In the present work, 2-propyl- and 2-heptyl-1H-benzo[d]imidazole were prepared by condensation reaction of o-phenylenediamine with n-butanoic acid and n-octanoic acid, respectively. The prepared products were characterized by FT-IR, 1H-NMR spectroscopy and melting point. These products were incorporated into acrylonitrile butadiene rubber (NBR) composites with two different fillers (Silica and High Abrasion Furnace carbon black HAF) as an antioxidant additive with different concentrations from 1 up to 2 phr as a comparison with 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) as a traditional antioxidant. Their effects on the rheometric, physico-mechanical and electrical properties of NBR composites were evaluated. Thermo-oxidative aging was carried out for NBR composites and distribution of the prepared products observed by Scanning Electron Microscope (SEM). The results showed that the prepared products can act as highly efficient antioxidants in acrylonitrile butadiene rubber vulcanizates comparing with commercial antioxidant TMQ and revealed that there was enhancement in mechanical properties of NBR composites that containing the prepared products, as well. The results also illustrated that the optimum ratio from 2-alkylbenzimidazole incorporated into acrylonitrile butadiene rubber vulcanizates is 1.5 phr if compared with the same ratio from traditional antioxidant (TMQ).

**Keywords:** 2-Alkyl-1H-benzo[d]imidazole, 2,2,4-trimethyl-1,2-dihydroquinoline, Antioxidant, Physico-mechanical and electrical properties.

**Introduction**

Acrylonitrile butadiene rubber (NBR) has been widely used all over the world due to its coveted chemical and physical properties such as good processability, mechanical properties, gas impermeability, resistance to oil, fuel and greases due to the polar character of NBR by presence of the polar nitrile group and moderate cost. NBR is a copolymer composed of butadiene and acrylonitrile, also used as a strategic material in automotive rubber products industries and incorporated in manufacturing of seals, oil resisting rubber hose [1-4]. Rubber products undergo deterioration which is generally occasioned by oxygen, ozone, heat and dynamics stress. Accordingly, there is a great effort to promote stability of rubber during processing, when exposed to the vulcanization thermal conditions and during the life time when exposed to the external environment.

A suitable technique was used to enhance the aging properties of rubbers by addition of antioxidants [5, 6]. Antioxidants protect the rubber materials from attack by air, heat, light and even ozone in the atmosphere. Herein, the commonly utilized antioxidants in polymers can be classified into two main classes, namely, hindered phenols and aromatic amines, depending on the nature of the matrix [7, 8]. Amine antioxidants are more common which perform their role by termination...
the free radical chain reactions during autoxidation of rubber by donating H-atoms to free radicals [9, 10].

Among these additions, reinforcement fillers play an important role in the rubber industry as they enhance rubber performance and reduce its cost. Carbon black and silica are the two most important fillers. SiO$_2$ is important white reinforcing filler due to its large specific surface, low density, and good dispersibility. It has attracted great attention because of its ability to reduce tire roll resistance, hysteresis loss, and fuel expense, since the concept of a “green tire” was first stated by Michelin in the beginning of the 1990s [11]. Also, carbon black is able to enhance the mechanical properties of rubber because of its excellent compatibility with rubbers. Thus, addition of carbon black to rubber formulation afford properties that meets the given service application.

In this manuscript, 2-Alkylbenzimidazole had been prepared by condensation reaction. The synthetic method was verified through melting point, FT-IR and $^1$H-NMR spectroscopy. The present study aims to discuss the probability and efficiency of using 2-Alkylbenzimidazole as a novel antioxidant for acrylonitrile butadiene rubber (NBR) and study its effect on physico-mechanical and electrical properties of the vulcanizates as compared to the traditional antioxidant, (2,2,4-trimethyl-1,2-dihydroquinoline) [TMQ]).

Experimental & Techniques

Materials

o-phenylenediamine, n-butanoic acid, n-octanoic acid and ethanol were supplied from El-Nasser pharmaceutical chemical company (Egypt). Acrylonitrile Butadiene Rubber (NBR), silica and carbon black (HAF) filler were supplied from Transport and Engineering, Alexandria, Egypt. All the rubber ingredients zinc oxide, stearic acid, dioctyl phthalate (DOP) and tetramethylthiuram disulfide (TMTD) were of commercial grades. N-cyclohexyl-2-benzothiazole sulfonamide (CBS), 2,2,4-tri- methyl-1,2-dihydroquinoline (TMQ) and sulfur were obtained from Aldrich company, Germany.

Synthesis and characterization of 2-Alkylbenzimidazole

A mixture of o-phenylenediamine (5.4 g, 0.05 mole) and n-butanoic acid (20 ml, 0.22 mole) or n-octanoic acid (20 ml, 0.13 mole) was heated under reflux for 5 hrs. The reaction mixture was cooled and diluted with cold water (10 ml), then basified by addition of (30%) sodium carbonate solution with continuous stirring. The separated solid was filtered off, washed with ice water several times, dried, and crystallized from the proper solvent to give compounds, 2-propyl-1H-benzo[d]imidazole, respectively. The compounds were also characterized by electro thermal apparatus melting point, Shimadzu FT-IR 8101 and Varian Mercury VX-300 NMR spectrometer.

Propyl-1H-benzo[d]imidazole

Deep yellow crystals, m.p. 150-152 °C (Toluene), yield 70%, FT-IR (KBr, $v$ cm$^{-1}$): 3447 (NH), 3086 (CH$_{ar}$), 2957 (CH$_{aliph}$), 1622 (C=N). $^1$H-NMR (DMSO- d$_6$) δ (ppm): 12.17 (s, 1H, NH, imidazole, exch. with D$_2$O), 7.08–7.46 (m, 4H, H$_{ar}$), 2.7–2.8 (t, 2H, -CH$_2$-CH$_2$), 1.75–1.84 (m, 2H, CH$_2$), 0.93–0.96 (t, 3H, CH$_3$).

Heptyl-1H-benzo[d]imidazole

Deep brown powder, m.p. 140-142 °C (1,4-dioxane: water [1:1]), yield 67%. FT-IR (KBr, $v$ cm$^{-1}$): 3425(NH), 3086 (CH$_{ar}$), 2954 (CH$_{aliph}$).
Preparation and characterization of NBR composites

NBR composites with the formulations were prepared using a laboratory two roll mill. The rubber compounds were left overnight before vulcanization. All compounds were compressed and molded using a hydraulic hot press according to their respective cure time (Tc) that was determined through TA instruments, MDR one [Moving Die Rheometer], USA.

Mechanical properties of vulcanizates were determined according to the standard methods using an electronic Zwick tensile testing machine (model Z010, German-anything), in accordance with ASTM D412 standard.

Thermal oxidative ageing was carried out at 90±1°C in an air circulating oven for different time periods according to ASTM: D 572-04, 2010. The reported results were averaged from a minimum five specimens.

The morphology of NBR composites were investigated by using scan electron microscope (SEM) Quanta instrument (model FEG250, FEI, Hillsboro, Oregon, USA). Samples were gold coated, and the electron microscope was operated at 10 kV of excitation potential. SEM was performed by mounting the polymer blends sample on standard specimens tube and then created with very thin layer of gold by deposition.

Dielectric Measurements

The permittivity ε′ and the dielectric loss ε″ in addition to the electrical conductivity s measurements were carried out using Novocontrol Alpha Analyzer (GmbH concept 40, tan δ > 10−4), over a frequency range from 10−1 Hz to 107 Hz. The samples were placed between two gold plated electrodes (the upper electrode’s diameter is 10 mm) of a parallel plate capacitor. This technique among others has the ability to probe molecular fluctuations and charge transport in a broad frequency range.

Results and Discussion

Effect of adding 2-Alkylbenzimidazole on physico-mechanical properties of NBR / Silica composites

2-propyl-, and 2-heptyl-, 1H-benzo[d]imidazole were incorporated into NBR at different concentrations from 1 up to 2 phr. As well as comparing their effect with the commercial applied antioxidant in rubber products, as (2,2,4-trimethyl-1,2-dihydroquinoline [TMQ] shown in Table 1.

The mechanical properties of the polymeric composites are one of the most significant performance parameters in the practical application of rubber material. The variations in tensile strength and elongation at break were shown in Fig.1 and Fig. 2, respectively. From figure 1, it was obvious that the highest tensile strength was achieved for NBR vulcanizates containing 1.5 phr from 2-heptyl-1H-benzo[d] imidazole followed by 2-propyl-1H-benzo[d] imidazole and finally TMQ and this is due to increase of crosslinking density between NBR chains. In addition, it was clear that the values of tensile strength of the NBR vulcanizates increased slightly with incorporation of traditional and prepared antioxidant up to 1.5 phr and then decreased with increase of antioxidant content up to 2 phr. Figure 2 also illustrated that the increase in the concentration of antioxidants from 1 up to 1.5 phr led to slight increase in the elongation at break and then decrease at 2 phr.

Effect of adding 2-Alkylbenzimidazole as a novel antioxidant on thermal oxidative aging for NBR/Silica composites

Figure 3 shows the tensile strength of the vulcanizates before and after ageing. All the vulcanizates show fairly good resistance to aging at 90°C. The vulcanizates containing 2-propyl-, and 2-heptyl-, 1H-benzo[d]imidazole show good resistance when the aging time increased more than traditional antioxidant. Figure 4 shows the variation in elongation at break of the vulcanizates before and after ageing. The vulcanizates containing 2-heptyl-1H-benzo[d] imidazole show better retention in elongation at break after ageing while vulcanizates containing 2-propyl-1H-benzo[d]-imidazole show slight less retention in elongation at break after ageing. In addition, the prepared antioxidants improve the aging resistance of NBR composites.

Effect of adding 2-Alkylbenzimidazole on physico-mechanical properties of NBR/HAF composites

Also, 2-propyl-, and 2-heptyl-, 1H-benzo[d] imidazole were incorporated into NBR containing HAF as black filler at different concentrations from...
TABLE 1. Formulation and rheometer characteristic of NBR /silica vulcanizates.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>1 Phr</th>
<th>1.5 Phr</th>
<th>2 Phr</th>
<th>1 Phr</th>
<th>1.5 Phr</th>
<th>2 Phr</th>
<th>1 Phr</th>
<th>1.5 Phr</th>
<th>2 Phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Basic recipe: ZnO 4, Stearic acid 2, Silica 20, Sulfur 2, TMTD 1, CBS 0.8, DOP 3 Phr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rheometer characteristic

| ML (d.Nm) | 0.64 | 0.60 | 0.61 | 0.64 | 0.64 | 0.61 | 0.6 | 0.59 | 0.59 |
| MH (d.Nm) | 11.56 | 10.55 | 11.22 | 11.83 | 11.61 | 11.29 | 11.08 | 11.18 | 11.06 |
| ts\(_2\) (min) | 1.56 | 1.41 | 1.31 | 1.38 | 1.39 | 1.37 | 1.43 | 1.42 | 1.42 |
| Tc\(_{90}\) (min) | 4.48 | 4.15 | 4.13 | 4.32 | 4.52 | 4.59 | 4.37 | 4.55 | 5.00 |

Notes:  
ML: Minimum torque  
MH: Maximum torque  
Ts\(_2\): Scorch time  
Tc\(_{90}\): Optimum curing time

Fig. 1. Tensile strength for NBR/ Silica composites

Fig. 2. Elongation at break for NBR/ Silica composites.
Fig. 3. Variation in tensile strength for NBR/Silica composites before and after thermal aging.

Fig. 4. Variation in elongation at break for NBR/Silica composites before and after thermal aging.

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Effect of adding 2-Alkylbenzimidazole as a novel antioxidant on thermal oxidative aging for NBR/HAF composites

Similarly, the mechanical properties of NBR/HAF composites with different concentrations of different antioxidants displayed a slight increase in the tensile strength and elongation at break before thermal aging time were shown in Fig. 5 and Fig. 6, respectively. Also, increase the concentration of antioxidants from 1 up to 1.5 phr leads to slight increase in the tensile strength and elongation at break and then decrease at 2 phr, however, a slight increase in 2-propyl-1H-benzo[d]imidazole was shown than in 2-heptyl-1H-benzo[d]imidazole.

**Effect of adding 2-Alkylbenzimidazole on dielectric properties of NBR vulcanizates.**

This work was extended to study the dielectric properties of NBR vulcanize upon addition of 2-alkylbenzimidazole. Accordingly, the obtained results for the permittivity $\varepsilon$ and dielectric loss $\varepsilon''$ were illustrated graphically versus the applied frequency ranging from 10-1 upto 10^7 Hz.

### TABLE 2. Formulation and rheometer characteristic of NBR/HAF vulcanizates.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>TMQ</th>
<th>2-propylbenzimidazole</th>
<th>2-heptylbenzimidazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

| Basic recipe: ZnO 4, Stearic acid 2, HAF 30, Sulfur 2, TMTD 1, CBS 0.8, DOP 3 Phr |

<table>
<thead>
<tr>
<th>Rheometer characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML (d.Nm)</td>
</tr>
<tr>
<td>MH (d.Nm)</td>
</tr>
<tr>
<td>$t_s$ (min)</td>
</tr>
<tr>
<td>$T_{c_{90}}$ (min)</td>
</tr>
</tbody>
</table>

Notes: $M_L$: Minimum torque $M_H$: Maximum torque $t_s$: Scorch time $T_{c_{90}}$: Optimum curing time
Fig. 5. Tensile strength for NBR/HAF composites

Fig. 6. Elongation at break for NBR/HAF composites

Fig. 7. Variation in tensile strength for NBR/HAF composites before and after thermal aging

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Fig. 8. Variation in elongation at break for NBR/HAF composites before and after thermal aging.

Fig. 9. SEM for NBR/Silica vulcanizate.
Hz and at room temperature \( \approx 25 \, ^{\circ}\text{C} \) in Figure (11) for various composites with fixed amount of different prepared antioxidants including the 2, 2, 4-trimethyl-1,2-dihydroquinoline as a traditional antioxidant and with fixed amount of silica.

The permittivity \( \varepsilon \) was found to decrease by increasing the applied frequency showing anomalous dispersion [12]. The decrease in \( \varepsilon \) values at lower frequency could be due to either space charge effects [13] and or the interfacial polarization [14].

From this figure it is seen that the \( \varepsilon \) values record the highest value for the traditional antioxidant followed by NBR with 2-propyl-1H-benzo[d]imidazole and the lowest value obtained for NBR with 2-heptyl-1H-benzo[d]imidazole which shows inverse proportional with the number of carbon atoms in the molecule. This is logic due to the lower polarity of 2-heptyl-1H-benzo[d]imidazole with respect to 2-propyl-1H-benzo[d]imidazole.

The dielectric loss \( \varepsilon'' \) as a function of the applied frequency was shown in Figure (11) illustrates a very complicated curves indicating more than one relaxation process. The higher values of \( \varepsilon'' \) at low frequency may be due to a combination between interfacial polarization and the dc electrical conductivity [15, 16].

Also, it is seen that at high frequency range a pronounced peak was detected. This relaxation process ascribes the movement of the side chain and the attached groups and found to be unaffected.
Fig. 11. The permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ of NBR/Silica vulcanizates with 1.5phr from different antioxidants.
Fig. 12. The permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ of NBR/HAF vulcanizates with 1.5phr from different antioxidants.

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by the type of antioxidant.

The permittivity $\varepsilon$ and the dielectric loss $\varepsilon''$ were measured for the same composites after replacing silica as reinforcing filler with HAF black one. The obtained data are given in Figure (12). Same trend is obtained but the values of $\varepsilon$ and $\varepsilon''$ are found to be higher when compared with those when silica was used as reinforcing filler.

The dc conductivity $\sigma$ was calculated from the measured ac conductivity and the obtained data were illustrated graphically in Figure (13). From this figure it is obvious that the electrical conductivity $\sigma$ follows the trend, TMQ > 2-propyl-1H-benzo[d]imidazole > 2-heptyl-1H-benzo[d]-imidazole which confirms the obtained dielectric data. Also it is clear that $\sigma$ values are much higher for HAF as reinforcing filler when compared with those of silica. This finding is logic due to the conducting nature of HAF [17-19].

**Conclusion**

Acrylonitrile butadiene rubber (NBR) has various desired properties but low resistant to oxidation, thus, the incorporation of antioxidants into NBR enhance some of its properties. Series from 2-alkylbenzimidazole were prepared by condensation reaction and characterized by utilizing FT-IR, $^1$H-NMR spectral techniques and melting points measurements.

The optimum ratio from 2-alkylbenzimidazole incorporated into acrylonitrile butadiene rubber...
vulcanizates is 1.5 phr if compared with the same ratio from traditional antioxidant (TMQ).

The vulcanizates containing 2-propyl-, and 2-heptyl-$H$-benzo[d]imidazole show good resistance when the aging time increased more than traditional antioxidant.

The synthesized compounds can act as highly efficient antioxidants in acrylonitrile butadiene rubber vulcanizates as compared to TMQ, a commercial antioxidant.

References


تتعرض منتجات المطاط إلى تدهور ملحوظ يحدث بشكل عام بواسطة الأكسجين، الأوزون والحرارة وكذلك الإجهاد الميكانيكي. لذا يضاف الي خلطات المطاط بعض المواد التي تلعب دورا هاما للحفاظ علي خواص المطاط الميكانيكية من التدهور أثناء التخزين أو التشغيل وهذه المواد تدعي المواد المضادة للأكسدة و تضاف %. كما يمكن تصنيف مضادات الأكسدة المستخدمة في البوليمرات إلى

٣-١
بكميات صغيرة من

٣-١
- بنزو١
- هيبتيل٢
- بروبيل٢
- ثلاثي ميثيل٣
- ثنائي هيدروكينولين كمادة مانعة للاكسدة كمادة مرجعية
- ٢،١- ثنائي هيدروكينولين كمادة مانعة للأكسدة كمادة مرجعية

إيثيميدازول بالإضافة إلى مضادات الأكسدة التقليدية. مثلاً، النتائج تلون في المركبات المحضرة يمكن أن تعمل كمضادات أكسدة عالية الكفاءة في مطاط الأكريلونيتربوتيدين كمضاد أكسدة جديد وتأثيره على الخواص الفيزيوكيميائية و الكهربية لمطاط الأكريلونيتربوتيدين

تحضير -ألكيل بنزاييميدازول كمضاد أكسباد أكسدة جديد وتأثيره على الخواص الفيزيوكيميائية والكهربائية لمطاط الأكريلونيتربوتيدين

أيمن محمد محمد علي حسن١، أحمد سعد سيف١، أحمد اسماعيل حسين٢، حامد احمد يونس دربالة١، احمد كامل الجماهير السيدة

قسم الكيمياء - كلية العلوم - جامعة عين شمس - القاهرة - مصر

قسم البلمرات والمخضبات - المركز القومي للبحوث - القاهرة - مصر


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