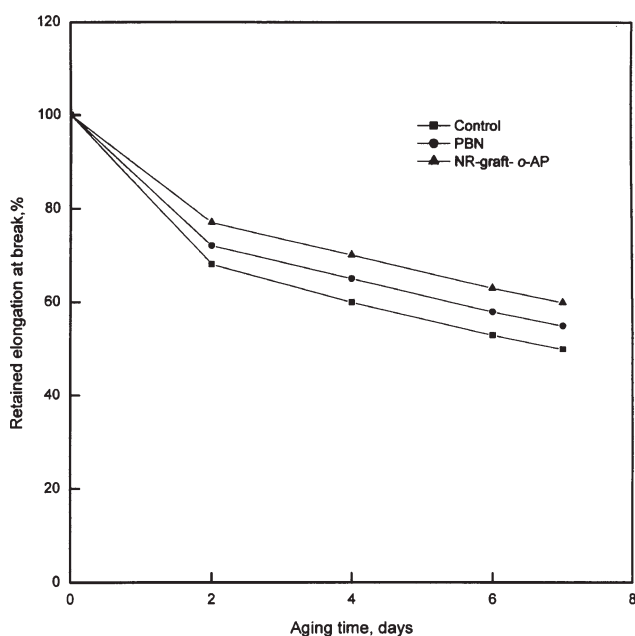


Figure 5  $^1\text{H-NMR}$  spectrum of natural rubber-g-*o*-aminophenol (NR-g-*o*-AP).



**Figure 6** Relation between retained tensile strength, % and aging time, days for NBR vulcanizates, which contain PBN, and NR-graft-*o*-AP and control vulcanizate.

samples were aged to 2, 4, 6, 7 days at 70°C in an aging oven. It is clear that the retained tensile strength, % and the retained elongation at break, % decreased with increasing the aging time duration from 2 up to 7 days for the NBR vulcanizates containing the commercial antioxidant, PBN, and the prepared grafted antioxidant, natural rubber-graft-*o*-



**Figure 7** Relation between retained elongation at break, % and aging time, days for NBR vulcanizates which contain PBN, and NR-graft-*o*-AP and control vulcanizate.

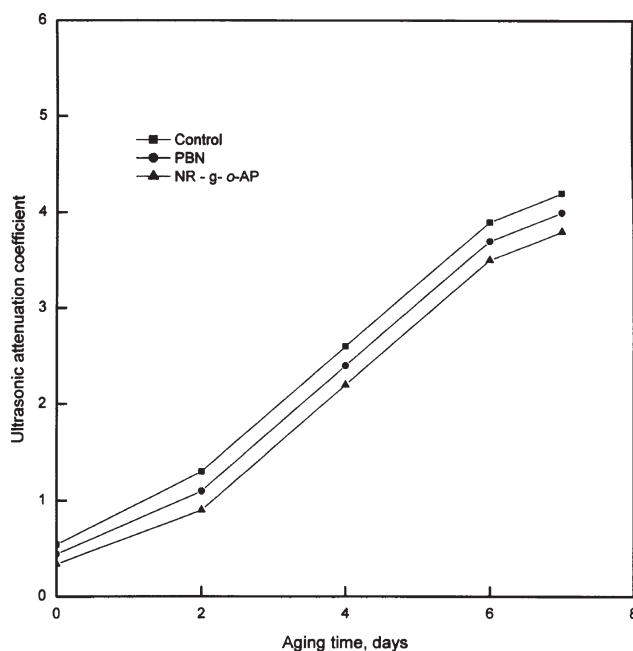
aminophenol, as well as the control vulcanizate. Because the aging time duration have undesirable effect on the mechanical properties of the NBR vulcanizates, increase the ultrasonic attenuation coefficient as shown in Figure 8, and cleavage the crosslinking density between the chains of the NBR vulcanizates.<sup>4,13</sup>

Figures 6 and 7 indicate that the retained tensile strength, % and the retained elongation at break, % of the NBR vulcanizate which contain the grafted antioxidant NR-graft-*o*-AP is higher than both of the NBR vulcanizate which contain PBN as commercial antioxidant and the control vulcanizate. Because the *o*-aminophenol part in the prepared NR-graft-*o*-AP is oxidized. Quinoneimines is the first product of the oxidation of *o*-Aminophenol, and also have a proven antioxidant activity.<sup>14</sup> The antioxidant activity of quinoneimines can be explained by considering their capacity to react with another peroxy radical or to give addition reactions with substrates containing reactive —CH groups.<sup>5</sup>

#### Effect of the prepared grafted antioxidant, NR-graft-*o*-AP, on the ultrasonic attenuation coefficient of nitrile rubber

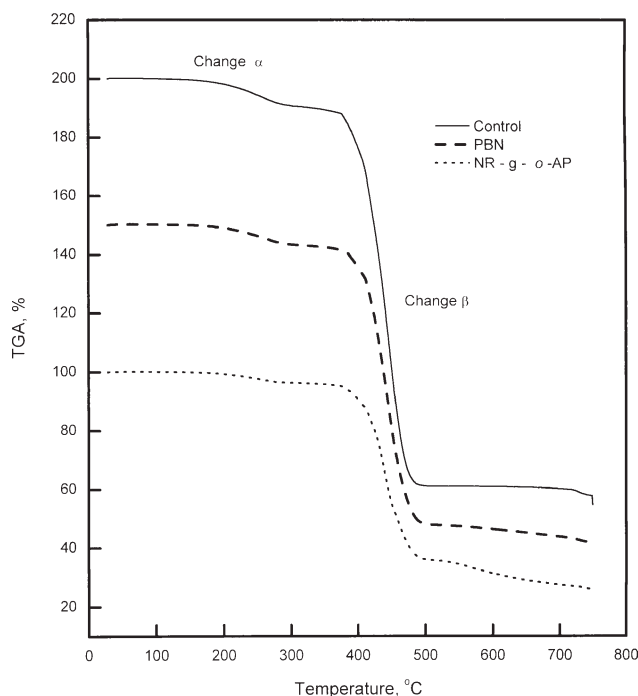
Figure 8 shows the relation between the ultrasonic attenuation coefficient and the aging time for NBR Vulcanizates.

Figure 8 shows that the NBR vulcanizate containing the NR-graft-*o*-AP has relatively lower the ultrasonic attenuation coefficient compared with both the



**Figure 8** Relation between ultrasonic attenuation coefficient and aging time for NBR vulcanizates which contain PBN, and NR-graft-*o*-AP.





**Figure 9** TGA thermogram for NBR vulcanizates contains PBN, NR-g-o-AP and control vulcanizate.

NBR vulcanizate containing PBN, and the control vulcanizate. Because, when the degradation of NBR chains increases, the homogeneity of NBR vulcanizate decreases and the NBR vulcanizate is more amorphous. It is clear that the ultrasonic attenuation coefficient increased with increasing the time of the thermal aging from 2 to 7 days. Therefore, it can be said that thermal aging activates molecules motion that promotes inherent weak point defect (e.g., voids) in the material to form minute cracks (stress raisers). Over periods of thermal aging, many sites of weak point defect can be traced to form the minute cracks. By increasing aging time, these minute cracks can grow and coalesce together to built main crack causing fracture.<sup>10,15</sup>

#### Effect of the prepared grafted antioxidant, NR-graft-o-AP, on the thermal stability of nitrile rubber

Thermogram of control mix, NBR mixes contains PBN, and NR-g-o-AP is given in Figure 9. Degradation

**TABLE II**  
Characterization of Change  $\alpha$

Properties samples	Change $\alpha$		Weight loss (%)
	Onset temperature (°C)	Endsed temperature (°C)	
A <sub>1</sub>	178	376.2	5.75
A <sub>2</sub>	200	384.2	6.05
A <sub>3</sub>	215	380.3	5.04

**TABLE III**  
Characterization of Change  $\beta$

Properties sample	Change $\beta$		Weight loss (%)
	Onset temperature (°C)	Endsed temperature (°C)	
A <sub>1</sub>	376.2	492.3	67.34
A <sub>2</sub>	384.2	505.9	65.81
A <sub>3</sub>	380.3	502.9	61.94

tion of NBR vulcanizates occurred in two steps,  $\alpha$  and  $\beta$  accompanied by weight loss. The first step degradation, change  $\alpha$ , starts at about 178°C and was completed at 384.2°C. Change  $\alpha$  is due to the loss of plasticizer and other ingredients and it corresponds to the volatilization of 5.04–6.05% of NBR content as shown in Table II.

The second step, change  $\beta$ , degradation start at 376.2°C and was complete at 505.9°C. Change  $\beta$  is due to the degradation of NBR vulcanizate at higher temperatures that leads to volatile products and also it is accompanied by weight loss for different NBR vulcanizates. Moreover, the thermal characterization of the change  $\beta$  is shown in Table III.

It is clear that, the second step of degradation occurs dramatically compared with first step degradation.

These results indicate the superior efficiency of the prepared NR-graft-o-AP to protect NBR against thermal treatment where that much better than the commercial antioxidant PBN, and control mix, respectively.

Thermogravimetric curves were analyzed mathematically to determine the non-isothermal kinetic parameters of the pyrolysis reactions. The function of the weight fraction  $\ln W_0/W$  was plotted versus the temperature factor,  $\theta$ . The activation energy of pyrolysis process was calculated from the slope of this straight line according to the equation

$$\ln W_0/W = \Delta E \theta / RT_s^2$$

where  $W_0$  and  $W$  are the initial weight and the weight at a given temperature, respectively.  $R$  is the gas constant,  $\Delta E$  is the activation energy,  $\theta$  is a temperature factor given as  $\theta = T - T_s$ <sup>16</sup> and  $T_s$  is the reference temperature. The values of the reference temperature,  $T_s$ , at which the maximum rate of

**TABLE IV**  
The Activation Energy of NBR Vulcanizates Containing PBN, and NR-graft-o-AP and Control Vulcanizate

Sample	$T_s$	$\Delta E$ Kcal/mole
A <sub>1</sub>	434	12.60
A <sub>2</sub>	441	15.11
A <sub>3</sub>	445	24.22

degradation occurred and the values of the activation energy ( $\Delta E$ ) were described in Table IV.

They show that the antioxidant NR-graft-*o*-AP has the higher activation energy ( $\equiv 24.22$  Kcal/mole) compared with commercial antioxidant, PBN ( $\equiv 15.11$  Kcal/mole), and finally the control mix ( $\equiv 12.60$  Kcal/mole). These results come in a good agreement with those obtained with the mechanical properties where NR-graft-*o*-AP is a superior antioxidant.

### CONCLUSIONS

The prepared NR-graft-*o*-Aminophenol is very active antioxidant in NBR copolymer compared with the commercial antioxidant, PBN. The NBR vulcanizate which contain the grafted antioxidant, NR-graft-*o*-AP, has higher mechanical properties than the NBR vulcanizate which contain PBN as commercial antioxidant and the control vulcanizate, respectively.

This study showed that thermal aging has significant effect on the ultrasonic attenuation coefficient. In addition, it promotes the degradation of NBR chains causing the decreasing of the mechanical properties. The results of thermal analysis indicate the superior efficiency of the prepared NR-graft-*o*-

AP to protect NBR against thermal treatment much better than the commercial antioxidant PBN and control mix, respectively.

### References

1. Kim, T. H.; Oh, D. R. *Polym Degrad Stabil* 2004, 84, 499.
2. Zhang, X. H.; Huang, L. H.; Chen, S.; Qi, G. R. *Exp Polym Lett* 2007, 1, 326.
3. Forsstrom, D.; Reitberger, T.; Terselius, B. *Polym Degrad Stabil* 2000, 67, 255.
4. El-Wakil, A. A. *J Appl Polym Sci* 2006, 101, 843.
5. Herdan, J. M.; Stan, M.; Giurginca, M. *Polym Degrad Stabil* 1995, 50, 59.
6. Ohkatsu, Y.; Nishiyama, T. *Polym Degrad Stabil* 2000, 67, 313.
7. Pospisil, J.; Nespurek, S. *Polym Degrad Stabil* 1995, 49, 99.
8. Avirah, S. A.; Joseph, R. *J Appl Polym Sci* 1995, 57, 1511.
9. El-Wakil, A. A. *Polym Plastics Technol Eng* 2007, 46, 661.
10. ASTM D 1998, 412.
11. Ward, I. M. In *Mechanical Properties of Solid Polymers*, 2nd ed.; John Wiley & Sons: Chichester, 1983.
12. Jha, A.; Bhowmick, A. K. *Polym Degrad Stabil* 1998, 62, 575.
13. El-Wakil, A. A. *J Appl Polym Sci* 2007, 104, 27.
14. Cain, M. E.; Gelling, J. R.; Knight, G. T.; Lewis, P. M. *Rubber Ind* 1975, 8, 216.
15. Mirham, A. Y. Barakat; El-Wakil, A. A. Presented at the 9th Cairo University International Conference on Mechanical Design and Production (MDP-9), 2008, Cairo, Egypt.
16. Horowitz, H. H.; Metzger, G. *Anal Chem* 1963, 35, 1464.