

Research Article

Enhancement the Thermal Stability and the Mechanical Properties of Acrylonitrile-Butadiene Copolymer by Grafting Antioxidant

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Monomeric antioxidants are widely used as effective antioxidants to protect polymers against thermal oxidation. Low molecular weight antioxidants are easily lost from polymer through migration, evaporation, and extraction. Physical loss of antioxidants is considered to be major concern in the environmental issues and safety regulation as well as long life time of polymers. The grafting copolymerization of natural rubber and *o*-aminophenol was carried out by using two-roll mill machine. The prepared natural rubber-graft-*o*-Aminophenol, NR-graft-*o*-AP, was analysed by using Infrared and ¹H-NMR Spectroscopy techniques. The thermal stability, mechanical properties, and ultrasonic attenuation coefficient were evaluated for NBR vulcanizates containing the commercial antioxidant, N-phenyl-β-naphthylamine (PBN), the prepared grafted antioxidant, NR-graft-*o*-AP, and the control vulcanizate. Results of the thermal stability showed 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.

1. Introduction

Polyolefin is one of the most widely used polymers and more susceptible to the oxidation. It well known that oxidation reactions increase at elevated temperatures during the processing of the polymer. 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 (O₂) 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 [1–3].

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, multifunctional 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 [4–7]. Therefore we synthesized Natural rubber-graft-*o*-Aminophenol and tested as grafted antioxidants.

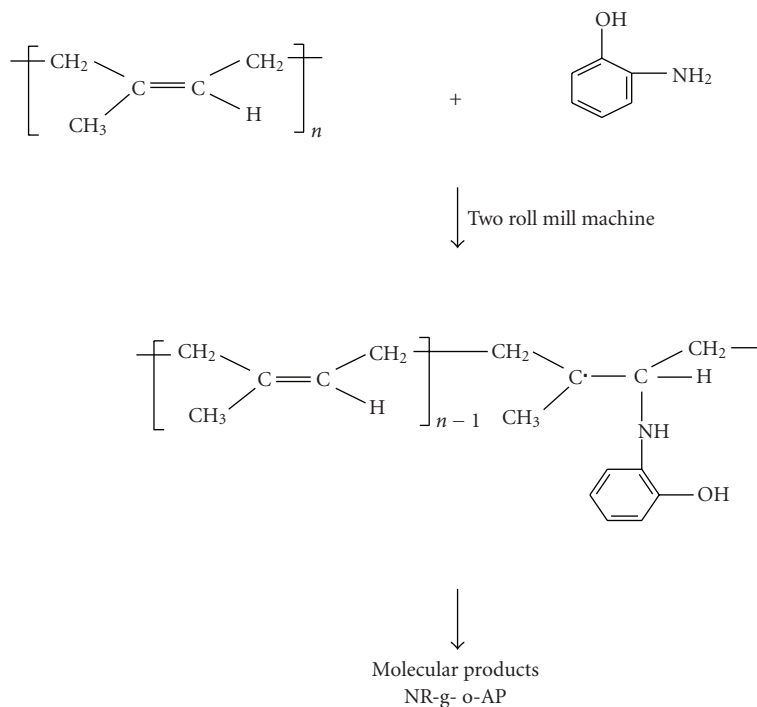


FIGURE 1

2. Experimental

2.1. Materials. *o*-Aminophenol was supplied by Sigma-Aldrich Co. Ltd. (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., Ltd., China). All laboratory grade solvents were obtained from Edwic (Cairo, Egypt).

2.2. Synthesis of NR-graft-*o*-AP. NR-graft-*o*-AP was synthesized by the reaction of natural rubber and *o*-Aminophenol using two-roll mill machine. Natural rubber was masticated on a water-cooled two-roll mill 150 mm in diameter and 300 mm wide. 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 is used to isolate the grafted NR. The product was dried in an oven at 40°C to constant weight within 24 hours. The percent graft was taken as the ratio of the graft yield to the natural rubber multiplied by 100 [8]:

$$\text{Degree of grafting} = \left(\frac{W_g}{W_{NR}} \right) * 100, \quad (1)$$

where W_g is the weight of graft yield and W_{NR} 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 Figure 1.

2.3. Formulation and Mixing of NBR Vulcanizates. The NBR rubber vulcanizates were compounded according to the recipe shown in Table 1. 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 Monosanto rheometer (Swindon, UK).

Zinc oxides and stearic acid 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 add to obtain the desirable properties. The most important of these materials is the organic accelerator. The most common method of crosslinking NBR is using sulfur. The function of sulfur is forming a bridge between large chains of NBR, linking them together in a fixed pattern.

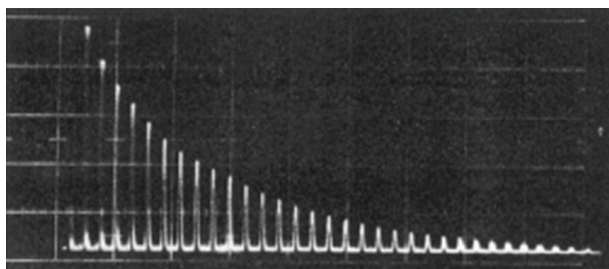
Antioxidants are substances that retard oxidation by atmospheric oxygen at moderate temperatures (autoxidation). Autoxidation is a free radical chain reaction that can be inhibited at the initiation and propagation steps.

2.4. Infrared and ¹H-NMR Spectroscopy. IR spectra and ¹H-NMR spectra were registered on Bruker, Vector22, FTIR Spectrometer, and Jeol-EX-270, respectively.

2.5. 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 [9].

TABLE 1: Formulation of NBR vulcanizates containing PBN, NR-*g-o*-AP, and control vulcanizate.

Ingredient (phr) ↓	Mix name		
	A1	A2	A3
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
Tetramethylthiuramdisulphide “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



Typical pulse-echo decay pattern

FIGURE 2

2.6. 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), and 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 (see Figure 2).

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 α [10]:

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

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.

2.7. Thermal Analysis. Thermogravimetric analysis (TGA) was 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 [11].

3. 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 hydroperoxides 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, 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.

3.1. Analysis of NR-graft-*o*-AP. Figures 3, 4, and 5 show the IR spectra of *o*-AP, original (ungrafted) NR, and the natural rubber-graft-*o*-aminophenol.

Figures 6 and 7 show the ¹H-NMR spectra of original (ungrafted) NR and the natural rubber-graft-*o*-aminophenol.

The assignments of various peaks found in Figures 3–5 show significant changes in the spectral behaviour of the natural rubber and *o*-aminophenol. The new absorption peak at 3375 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 6 and 7 show the ¹H-NMR spectra of the natural rubber and natural rubber-graft-*o*-aminophenol. Figure 7 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 that the *o*-aminophenol was grafted onto the natural rubber.

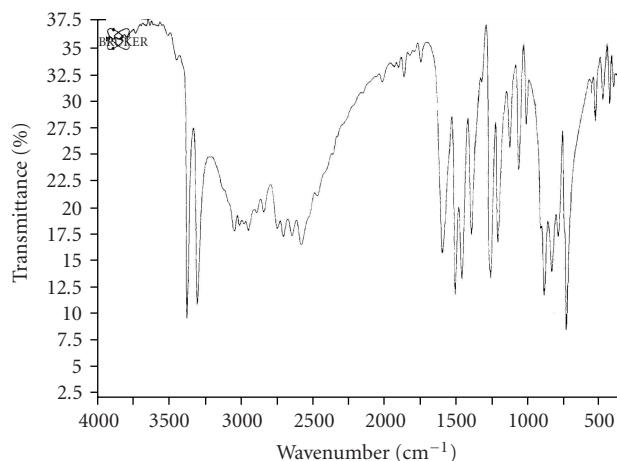
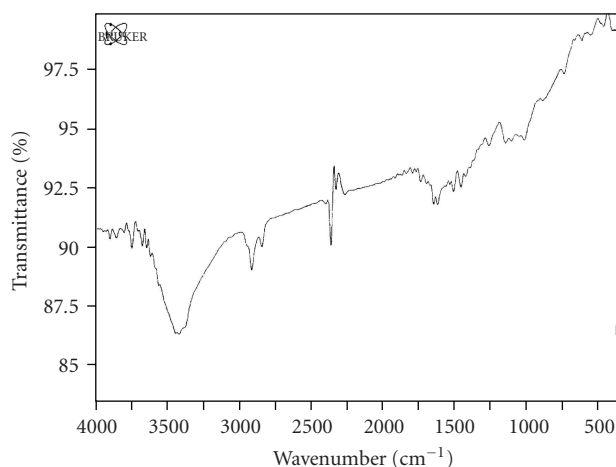
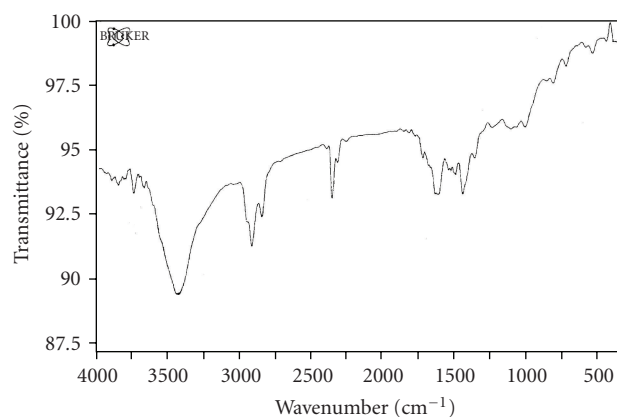
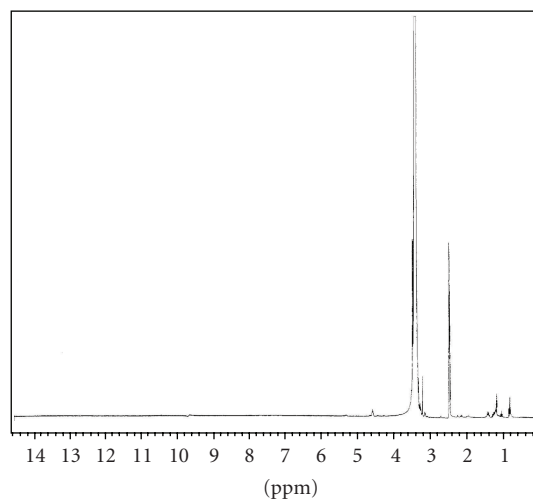
FIGURE 3: IR spectrum of *o*-aminophenol (*o*-AP).FIGURE 5: IR spectrum of natural rubber-g-*o*-aminophenol (NR-g-*o*-AP).

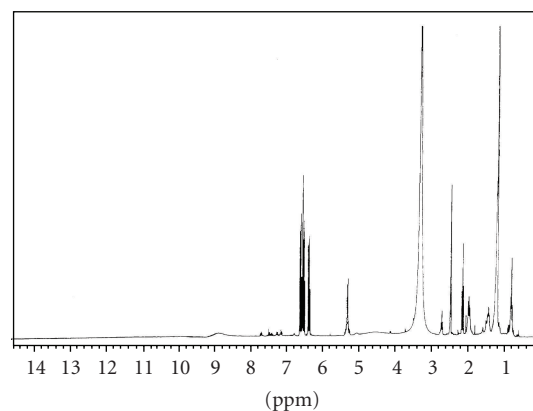
FIGURE 4: IR spectrum of natural rubber.

FIGURE 6: ¹H NMR spectrum of natural rubber.

3.2. Effect of the Prepared Grafted Antioxidant, NR-g-*o*-AP, on the Mechanical Properties of Nitrile Rubber. Figure 8 shows the retained tensile strength as a function of the aging time and Figure 9 shows the relation between the retained elongation at break and the aging time.

The NBR-tested samples were aged to 2, 4, 6, and 7 days at 90°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 durations from 2 days up to 7 days for the NBR vulcanizates containing the commercial antioxidant, PBN, and the prepared grafted antioxidant, natural rubber-graft-*o*-aminophenol, as well as the control vulcanizate. Because the aging time duration has undesirable effect on the mechanical properties of the NBR vulcanizates, increase the ultrasonic attenuation coefficient as shown in Figure 10, and cleavage the crosslinking density between the chains of the NBR vulcanizates [4, 12].

Figures 8 and 9 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 are higher than both of the NBR vulcanizate which contains PBN as commercial antioxidant and the

FIGURE 7: ¹H NMR spectrum of natural rubber-g-*o*-aminophenol (NR-g-*o*-AP).

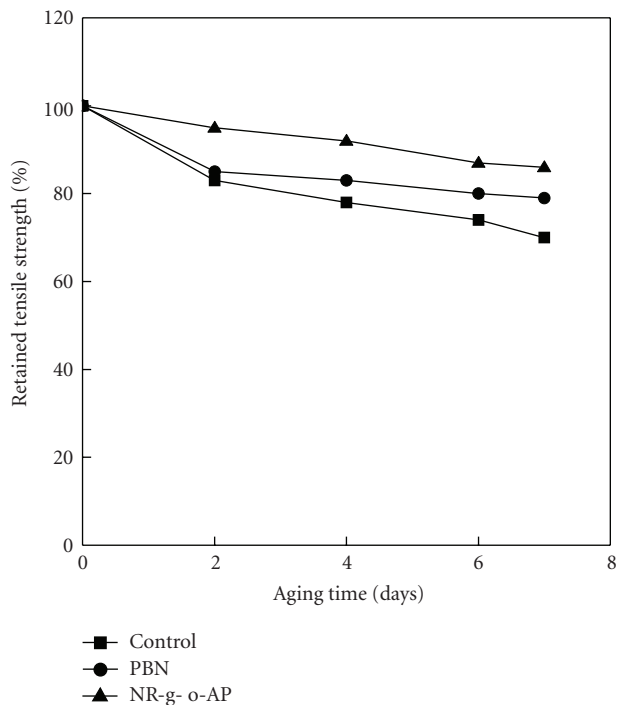


FIGURE 8: Relation between retained tensile strength and aging time for NBR vulcanizates containing PBN, NR-graft-*o*-AP, and control vulcanizate.

control vulcanizate. Because the *o*-aminophenol part in the prepared NR-graft-*o*-AP was oxidize, quinoneimines is the first product of the oxidation of *o*-Aminophenol and also has antioxidant activity [13]. 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 [5].

3.3. *Effect of the Prepared Grafted Antioxidant, NR-graft-*o*-AP, on the Ultrasonic Attenuation Coefficient of Nitrile Rubber.* Figure 10 shows the relation between the ultrasonic attenuation coefficient, and the aging time for NBR Vulcanizates.

Figure 10 shows that the NBR vulcanizate containing the NR-graft-*o*-AP has relatively lower ultrasonic attenuation coefficient compared with both the NBR vulcanizate containing PBN and the control vulcanizate. when the degradation of NBR chains increased, the homogeneity of NBR vulcanizate decreased and the NBR vulcanizate became 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 the fracture [10, 14].

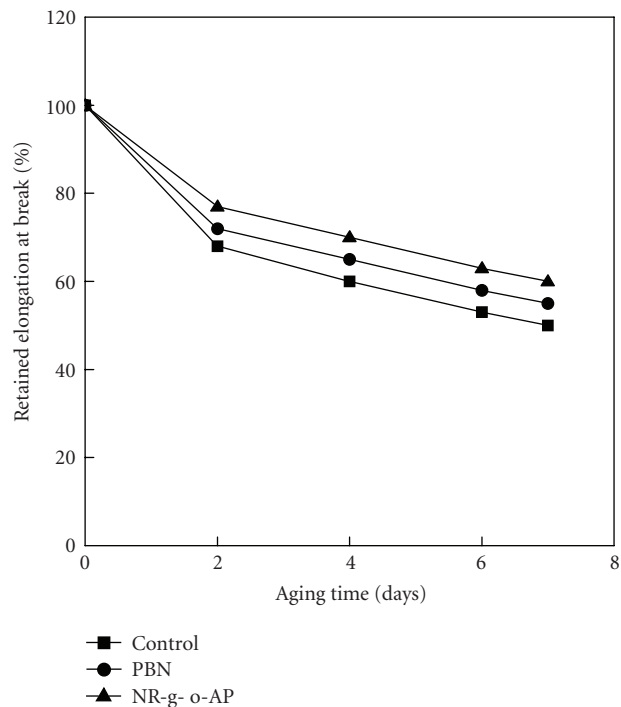


FIGURE 9: Relation between retained elongation at break and aging time for NBR vulcanizates containing PBN, NR-graft-*o*-AP, and control vulcanizate.

TABLE 2: Characterization of change α .

Properties	Change α			
	Samples	Onset temp. °C	Endsed temp. °C	Weight loss %
A1		178	376.2	5.75
A2		200	384.2	6.05
A3		215	380.3	5.04

TABLE 3: Characterization of change β .

Properties	Change β			
	Samples	Onset temp. °C	Endsed temp. °C	Weight loss %
A1		376.2	492.3	67.34
A2		384.2	505.9	65.81
A3		380.3	502.9	61.94

3.4. *Effect of the Prepared Grafted Antioxidant, NR-graft-*o*-AP, on the Thermal Stability of Nitrile Rubber.* Thermograms, of control mix, NBR mixes containing PBN, and NR-g-*o*-AP are given in Figure 11.

Degradation of NBR vulcanizates occurred in two steps, α and β accompanied by weight loss. The first step degradation, change α , starts at about 178°C and is completed at 384.2°C. Change α 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 2.

The second step, change β , degradation starts at 376.2°C and is completed at 505.9°C. Change β is due to the degradation of NBR vulcanizate at higher temperatures that

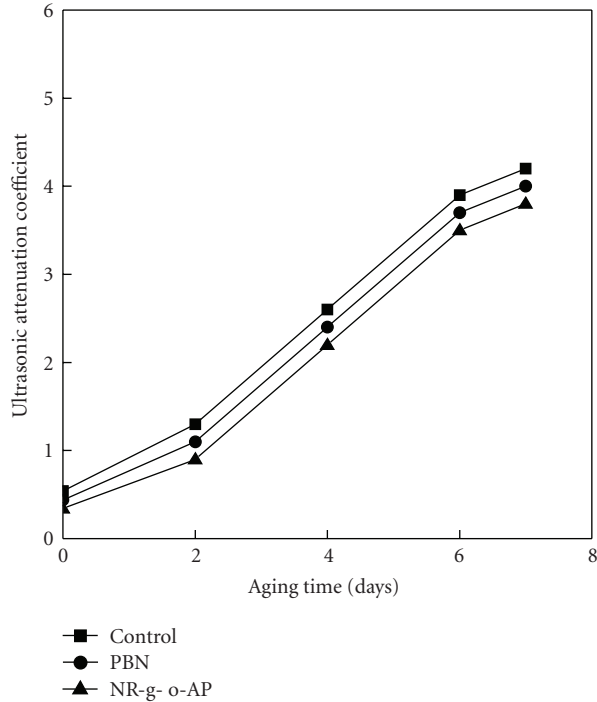


FIGURE 10: Relation between ultrasonic attenuation coefficient and aging time for NBR vulcanizates containing PBN and NR-graft-*o*-AP.

leads to volatile products and also it is accompanied by weight loss for different NBR vulcanizates. Moreover, the thermal characterization of change β is shown in Table 3.

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 is much better than the commercial antioxidant PBN and control mix, respectively.

Thermogravimetric curves were analysed mathematically to determine the nonisothermal kinetic parameters of the pyrolysis reactions. The function of the weight fraction $\ln \ln W_0/W$ was plotted versus the temperature factor, θ . The activation energy of pyrolysis process was calculated from the slope of this straight line according to (3):

$$\ln \ln \frac{W_0}{W} = \frac{\Delta E \theta}{RT_s^2}, \quad (3)$$

where W_0 and W are the initial weight and the weight at a given temperature, respectively. R is the gas constant, E is the activation energy, θ is a temperature factor given as $\theta = T - T_s$ [15], and T_s is the reference temperature. The values of the reference temperature, T_s , at which the maximum rate of degradation occurred, and the values of the activation energy (ΔE) were described in Table 4.

They show that the antioxidant NR-graft-*o*-AP has the higher activation energy ($\cong 101.72$ KJ/mole) compared with commercial antioxidant, PBN ($\cong 63.46$ KJ/mole), and finally the control mix ($\cong 52.92$ KJ/mole). These results come in a

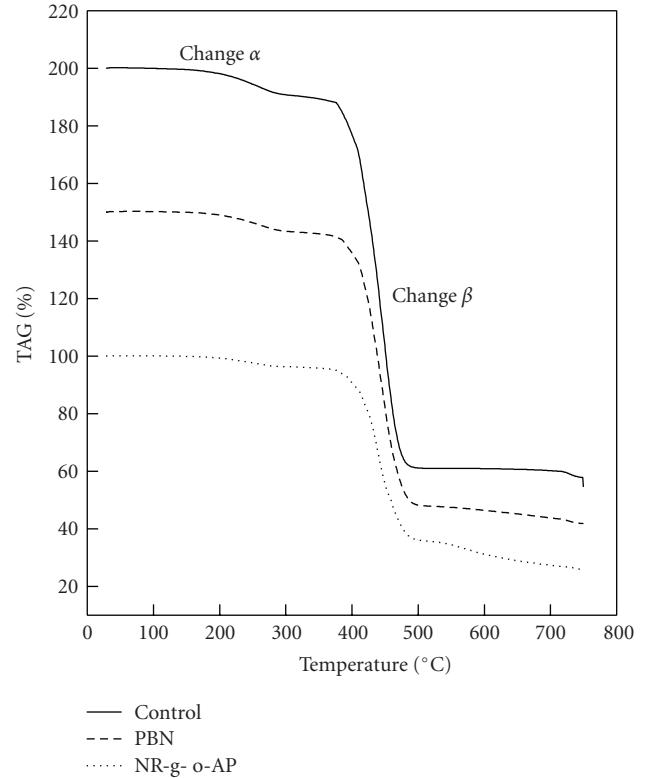


FIGURE 11: TGA thermogram for for NBR vulcanizates containing PBN, NR-g-*o*-AP, and control vulcanizate.

TABLE 4: The activation energy of NBR vulcanizates containing PBN, NR-graft-*o*-AP, and control vulcanizate.

Sample	T_s	E KJ/mole
A1	434	52.92
A2	441	63.46
A3	445	101.72

good agreement with those obtained with the mechanical properties where NR-graft-*o*-AP is a superior antioxidant.

4. Conclusions

The prepared NR-graft-*o*-AP is very active antioxidant in NBR copolymer if it is compared with the commercial antioxidant, PBN. The NBR vulcanizate which contains the grafted antioxidant, NR-graft-*o*-AP, has higher mechanical properties than the NBR vulcanizate which contains 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.

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