**Multipurpose Additive for Ethylene Propylene Diene and Acrylonitrile Rubber Blend**

There are different industrial applications, which need rubber products that are withstandin for oils and having thermal stability, like hoses, gaskets and motor mounts. In fact, there is no existing rubber which can satisfy these requirements. This task attracts the sight of researchers and technologists to tailor special blends which contain two or more rubbers [1-9]. So that one of them resists swelling in oils and the other shows high thermal stability. It is well known that ethylene propylene diene rubber exhibits high resistance to thermal degradation due to the absence of unsaturated double bonds across its main backbone chain [10, 11], on the other hand acrylonitrile butadiene rubber shows high re-sistance to swelling in oils [12] due to the pronounced difference between its solubility parameters and that of the oil. M. V. Duin et al. grafted EPDM rubber with maleic anhydride to acquire it some polarity to resist oils [13]. Blending of EPDM/ NBR rubbers will lead to rubbery goods which withstand for both thermal aging and swelling in oils. The problem which may be arise here is, that this blend is consisting of two incompatible rubbers due to the marked differences in their polarities. The drawback of such incompatible blend is attributed to the differences in chemical affinities of the curing ingredients towards the two phases which are generated in the incompatible blend [14, 15]. The migration of either sulphur or accelerators towards a definite phase of the rubber blend influences the crosslinking density of this phase which in turn affects the carbon black existence. Effect of carbon black loading to EPDM/ NBR blend had been studied by V. Jovanovic et al. [16]. Also, the effect of white fillers like kaolin or silica were studied [17]. Consequently, a distinct different reinforcing distribution across the rubber blends takes place [18]. The first challenge of this work is to find an efficient compatibilizer for this blend, in a previous work, it was found that the use of small amounts of maleated EPDM as a compatibilizer for EPDM/ NBR blend produced compatible blend, also using of bromobutyl rubber enhanced the compatibility of this blend [19, 20]. L. I. Kraf tofi et al. investigated that compatibilization between EPDM and styrene acrylonitrile (SAN) was achieved by reactive extrusion, at which a compatibilizer EPDM- g- SAN is formed in situ [21]. The second challenge is to present a single additive which provides multiple functions, to abbreviate the number of additives which must be added to formulate a rubber compound. Moreover, the product must be characterized by its availability with low cost. The use of efficient compatibilizer reflects improve in mechanical properties. Investigation of the compatibility effectiveness is carried out using different tools such as microthermal analysis [22]. The current work aims to study the synthesized aminated epoxy oil to be used as a compatibilizer for EPDM/ NBR rubber blend, in addition to its activity as antioxidant and plasticizing agent.

**Materials and Experimental techniques**

**Materials**

EPDM; Dutral Ter447, propylene content 41, Mooney viscosity ML (1+4) 125°C 60-66, total ash (550 +20 °C) 0.5 % max, volatile matter(105+2 °C 0.1 % max, Versalis, S.P.A. NBR; Krynac 33/45, Mooney viscosity (1+4) 100 °C 45, Bayer Chemicals, Germany. Epoxidized oil; Paints and Pigments.

**Authors**

M. L. Tawfic, A. I. Hussein, Dokki, Cairo, Egypt

Corresponding author: M. L. Tawfic
Polymer and Pigments Department
National Research Center
Dokki, Cairo, Egypt
Tel: +20 2 01005007323
Fax: + 20 2 33371728
E-mail: medhat_lotfy2000@yahoo.com
Chemical Industries, Egypt. N- methyl-p-phenylene diamine, Across Organics. Mercapto-benzothiazol (MBT); creamy colored powder, ash content 0.5 % max., Zengzhou Welcome, China. Methanol; ElNasr company (ADWIC), Egypt. Tetramethyl thiuram disulphide (TMTD); Zengzhou Welcome, China. Antioxidant Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), Zhengzhou Double Vigour Chemical Product Co., Ltd China. Carbon black (HAF); Amerya Company for carbon black, Egypt. All the following ingredients were of technical grade, Zinc oxide, Sulphur and Paraffinic oil.

Experimental techniques:

**Synthesis of N- methyl-p-phenylene diamine and epoxidized oil adduct**

In a two-necked round bottom flask, equipped with a mechanical stirrer and nitrogen gas purging, 100 ml of epoxidized oil was added with 5 gm N-methyl-p-phenylene diamine. The reaction was carried out in an oil bath at 180°C, for three hours. The produced adduct was recrystallized from methanol, to get rid of excess N-methyl-p-phenylene diamine. This adduct was then investigated by both FT-IR and 1H-NMR spectroscopy.

**Spectrometry and differential thermal analysis**

FT-IR was carried out using Nexus 670 FT-IR spectrophotometer, Nicolet, USA, with resolution 4 cm⁻¹ ranging from 4000 to 200 cm⁻¹.

1H-NMR spectroscopy was performed on a JEOL ECA-500 NMR instrument (Akashima, Japan) at 500 MHz with tetramethylsilane as the internal reference for 1H-NMR spectra. The samples were dissolved in deuterated chloroform.

The glass transition temperature was evaluated on a Perkin Elmer differential scanning calorimeter (DSC), using about 20 mg of the samples. The samples were cooled down to -100°C, and then heating was done with a rate of 5°C/min. under nitrogen atmosphere. This test was carried out on unfilled samples and in absence of both activators and curatives.

**Mixing, vulcanizing, and testing of rubbers**

An open two-roll mill of 170 mm diameter and 300 mm working distance, 24 rpm speed of slow roll and 1 : 1.25 gear ratio, was used to prepare rubber mixes. The rheological characteristics were assessed by using a Monsanto Oscillating Disc Rheometer R-100, at 152+1°C, according to ASTM D2084-95. The rubber blends were vulcanized at their optimum cure times (t90) by the aid of a hydraulic hot press at the same temperature. The physico-mechanical properties were measured using Zwick-1425 tensile tester according to ASTM D412-98a. Accelerated thermal aging was carried out at 90°C for different periods up to 7 days, according to ASTM D573-88.

**Scanning electron microscopy (SEM)**

Scanning electron microscopy (SEM) was done using (JXA-840A) electron probe micro-analyzer Japan JOEL. Rubber specimens were cut under liquid nitrogen; the cross-section surface was covered with a very thin layer of gold to avoid electrostatic charging during examination. The examined samples were the gum rubber blends 50/50 EPDM/ NBR without any additive and in presence of 5, 7.5 and 10 phr (Am –Ep).

3. Results and discussion

**Elucidation of the structure of (Am-Ep) adduct**

Fig.1a, 1b show the FT-IR spectra of both epoxidized oil (spectrum a) and N-methyl-p-phenylene diamine adduct with
epoxidized oil (Am-Ep). It is obvious from spectrum (b) that upon amination of the epoxidized oil, new peaks appear at 1630, 3300 and 3500 cm\(^{-1}\). These peaks are characteristic for the imine groups which are generated via the addition reaction to the oxirane rings of the epoxidized oil.

Fig. 2: exhibits \(^1\text{HNMR}\) of both epoxidized oil, spectrum(a) and its aminated form, the doublet signal in spectrum (b) at 7.15 ppm characterizes the aromatic protons of the produced (Am-Ep) adduct, while the singlet signal at 3.45 ppm characterizes the proton of the hydroxyl group, which was generated upon opening of the oxirane ring in the epoxidized oil. Consequently, the possible reaction pathway may be represented as shown in scheme (1).

**Determination of the optimum ratio of the compatibilizer**

In order to investigate the optimum amount of (Am-Ep) which must be added to achieve efficient compatibilization, blending of 50/50 EPDM/NBR rubbers were carried out in presence of 2.5, 5, 7.5 and 10 phr of the adduct in absence of fillers. These unfilled blends were cured and molded using the same activator and curing system which are listed in table 1.

The tensile strengths of these unfilled blends of EPDM/NBR, versus the amounts added of (Am-Ep) are illustrated in fig. 3. It is clearly seen that the tensile strength of the blend increases gradually by increasing the amount of the adduct. The use of 7.5phr (Am-Ep) shows the highest value of tensile strength. On the other hand, the addition of 10 phr of the adduct decreases the tensile strength. It is concluded that the ratio 7.5 phr is the most efficient for achieving compatibility between the two rubbers under investigation. Consequently, this study is focusing on confirming the performance of this ratio of (Am-Ep) as a compatibilizer for EPDM/NBR beside its activity as both antioxidant and plasticizer.

**Investigation of EPDM/NBR Compatabilization**

Fig. 4 a-d: show SEM of the blend under investigation in absence of (Am-Ep) and in presence of 5, 7.5 and 10 phr of (Am-Ep) respectively. It is clearly seen that the domains size are large without using any compatibilizer. Upon using 5 phr (Am-Ep) the domain size decreases and almost totally disappeared by using 7.5 phr. On the other hand, the use of 10phr adduct makes the domains to be appeared again as shown in fig.4d. The explanation of this observation may be due to the fact that, compatibilization performance is governed by the location of the compatibilizer at the interface between the two polymers to reduce the interfacial tension [23], so that the non-polar moiety (Tail) of the compatibilizer is oriented towards the lower polarity polymer, whereas the polar moiety (Head) is oriented towards the higher polarity polymer. Furthermore, the amount of the compatibilizer must be enough to cover the interface region. It is seen that using 7.5 phr satisfies the aforementioned requirements. Using of 10 phr may lead to an excess of the compatibilizer than the required amount to cover the interface, this excess are located tail to tail or head to head and lead to phase inversion [24] and consequently to agglomerate of one rubber into another and new domains appear again. This result confirms the activity of 7.5 phr (Am-Ep) as optimum concentration as compatibilizer.

Further confirmation for the compatibilization activity of (Am-Ep) is estimated from DSC results of the 50/50 rubber in absence and in presence of 2.5, 5 and 7.5 phr (Am-Ep), as shown in fig. 5 a-d. It is well known that for two different rubbers to be thermodynamically miscible, they must have one glass transition temperature (Tg). It is noticed from the aforementioned figure that the difference between the glass transi-

---

**Tab. 1: Formulations and rheometric characteristics and mechanical properties of the prepared EPDM/NBR rubber blends**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>–</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NBR</td>
<td>50</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Am-Ep</td>
<td>7.5</td>
<td>–</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Paraffinic oil</td>
<td>–</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>TMQ antioxidant</td>
<td>–</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Rheometric characteristics at 152 +1°C**

<table>
<thead>
<tr>
<th></th>
<th>Min., torque (ML), dNm</th>
<th>Max., torque (MH), dNm</th>
<th>Scorch time, (t(_s)), min</th>
<th>Optimum cure time, (t(_c)), min.</th>
<th>Cure rate index, (CRI), min(^{-1})</th>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>9</td>
<td>10</td>
<td>10</td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>86</td>
<td>75</td>
<td>68</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.2</td>
<td>3.5</td>
<td>3.5</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>11.5</td>
<td>14.5</td>
<td>15.1</td>
<td>8.5</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>9.7</td>
<td>9.1</td>
<td>8.6</td>
<td>14.3</td>
<td>6.8</td>
</tr>
</tbody>
</table>

**Zinc oxide 3phr, Carbon black (HAF) 40 phr, Stearic acid 2 phr, MBTS 1.2 phr, TMTD 0.6 phr, Sulphur 2.5 phr**

---

**Fig. 3: The tensile strength, MPa, of the unfilled 50/50 EPDM/NBR versus the amounts added phr of Am-Ep.**
tion temperatures of the parent rubbers is 39 °C, this difference does not change upon using 2.5 phr of the adduct. By increasing the ratio of (Am-Ep) up to 5 phr the difference between the glass transition temperatures decreases to 22 °C. In case of adding 7.5 phr adduct, one glass transition point (-37 °C) is obtained. This result is attributed to the formation of one phase of the two rubbers in the blend.

**Determination of the mechanical properties**

The ultimate advantage of using compatible blends is to obtain more enhanced properties than each of the individual rubbers participating in the blend. Table 1: lists the different formulations and the rheometric characteristics of the rubber blends and the two individual rubbers under investigation either in presence or in absence of 7.5 phr (Am-Ep). It can be seen from this table that the optimum cure time ($t_{	ext{opt}}$) of the blend in presence of the given ratio of (Am-Ep) is lower than that of the blend in absence of it, whereas the scorch time of the former ($t_{	ext{sc}}$) is higher than that of the latter. Therefore, it is concluded that (Am-Ep) has an accelerating and anti-scorching effects. Fig. 6: illustrates the tensile strength at break (MPa) against thermal aging time (day) of the two individual rubbers EPDM and NBR and their 50/50 blends, in absence and in presence of 7.5 phr (Am-Ep). It is obvious that the lowest tensile strengths are given by EPDM / NBR vulcanize, this result can be attributed to the formation of two separate phases in the blend at which the chemical affinities of the the curing agents and the accelerator are different. The highest values of tensile strength are exhibited by NBR vulcanize, while EPDM vulcanize shows moderate values these results are due to that NBR rubber has more unsaturated double bonds available for vulcanization than EPDM. On the other hand, upon blending EPDM/NBR (50/50) using 7.5 phr of (Am-Ep), the tensile strength increases gradually till it reaches a steady state of thermal aging stability after two days of aging and the tensile strength values tend to be close to those values of NBR vulcanize rather than the lower values of EPDM vulcanize. The obtained results are seen to be greater than the values which may be obtained by the additively rule. On the other hand, these values are higher than those for the blend under investigation.

**Fig. 4:** Scanning electron microscope (SEM) of 50/50 EPDM/ NBR (a) in absence of Am-Ep, (b) in presence of 5 phr Am-Ep, (c) in presence of 7.5 phr Am-Ep and (d) in presence of 10 phr Am-Ep.

**Fig. 5:** Differential scanning calorimetric (DSC) of the 50/50 EPDM/NBR rubber blend, (a) without Am Ep, (b) with 2.5 phr Am-Ep, (c) with 5 phr Am-Ep and (d) with 7.5 phr Am-Ep.

**Fig. 6:** Tensile strength at break in MPa, versus thermal aging time, day, of the two individual rubbers EPDM and NBR and their 50/50 blends both in absence and in presence of 7.5 phr Am-Ep.
in absence of (Am-Ep), it means that synergistic state is obtained. Furthermore, NBR vulcanizate in presence of 7.5 phr (Am-Ep) shows low values of tensile strength and even lower than EPDM in presence of 7.5 phr (Am-Ep). This last observation is due to that the prepared adduct is polar and may have solubility parameter close to that of NBR, which in turn facilitates its mixing and leads to more plasticization of this rubber.

As shown in fig. 7: the elongation at break of the blend in presence of (Am-Ep) and in absence of paraffinic oil exhibits nearly the same elongation at break (235%) as in case of the blend in presence of paraffinic oil and in absence of (Am-Ep) (275%). Furthermore, more steady state of thermal aging stability of the compatibilized blend is observed, where the loss of elongation at break of it after aging for 7 days is 11% whereas the corresponding loss in case of uncompatibilized blend is 15%, this latter observation confirms the activity of the prepared (Am-Ep) adduct as both antioxidant and plasticizer at the same time.

**Conclusion:**

The reaction of epoxy oil with N- methyl -p- phenylene diamine results in an adduct, where its structure is confirmed by spectrometric tools such as FT-IR and 1HNMR. The optimum amount of the adduct is estimated from measuring the tensile strength of the unfilled EPDM/NBR blend (50/50). Using 7.5 phr of (Am-Ep) adduct, as the optimum amount, in EPDM/ NBR rubber blend enhances its compatibility, as investigated by both SEM and DSC. The thermal stability beside the mechanical properties of the blend are improved. The synthesized adduct acts as multifunction agent. These functions are compatibilization, acceleration, anti-scorching, anti-oxidation and plasticization.

**References**