Effect of Nanoclay on EPDM Composites under Gamma Irradiation

Samaa. A. Wasfy¹, Elham M. Hegazi¹, A.A. Abd El-megeed², T. S. Mahmoud³ and E.Y. El-Kady ³

¹Nuclear & Radiological Regulatory Authority, Cairo, Egypt
²National Institute for Standards, Cairo, Egypt
³Shobra Faculty of Engineering, Benha University

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ABSTRACT

The polymers used for the insulation and jacket materials for electric cables are susceptible to degradation mechanisms caused by exposure to many of the stressors encountered in nuclear power plant service environments. Ethylene propylene diene monomer rubber (EPDM) is the most common type of polymer used in cables insulations used in NPP. In order to improve the EPDM insulation rubber performance, many additives can be added to the EPDM compounds. Nanoclay is selected to improve the resistance of EPDM rubber against gamma irradiation up to 600KGY. The effect of different concentration of nanoclay on the mechanical and physical properties of the EPDM rubber is investigated. The physical and mechanical properties of the EPDM rubber compounds were evaluated by measuring swelling ratio, crosslinking density, tensile strength, elongation at break and hardness. The results of the present study show that the addition of Nanoclay as an additive improves the physical and mechanical performance of EPDM.

Keywords: EPDM, Nanoclay, Gamma ray

INTRODUCTION

The polymers used for the insulation and jacket materials for electric cables, cable splices, and terminations are susceptible to aging and degradation mechanisms caused by exposure to many of the stressors encountered in nuclear power plant service environments. Longer cable circuits may pass through several different operating environments over the length of their routing throughout the plant. Portions of a cable circuit may pass through areas experiencing more harsh environmental conditions, such as high temperature, high radiation, high humidity, or flooding of underground cables. There has been a concern that such local adverse environmental stressors can cause excessive aging and degradation in the exposed sections of a cable that could significantly shorten its effective service life and cause unexpected early failures.

Insulation is a material having good dielectric properties used on wire components in cables usually as direct covering on conductors. Insulation selection is determined by a number of factors such as stability and long life, dielectric properties, resistance to high temperature, resistance to moisture, mechanical strength and flexibility. It is necessary to select a cable with the type of insulation that fully meets the requirements of the application.

Insulation and jacket materials, used in electrical cables, are based on polymeric materials combined with a number of additives and fillers to provide the required mechanical, electrical and thermal properties. The most commonly used insulation materials are XLPE, EPR/EPDM and PVC. For example, in NPPs in the USA, XLPE and EPR/EPDM are the dominant insulations in cables. EPDM is the most common type of polymer used in cables insulations used in NPPs.
Recently, using nanoclay in polymer nanocomposites attracts a great interest, both in industry and academia, since it is possible to achieve remarkable property enhancements as compared to pure polymer or conventional microcomposites. These improvements include increasing strength and heat resistance, decreasing gas permeability and flammability, and increasing biodegradability of biodegradable polymers\(^{(7,8,9)}\).

The effect of gamma irradiation on the properties of EPDM with nanoclay as an additive was studied, the experimental data showed that the gamma irradiation has a strong influence on the properties of EPDM/clay nanocomposite, EPDM conventional composite, and unfilled EPDM\(^{(10)}\).

EPDM possesses an excellent mechanical strength and tracking resistance and it is a comparatively lower cost material. Blending of polymers has gained a considerable importance for achieving property improvement and economic advantages. Inorganic fillers have a major role in the improvement of the desired electrical and mechanical properties of polymers\(^{(11,12)}\).

EPDM nanocomposites were developed with varying proportions of nanoclay. The effects of nanoclay content on physical and mechanical, properties have been investigated. The results obtained for mechanical properties showed a significant improvement in tensile strength and elongation at break of nanocomposites. The experimental results showed that the EPDM nanocomposite could be a better candidate for electrical insulators due its enhanced physical and mechanical characteristics.

### EXPERIMENTAL

#### 1. Materials

Materials used in this work are commercial grade of EPDM (ethylene-propylene rubber; Herlene, grade HS63) manufactured by Unimers India Limited (in collaboration with Uniroyal Chemical Co., USA). The additives used are nanoclay, surface modified, contains 25-30 wt. % methyl dihydroxy-ethyl hydrogenated tallow ammonium (Montmorillonite clay, Nanomer 1.34MN, SIGMA-ALDRICH, Co., USA, and ATH(Aluminum Hydroxide Al(OH)\(_3\), Oxford Laboratory). Other rubber additives such as stearic acid, zinc oxide, processing oil, antioxidant, and sulfur were of commercial grades, and purchased from El Nasr Pharmaceutical Chemicals Co. Cairo, Egypt.

#### 2. Preparation of samples and irradiation

EPDM rubber samples are mixed with different amounts of Nanoclay the compounding recipe is given in Table 1. The mixing of the rubber is carried out on a laboratory two-roll mill (Farrel-UK,152 mm and 330 mm) at a friction ratio of 1:1.4, according to ASTM D3182\(^{(13)}\). The Oscillating Disk Rheometer (Alpha-UK, MDR 2000) measures the complete curing characteristics of an elastomer compound. Samples of about 5 g were cut from a milled sheet and placed in the rheometer, at a specified temperature according to ASTM D-2084\(^{(14)}\), at 160°C for EPDM compounds. The samples were vulcanized in a hydraulic press (Farrel-UK) at 160°C and pressure of 150 kg/cm\(^2\) for a period of 4.5 min for EPDM compounds. Gamma irradiation of the EPDM compounds was carried out at a rate of 2 KGy/h using the C\(^{60}\) source at the Canadian Gamma Cell (Ge 220) located at the National Center for Radiation Research and Technology (NCRRT).

#### 3. Swelling measurements

Swelling experiment procedure according to ASTM D-471\(^{(15)}\) is carried out by immersing three circular samples cut from the rubber sheets with 5-mm diameter and 2-mm thick in toluene solvent for 48 h to reach equilibrium at room temperature. The swelling ratio, Q(t)\(^{\%}\), of the EPDM rubber in the solvent was calculated by the equation:

\[
Q(t)\% = \frac{M_t - M_i}{M_i} \times 100
\]

Where \(M_i\) is the initial weight of the sample, \(M_t\) is the weight of the swollen sample.
Table (1): List of all ingredients of the mixture

<table>
<thead>
<tr>
<th>Ingredients (phr)</th>
<th>N0</th>
<th>N3</th>
<th>N5</th>
<th>N7</th>
<th>N10</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Oil</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>MBTS b</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>6PPD c</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CaC3e</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>ATH f</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Nanoclay</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>10</td>
</tr>
</tbody>
</table>

a Part per hundred part by weight of rubber
b MBTS Dibenthiazyl Disulfide
c 6PPD N-(1, 3-dimethylbutyl)-N’-phenyl-p-phenylene diamine
d CaC3 calcium carbonate
e ATH aluminum tri hydroxide

Table (2): Vulcanization Parameters for EPDM samples with deferent Nanoclay additive

<table>
<thead>
<tr>
<th>property</th>
<th>N0</th>
<th>N3</th>
<th>N5</th>
<th>N7</th>
<th>N10</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML (Lb. in)1</td>
<td>1.25</td>
<td>1.15</td>
<td>1.17</td>
<td>1.24</td>
<td>1.51</td>
</tr>
<tr>
<td>MH (Lb. in)2</td>
<td>7.87</td>
<td>8.06</td>
<td>8.28</td>
<td>7.79</td>
<td>8.41</td>
</tr>
<tr>
<td>Ts2 (min)3</td>
<td>3.23</td>
<td>2.75</td>
<td>2.72</td>
<td>3.12</td>
<td>2.98</td>
</tr>
<tr>
<td>Tc90 (min)4</td>
<td>14.78</td>
<td>14.15</td>
<td>14.7</td>
<td>14.92</td>
<td>15.12</td>
</tr>
<tr>
<td>CRI (min-1)5</td>
<td>8.66</td>
<td>8.77</td>
<td>8.34</td>
<td>8.48</td>
<td>8.24</td>
</tr>
</tbody>
</table>

1 ML minimum torque 2 MH maximum torque 3 Ts2 Scorch Time 4 Tc90 Time of 90% cure 5 CRI cure rate index

4. Crosslinking measurements

The most important changes of gamma irradiation effect in rubber is crosslinking (intermolecular bonds), and degradation (the scission of bonds in the main polymer chain and inside chains). The number of the formed crosslinks is proportional to the dose rate. The crosslinking, \( \nu_c \), of the EPDM rubber compounds was calculated by the equation:

\[
\nu_c = \rho_r N/M_c \tag{2}
\]

Where \( \rho_r \) is the density of the rubber

\( N \) is Avogadro’s number = 6.02214179 \times 10^{23} \text{ mol}^{-1}

\( M_c \) is the average molecular weight between crosslinks of rubber and it can be calculated according to the theory of Flory and Rehner \(^{(16)}\) by:

\[
M_c = -V_1 \rho_r \left\{ \Phi_r^{16} - \Phi_r^{12} \right\} / \left\{ \ln \left( 1 - \Phi_r \right) + \Phi_r + \mu \Phi_r^2 \right\} \tag{3}
\]

where \( V_1 \) is the molar volume for toluene = 106.3 cm\( ^3 \)/mole

\( \Phi_r \) is the volume fraction of polymer and it can be determined from the equilibrium degree of swelling \( Q_m \) as follows:

\[
Q_m = 1/\Phi_r = 1 + \{M_S \rho_r / M_T \rho_S \} \tag{4}
\]

Where \( M_T \) and \( M_S \) are the weights of the dried rubber and absorbed solvent, respectively, also, \( \rho_r \) and \( \rho_s \) are the densities of the solvent used and the rubber compound, respectively.
\( \mu \) is the Huggins (17) interaction parameter between solvent and polymer and it can be calculated as follows:

\[
\mu = \left( \delta_s - \delta_r \right)^2 V_1 / RT
\]

(5)

Where \( \delta_s \) and \( \delta_r \) are the solubility parameters of the solvent and rubber compounds respectively.

R is the Universal gas constant = 8.314 J·K\(^{-1}\)·mol\(^{-1}\)

T is the absolute temperature.

5. Mechanical tests

The tensile strength and elongation at break are measured by using a Zwick (Germany) Tensile Testing Machine (Model Z010) and a crosshead speed of 500 mm/min using five dumb-bell tensile specimens being shaped according to ASTM D-412(18). The hardness test is measured by a Shore Hardness Tester Machine (TH200) according to ASTM D-2240(19).

RESULTS AND DISCUSSION

A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Fillers are employed to improve the desired properties of the polymer or simply reduce the cost. Polymer composites with improved mechanical, thermal, barrier and fire retardancy properties are widely used in very large quantities in variety of applications. (20) Development of polymer nanocomposites is an interesting area in advanced research because of its capability of providing improved mechanical, thermal and electrical properties. The main application areas of polymer nanocomposites are aerospace, automotive, electrical, electronics and consumer products etc. The commonly used polymeric materials for electrical insulators are ethylene propylene rubber, ethylene propylene diene monomer rubber (EPDM), silicone rubbers etc. (21)

1. Swelling properties

Fig. (1) shows EPDM/ nanoclay compounds (N0, N3, N5, N7, and N10) at different gamma doses. Fig. (1) shows that the swelling ratio generally decreases with increasing gamma doses. However, the present results show that N0 (EPDM without nanoclay) have the lowest value of swelling ratio while N5 (EPDM with 5phr Nanoclay), and N7 (EPDM with 7phr Nanoclay) have the highest value. The other two studied rubber compounds: N3 (EPDM with 3phr Nanoclay) and N10 (EPDM with 10phr nanoclay) have nearly similar values.

Fig. (2) shows the effect of gamma rays on the crosslinking density of EPDM rubbers with different amount of nanoclay. The results of crosslinking density measurement of EPDM rubber showed that there is an increase in the crosslinking with increasing gamma doses. All rubbers suffer modifications at their properties at exposure to gamma doses, a loss of their mechanical properties is obtained. The results show that EPDM rubber with 5, and 7 phr of nanoclay have lower values of crosslinking density, while N0 (EPDM without nanoclay) has the highest value. This means that nanoclay plays a good role in protecting the rubbers against gamma irradiation.
Determination of the swelling ratio of the radiation vulcanized EPDM rubber was carried out and their results are shown in Fig. (1). The results of swelling have already recognized that the restriction of swelling is related to the different amounts of nanoclay and the gamma doses. From the results, all the EPDM rubber samples with different amounts of nanoclay have high swelling ratios at lower doses up to 200 KGY and it decreases with increasing in the doses up to 600 KGY. This change is due to the crosslinking density. The most important effect of gamma irradiation on rubber is crosslinking (intermolecular bonds), and/or degradation (the scission of bonds in the rubber chains). It can be observed that the EPDM compounds swelled more at low doses and the swelling ratio decreases with increasing gamma doses. The crosslinking density of rubber compounds increased as gamma doses increased as can be observed in Fig. (2). The present results showed that EPDM rubber with different amounts of nanoclay (5, and 7phr) has lower values of crosslinking density and this means that the addition of nanoclay has a good effect on protecting the rubbers against gamma irradiation.

2. Mechanical properties

Fig. (3) shows the effect of gamma irradiation doses on tensile strength of different samples of EPDM rubber with different amounts of nanoclay. The figure reveals that N0 has the highest value, while N5 and N7 have the lowest values up to 200 KGY. Then all the other samples have similar values.

Fig (1): Effect of gamma doses on swelling ratio of EPDM samples with different amounts of nanoclay

Fig (2): Effect of gamma doses on crosslinking density of EPDM samples with different amounts of nanoclay
Fig. (3): Effect of gamma doses on tensile strength of EPDM samples with different amounts of nanoclay

Fig. (4): Effect of gamma doses on elongation at break of EPDM samples with different amounts of nanoclay

Fig. (4) shows the effect of gamma irradiation dose on the elongation at break (Eb) of different samples of EPDM rubber with different amount of Nanoclay. Without exposure to gamma irradiation the Eb values show the minimum value for N0 and the maximum value for N3. Eb values for all rubber compounds decrease with increasing the γ-doses until 600 KGy. The elongation at break decreased with dose increasing for all samples due to more crosslinked structures produced in the sample matrix, which prevents the structural organization during drawing and brings about a decrease in the internal chain mobility and elongation (22). This observation is further supported by the explanation provided for the swelling ratio and crosslinking density behavior with high radiation dose discussed as mentioned above.

There is number of reports on the reduction of tensile strength by the addition of clay minerals (Alexandre & Dubois (23), Finnigan et al. (24)). Similar to modulus, any factor affecting the degree of intercalation/exfoliation has an impact on the tensile strength of nanocomposites. The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers. The stronger interfacial interaction causes an increase of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposites. Ultimate tensile stress is even much decreased compared to PP matrix and further drops down at higher filler content. This lack of strength properties can be attributed to the fact that only weak interactions exist at the poly(styrene)-clay interface contrary to the previous compositions in which (stronger) polar interactions may take place, strengthening the filler matrix interface (25). Norkhairunnisa et al. (26), reported that the decrease in flexural strength for above 2 wt% of clay may be due to the agglomeration of clay in the resin which acts as stress concentrators and leads to the reduction of flexural strength.
Kusmono et al.(27), reported that the intercalated structure or agglomerated clay particles that occurred for the epoxy nanocomposites with high clay content (above 3 wt%) was believed to be responsible for the decrease in tensile strength. This intercalation structure leads to low aspect ratio of clay platelets and low contact surface area, resulting in weak adhesion between polymer matrix and clay, which subsequently leads to lowering their tensile strength. In addition, this behavior was probably attributed to the filler-filler interaction which resulted in agglomerates.

3. Hardness properties

Shore A Hardness measurement is the most common instruments used for rubber and elastomer hardness characterization(28). The measurement of changes in the hardness of materials can provide important measurement about the effects of gamma irradiation on the rubber material. Fig.( 5) shows the effect of $\gamma$-doses on hardness of EPDM samples with different amounts of nanoclay. From the figure, N0 has the highest value; while N5 and N7 have the lowest values up to 400 KGY then all samples almost have the same values. The present results showed that the hardness increased with increasing $\gamma$-doses for all EPDM compounds as a result of the increase in the crosslinking density of the rubber.

![Fig (5): Effect of gamma doses on hardness of EPDM samples with different amounts of nanoclay](image)

CONCLUSIONS

In the present study, nanoclay additives are selected to study their effect on the physical and mechanical properties of EPDM rubber samples under gamma radiation up to 600 KGY. From the present results it can be concluded that the addition of nanoclay to the EPDM rubber plays a good role in the protection of the insulation rubber against gamma radiation up to 600KGY as improving their mechanical properties. EPDM with 5, and 7phr of nanoclay showed the best physical and mechanical properties compared with the other samples. It can be concluded that nanoclay is a good additive represents a good protective material for the EPDM rubber at gamma radiation.

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