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New Thermoplastic Ionic Elastomers Based on MA-g-EPDM with Advanced Characteristics

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1. Introduction

Ionic thermoplastic elastomers or ionomers are copolymers involving a major non-polar constituent (which can be crystallized or not) and a minor ionizable constituent, partly or entirely neutralized with mono- and divalent inorganic ions as a salt at a concentration not exceeding 10 mol % (Andrei & Dobrescu, 1987; Stelescu, 2011).

In order to obtain ionic thermoplastic elastomers, one or more of the techniques listed below can be used:

a. Synthesis of elastomers containing ionizable monomers or just preparing the thermoplastic ionic elastomers on the same equipment where polymerization, copolymerization or polycondensation of the basic monomers in the polymer chain are performed, but adding small amounts (5-7%) of other monomers resulting in ionic or ionizable groups in the polymer chain.

b. Converting chemically some elastomers containing double bonds in their macromolecules.

c. Processing elastomers containing ionizable groups with metal salts, metal alkali or metal oxides which can react with the functional groups in the ionizable groups, thus yielding ionic ranges; fillers, ionic plasticizers, polyolefins, antioxidants etc. can be also added in order to obtain ionic thermoplastic elastomer compounds with a large variety of applications depending on their composition (Zuga, 2005).

The ionic elastomer compounds resemble highly with the traditional rubber compounds but there are some differences. Because the former are thermoplastics, there is no curing stage and, therefore, no sulfur and vulcanization accelerators or peroxides are added. Another significant difference is the use of an ionizing agent - ionic plasticizer in preparing ionic thermoplastic elastomers. It plays the role of promoting the ionic break-up of the ionic interactions at high temperatures to enable the shearing flow of the compound; at room

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temperature it behaves like a filler. Zinc stearate is the most largely used ionic plasticizer but some others can be also used, like calcium stearate, zinc acetate, stearamide (Nahmias & Marco Serra, 2002; Zuga et al., 2009; Stelescu et al., 2011).

A formulation of ionic thermoplastic elastomer compound consists generally of a neutralized ionomer, ionic plasticizer, non-ionic plasticizer, filler, antioxidants, other polymers, etc. (Zuga & Cincu, 2006a). A significant increase of vitrifying point by incorporating ions into polymers was proved (Eisenberg, 1977). This increase depends on the nature of the basic ion, the effect being stronger as the ionic forces are larger. They have also shown that the nature of the basic ion influences not only the value of $T_g$ (glass transition temperature), but also the position and shape of the module – temperature curve. The increase of ion content leads to an increase of the module and the increase of the specific plateau of vulcanized rubber.

An important contribution to establishing the relation between properties and the ion content in ionomers has been brought by research on carboxylated elastomers. Ionomer-rubbers have remarkable properties such as: high module, large elongation at break and a constant plateau in the module – temperature curve. This constant plateau can be explained through the presence of a small concentration of stable interchain bonds, called multiplets. Elongation at break has been attributed to the loosening of ionic bonds by exchange reactions between crosslinking bridges of various chains, thus hindering an excessive strain. Finally, due to the presence of ionic aggregates which may act as “filling materials”, of reinforcement and of quasi-crosslinking, the initial high module of materials can be explained.

Rheological studies on ionomers in melt (Szymczyk & Roslaniec, 1999) have highlighted a remarkably large increase of melt viscosity, as a result of introducing ions into polymers. This increase depends on the ion concentration or on the neutralization degree and less on the nature of ions. Also, the non-Newtonian character of ionomers in melt is noticed, probably due to the fact that the movement of chain segments and chains implies dissociation of ion pairs in cluster aggregates. This dissociation certainly has a determining influence on rheological properties in melt. In partially neutralized ionomers, hydrogen bonds between the carboxyl functional groups may also have a significant effect on flow properties.

There are a few studies (Zuga & Cincu, 2006b, 2006c; Datta & Kharagpur, 1997; Paeglis & O’Shea, 1988) on ionomers based on maleated and/or sulphonate EPDM rubber indicating the fact that, by introducing neutralization agents (zinc oxide, sodium hydroxide etc.) when a metal base is obtained, modifications of physico-mechanical properties which take place in system are assumed to be due to the rigid phase resulted from the restriction of chain mobility in the ionic aggregate area and a reduction of crystallinity compared to that existing in the initial elastomer is noticed (Stelescu, 2010).

This review gives an overview about our research on ionic thermoplastic elastomers based on maleated ethylene propylene diene terpolymer (EPDM-g-MA). The investigations were aimed to obtain some new generations of ionic thermoplastic elastomers with high technical and processing characteristics intended to be processed on the injection moulding machines, resulting in high quality products complying with the international market requirements. Two types of maleated ethylene propylene terpolymer elastomers (EPDM-g-MA) with various levels (0.5 and 1.0 %) of maleic anhydride were used. The EPDM-g-MA rubbers were modified by neutralizing them with zinc oxide and stearic acid, and then the ionomer
has been converted into a thermoplastic ionic elastomer by adding various percentages of ionic plasticizer to the blend. The behaviour of the thermoplastic ionic elastomers resulted by adding fillers like as precipitated silica and carbon black in various percentages was assessed. The extent of the neutralization agent, ionic and non-ionic plasticizers, filler, polyolefin’s which influence the characteristics of the resulting products was determined with the purpose of selecting the best types of ionic thermoplastic elastomer based on EPDM-g-AM. All the laboratory prepared compounds were tested for the physico-mechanical characteristics; based on the results, three thermoplastic ionic elastomers with the best characteristics were selected and the applications of these were set up.

To obtain better characteristics, the creation of nanocomposites from a selected EPDM-g-AM compound and organically modified montmorillonite clay (OMMT) was targeted. Nanocomposites based on maleated ethylene propylene diene terpolymer and organically modified montmorillonite (OMMT) has been prepared by melt intercalation procedure. The materials were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC) and mechanical tests. XRD data show the increase of the distance between the silicate layers indicating the intercalation of polymer chains in the montmorillonite galleries. The incorporation of OMMT in composites determines the increase of melting peak temperature (Tm) and heat of fusion (ΔHf) suggesting a supplementary nucleation increase due to the OMMT presence. The mechanical properties were analyzed as a function of the OMMT level in the composite and the results reveal remarkable improvement relative to the conventional composite.

Ionic thermoplastic elastomer compounds can be used in many applications such as: to manufacture a wide range of consumer goods (hoses, soles etc), as modifier for other materials, to make adhesives, to obtain impermeable flexible thin membranes such as cover membranes etc. (Swapan et al., 2001; Zhao-Hua et al., 2002; Einsenbach et al., 1998; Piere, 2002; Ronatti, 1990; Nachmias & Sera, 2002).

The new types of thermoplastic elastomers can be processed by specific techniques for thermoplastic materials, thus removing the vulcanization stage involving high power expenditure and release of noxious products, improved characteristics (higher values for elasticity, ageing resistance, abrasive resistance, acid and alkali fastness) of these materials can be assured.

The potential users of the new rubber materials will be economic operators processing rubber and plastics, footwear and car component manufactures etc. They can be used in the manufacture of a large range of products like as hoses, gaskets, rubber shoes, protective equipment etc.

2. Preparation

Ionic thermoplastic elastomers can be obtained by processing of ethylene propylene diene elastomers (EPDM) grafted with maleic anhydride (EPDM-g-MA) having different contents of maleic anhydride. The compositions of thermoplastic elastomers contain besides EPDM-g-MA the following elements: neutralizing agents of the ionic groups (zinc oxide in the presence of stearic acid), ionic plasticizers (zinc stearate), nonionic plasticizers (paraffin oil), fillers (precipitated silica, carbon black, chalk), polyolefins (high density polyethylene
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(HDPE), polyethylene grafted with maleic anhydride (PE-g-MA), polypropylene (PP), clays, antioxidants (Irganox 1010).

EPDM-g-MA elastomers exhibit the peculiar features of EPDM elastomers, but they can react with divalent metal oxides salts leading to the crosslinking by ionic bonds. The structure of EPDM-g-MA is shown in Fig. 1. The most used EPDM-g-MA elastomers contain 0.5% MA having semicrystalline structure and 1% MA with amorphous structure. The ionic plasticizer solvates the ionic domains at higher temperatures improving flow and at the room temperature it has the role of a filler.

Fig. 1. Chemical structure of EPDM-g-MA elastomers

In the compositions of thermoplastic elastomers, plasticizers assure the decrease of blend stiffness, suitable adherence, improvement of extruding, calendering or elongation, the decrease of freezing temperature of vulcanizates, the enhancing of ozone resistance and the price reducing. Due to their property to dissolve in rubber, the pasticizers get into the polymer chains diminishing the intermolecular interactions but in the same time new polymer plasticizer interaction appear in system.

The fillers are fine powder materials incorporated in blends in order to improve the composition properties (active fillers) and to reduce price (inactive fillers). The active fillers determine improving of some mechanical properties of elastomer composition namely tensile strength, shearing strength, abrasion resistance, repeated strain resistance.

Carbon black is a filler for many rubber materials having concomitantly the function of reinforcement, filling and coloring material. In rubber blends the particle sizes, structure and pH were affected by the carbon black content. Higher specific surface higher the break and tear resistance of the rubber. The increase specific surface leads to the energy consumption for mixing, rendering difficult the blend processing and the decrease of elasticity of the vulcanized products. The use of carbon black in rubber compositions provides a higher thermal and dimensional stability, increased hardness, enhanced thermal and electrical conductivities, better processing ability.

Polyolefins are utilized in elastomer compositions in order to improve tensile strength, tear strength, chemical reagent resistance.

Thermoplastic compositions were prepared by melt blending technique, on a laboratory electrically heated roller mill equipped with a cooling system. The process flow for the preparation of ionic thermoplastic elastomer compositions is shown in Fig. 2. After the raw materials were tested, the ingredients were weighed according to the processing formulations. The blend constituents were added in the following sequence: roll binding of maleated EPDM (and HDPE) (5-8 min), embedding zinc oxide, stearic acid and antioxidant
(2 min), introducing zinc stearate, paraffin oil and filler (5 min), homogenizing the blend and removing it from roll in 2 mm thick sheets (4 min). The working parameters were: friction 1:1.1 and temperature 150-170°C, for blends without polyolefins.

| No. | Ingredient                                      | Quantity (phr) |
|-----|------------------------------------------------|----------------|
| 1.  | EPDM-g-MA (Royaltuf 485, Royaltuf 498)         | 100            |
| 2.  | Zinc oxide                                     | 5-20           |
| 3.  | Stearic acid                                   | 0.5-2          |
| 4.  | Ionic plasticizer                              | 0-40           |
| 5.  | Nonionic plasticizer (Paraffin oil)            | 0-50           |
| 6.  | Filler (carbon black, precipitated silica, chalk)| 0-90          |
| 7.  | Polyolefins (PE, PP)                           | 0-160          |
| 8.  | Antioxidants (Irganox 1010)                    | 2.0            |

Table 1. Mix formulation of thermoplastic composition

Fig. 2. Laboratory processing stages for ionic thermoplastic elastomers
When the thermoplastic compositions are formulated the resulting compound characteristics depend on the quantity of ionic or nonionic plasticizer, neutralizing degree, the ratio elastomer/filler and filler type, the quantity and type of polyolefins.

A basic formulation for ionic thermoplastic elastomers contains the components from Tab. 1. The quantities from Tab. 1 are expressed in parts per hundred parts of rubber (phr).

The resulting blends were granulated on an extruder-granulator equipped with feeder hopper, screw with three heating zones, granulating device and rotary cutter. Feeding was done using materials under the form of strips with 2-3 mm thickness and 20-30 cm length, obtained as a result of blend homogenizing. The thermal regime of extruder-granulator in obtaining EPDM-g-MA rubber granules is presented in Tab. 2. The maleated EPDM-blend granules were then cooled and homogenized. The temperatures during granulation process are given in Tab. 3. Upon the granulation operation we must be sure that the keeping time of EPDM-g-MA rubber blend in extruder-granulator correspond to that required to achieve ionic crosslinking, determined using a rheometer (20 min).

| Types of ionic thermoplastic elastomer granules | Area 1 (°C) | Area 2 (°C) | Area 3 (°C) | Jet (°C) |
|-----------------------------------------------|-------------|-------------|-------------|---------|
| Blends without polyolefins                    | 145-155     | 160-170     | 145-155     | 150     |
| Blends with polyolefins                       | 150-180     | 160-190     | 150-170     | 160     |

Table 2. Thermal regime for obtaining EPDM-g-MA rubber granules

| No. | Heating zone in granulating machine | Temperature range (°C) |
|-----|------------------------------------|------------------------|
| 1.  | Pre-heating                        | 145-155                |
| 2.  | Blending                           | 160-170                |
| 3.  | Cooling                            | 145-155                |

Table 3. Process variables for granulation of thermoplastic ionic elastomer composition

The pellets needed to determine the physico-mechanical characteristics of resulting ionic thermoplastic elastomer compositions were obtained by injection moulding in a mould with two cavities using an electrically heated injection moulding machine. The test samples were prepared in the following stages: 1) electrical supply, adjusting the process temperature and bringing the machine up to the process temperature; 2) feeding the ionic thermoplastic elastomer pellets in feeder hopper; 3) heating the pellets up to 165-170°C within the injection machine screw; 4) injecting the melt composition in the mould; 5) cooling the plates for 3 min; 6) taking the plates off the mould.

Laboratory tests aim to measurements of tensile strength, tear strength, hardness, elasticity, melt flow index, abrasion resistance, flexion resistance, accelerated aging, etc.

3. Influence of the crosslinking degree on EPDM-g-MA ionic elastomer characteristics

In order to study the effect of neutralizing degree on the physico-mechanical properties of EPDM-g-MA rubber, zinc oxide was used as neutralization agent (Stelescu, 2010). Chemical structure of an EPDM-g-MA elastomer which subjected to the neutralization reaction with
zinc oxide is presented in Fig. 3, the resulting carboxylic salts can act as ionic crosslinkings (Setua & White, 1991).

Fig. 3. Schematic representation of ionic elastomers obtained by neutralization with zinc oxide

Analyzing physico-mechanical properties of blends based on EPDM-g-MA (Royaltuf 485 and 498 elastomers) with 0.5 % and 1.0% maleic anhydride, respectively, neutralized with zinc oxide the following are noticed:

Hardness of ionic thermoplastic composition shows an increase from 71 to 74 °ShA when introducing 5 phr of zinc oxide, while for composition with Royaltuf 498, hardness exhibits an increase from 55 to 66 °ShA, then further increasing of zinc oxide quantity does not lead to the improving of this property (Fig. 4). Elasticity has very good values especially in the case of Royaltuf 498 elastomer utilization (Fig. 5), but the elasticity practically does not increase to zinc oxide quantity increasing in blend, values of 60% being obtained for Royaltuf 498 composition.

![Graph of hardness vs. ZnO level](image1)

Fig. 4. Dependence of hardness on variation of ZnO level

![Graph of elasticity vs. ZnO level](image2)

Fig. 5. Elasticity variation depending on ZnO quantity

The tensile strength increase from 10.4 to 18.5 N/mm² for Royaltuf 485 blends when the maximum value is observed for 5 phr of zinc oxide, after which it exhibit a slight decrease.
while the zinc oxide quantity continues to increase (Fig. 6). Module increases together with the increase of neutralization degree in the elastomer compositions (Figs. 6, 7). Elongation at break exhibits very high values and a maximum between 5-15 phr of zinc oxide was observed for the two elastomer compositions.

By increasing of neutralization degree this parameter decreases (Fig. 8). Tear strength exhibits a significant and continuous increase for Royaltuf 485 composition when an increase from 38.5 to 53.5 N/mm was observed at the increase of ZnO quantity from 0 to 10 phr. After this ZnO content a slight decrease of tear strength was noticed for Royaltuf 498 composition (Fig. 9).

Comparing characteristics of blends made with Royaltuf 485 rubber with those made with Royaltuf 498 elastomer, both neutralized with zinc oxide, it is noticed that physico-mechanical properties are better in blends in which Royaltuf 485 rubber was used. This behaviour is determined by the composition and structure of the two types of rubber; thus, blends containing elastomer with semi-crystalline structure (Royaltuf 485) have exhibited higher values of hardness, module, tensile strength, elongation at break and tear strength than blends containing Royaltuf 498 elastomer which has an amorphous structure.

The rheological properties of compositions based on EPDM-g-MA elastomer containing different ZnO levels are presented in Tab. 4. It is noticed that zinc oxide replaces sulfur and vulcanization agents in these blends. The optimal time of vulcanization decreases as the quantity of neutralization agent (ZnO) increases, and the minimum and maximum moments increase as a result of the reinforcing effect due to ionic bond formation.
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From the analysis of physico-mechanical properties of blends based on EPDM-g-AM Royaltuf 485 rubber and Royaltuf 498 rubber, respectively, it is noticed that, together with the increase of the neutralization degree, due to the property of groups specific to maleic anhydride existing on the macromolecular chain of reacting with oxides of divalent metals (zinc oxide), ionic bonds form similar to sulphur bridges from vulcanized rubber. This ionic crosslinking has led to an improvement in the value of the module, in tensile and tear strength. It can be inferred that EPDM-g-AM elastomers have reacted chemically with the zinc oxide.

| Characteristics / ZnO level | 5 phr ZnO | 10 phr ZnO | 15 phr ZnO | 20 phr ZnO |
|-----------------------------|-----------|------------|------------|------------|
| **Blends with Royaltuf 485** |           |            |            |            |
| Minimum moment, Nm          | 3.8       | 5          | 9          | 7          |
| Maximum moment, Nm          | 6         | 17.5       | 19         | 20         |
| Optimal vulcanization time  | 25'       | 22'45"     | 17'30"     | 16'15"     |
| **Blends with Royaltuf 498** |           |            |            |            |
| Minimum moment, Nm          | 4.4       | 5.6        | 13.4       | 11.4       |
| Maximum moment, Nm          | 9         | 16.6       | 16.7       | 17.5       |
| Optimal vulcanization time  | 25'       | 22'30"     | 16'15"     | 11'15"     |

Table 4. Rheological characteristics of EPDM-g-AM blends containing zinc oxide
4. Effect of fillers on the properties of thermoplastic elastomers based on maleated EPDM

Fillers are used to improve some properties of thermoplastic compositions. It is well known that the fillers interact with ionic elastomers leading to the formation of ionic, covalent or hydrogen bonds with them. The appearance of these bonds determines a reinforcing effect of rubber composition and the improving of modulus, tear strength or of tensile strength (Zuga et al., 2004).

The filler nature (carbon black, precipitated silica or chalk) will influence the properties of ionic thermoplastic elastomers and it is very important to select the type of filler and optimum quantity which must be incorporated in a composition designated to be utilized in light industry.

| Ingredients/Sample | O1 | U1 | U2 | U3 | C1 | C2 | C3 | F1 | F2 | F3 |
|--------------------|----|----|----|----|----|----|----|----|----|----|
| EPDM-g-AM Royaltuf 485, g | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide, g | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Stearic acid, g | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Zinc stearate, g | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Precipitated silica | - | 30 | 60 | 90 | - | - | - | - | - | - |
| Perkasil, g | - | - | - | - | 30 | 60 | 90 | - | - | - |
| Chalk, g | - | - | - | - | - | - | - | 30 | 60 | 90 |
| Carbon black HAF, g | - | - | - | - | - | - | - | - | 30 | 60 |
| Paraffin oil Texpar 22, g | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Antioxidant Irganox 1010, g | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

| Characteristics | O1 | U1 | U2 | U3 | C1 | C2 | C3 | F1 | F2 | F3 |
|-----------------|----|----|----|----|----|----|----|----|----|----|
| Hardness, °ShA | 63 | 72 | 81 | 89 | 66 | 67 | 72 | 67 | 77 | 84 |
| Elasticity, % | 34 | 34 | 36 | 36 | 34 | 36 | 32 | 30 | 32 | 30 |
| Tensile strength, N/mm² | 8.8 | 8.2 | 5.2 | 5.2 | 4.7 | 4.7 | 6.9 | 5.8 | 9.3 | 9.6 |
| Elongation at break, % | 767 | 580 | 273 | 100 | 567 | 473 | 473 | 633 | 633 | 633 |
| Residual elongation, % | 83 | 61 | 24 | 9.3 | 59 | 49 | 53 | 75 | 50 | 60 |
| Tear strength, N/mm | 36 | 43.5 | 46 | 48 | 37.5 | 41 | 44 | 53 | 50 | 74 |
| Specific weight, g/cm³ | 1.07 | 1.12 | 1.16 | 1.23 | 1.14 | 1.25 | 1.35 | 1.11 | 1.16 | 1.22 |
| Abrasion resistance, mm³ | 102 | 135 | 182 | 246 | 165 | 176 | 196 | 149 | 162 | 161 |

Table 5. Formulations and characteristics of rubber blends based on EPDM-g-MA (Royaltuf 485)

Some formulations and properties of rubber blends based on EPDM-g-MA are given in Tab. 5 and 6 in order to reveal the influence of filler nature on the resulting compositions. From these tables it can be seen that the hardness of composition increases together with filler incorporation due to the reinforcing effect of fillers. This improvement of hardness is more
pronounced for compositions with active fillers (carbon black, silica) as compared to compositions containing inactive fillers (chalk). For the compositions containing Royaltuf 485 the increase of filler level determines an increase of hardness of 41 % for compositions having precipitated silica and of 33 % for compositions with carbon black, respectively. The same effect was observed for compositions containing Royaltuf 498, where the hardness increase with 34.8% introducing precipitated silica and with 28.8 % for compositions having carbon black as filler. The introducing of chalk determines a lower increase of hardness (about 15 %, Tab. 5).

The elasticity decreases by introducing fillers in composition. For compositions containing Royaltuf 485 the elasticity was diminished from 34 to 26 % in the case of carbon black utilization and lower decrease together with the increase of chalk level (from 34 to 30 %). The elasticity shows a nonuniform variation in compositions with silica or chalk and it decreases till 28% in compositions with carbon black (compositions with Royaltuf 498).

| Ingredients / Sample | O2 | U1 | U2 | U3 | C1 | C2 | C3 | F1 | F2 | F3 |
|----------------------|----|----|----|----|----|----|----|----|----|----|
| EPDM-g-AM Royaltuf 498, g | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide, g | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Stearic acid, g | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Zinc stearate, g | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Precipitated silica | - | 30 | 60 | 90 | - | - | - | - | - | - |
| Perkasil, g | - | - | - | - | 30 | 60 | 90 | - | - | - |
| Chalk, g | - | - | - | - | 30 | 60 | 90 | - | - | - |
| Carbon black HAF, g | - | - | - | - | - | - | - | 30 | 60 | 90 |
| Paraffin oil, Texpar oil 22, g | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Antioxidant Irganox 1010, g | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Characteristics | | | | | | | | | | |
| Hardness, °ShA | 66 | 70 | 83 | 89 | 67 | 70 | 73 | 79 | 80 | 85 |
| Elasticity, % | 32 | 35 | 32 | 30 | 34 | 32 | 32 | 23 | 23 | 25 |
| Tensile strength, N/mm² | 7.7 | 5.5 | 6.5 | 6.6 | 6.1 | 6.5 | 10.6 | 9.2 | 8.2 |
| Elongation at break, % | 753 | 553 | 487 | 200 | 660 | 527 | 513 | 460 | 433 | 313 |
| Residual elongation, % | 77 | 53 | 41 | 12 | 67 | 44 | 49 | 69 | 60 | 51 |
| Tear strength, N/mm | 36 | 34.5 | 44.5 | 57 | 33 | 49 | 43.5 | 59.5 | 70 | 57 |
| Specific weight, g/cm³ | 1.02 | 1.07 | 1.16 | 1.21 | 1.14 | 1.18 | 1.21 | 1.08 | 1.15 | 1.22 |
| Abrasion resistance, mm³ | 111 | 162 | 211 | 257 | 147 | 220 | 252 | 150 | 169 | 198 |

Table 6. Formulations and characteristics of rubber blends based on EPDM-g-MA (Royaltuf 498)

Tensile strength also decreases together with the increase of silica and chalk levels for the both compositions. In case of compositions containing carbon black the tensile strength
increases with 25% as the filler level increases, while in compositions containing Royaltuf 498 the tensile strength increases with 37.7 % for carbon black level of 30 phr and then it decreases until 22.6 %. The elongation at break decreases together with the increase of filler level. The most increase was observed in compositions containing precipitated silica. Tear strength increases against filler level for all compositions, the high values were obtained for compositions containing carbon black.

Also, the specific weight and abrasion resistance increase as the filler level becomes higher. However, the values of specific weight for compositions containing more than 60 phr of filler are very high and inadequate for use in shoes fabrication. The values of abrasion resistance confirm that these compounds can be used to manufacture „every day” shoes.

From Tabs. 5 and 6, the best characteristics of the compositions based EPDM-g-MA were obtained using as fillers carbon black and silica, occurring an increase of hardness, tensile strength and tear strength. Taking into account that a higher filler level leads to the decrease of melt composition viscosity and to the increase of specific weight and abrasion resistance, a rubber composition containing 30 phr carbon black or 30 phr precipitated silica could be selected in order to utilize in EPDM-g-MA compounds (Zuga et al., 2004).

5. Influence of plasticizers on the properties of maleated EPDM ionic elastomers

Ionic plasticizers play the role of promoting the ionic break-up of the ionic interactions at high temperatures to enable the shearing flow of the compound; at room temperature they behave like a filler. The most largely used ionic plasticizer is zinc stearate but some others can be also used, like calcium stearate, zinc acetate, stearamide.

Non-ionic plasticizers play the role of solvatating the non-ionizing elastomer chains. They are chemically and thermally stable materials which are added to polymers to facilitate their processing, imparting flexibility and softness to the finished products. The major plasticizer functions in the polymer blends are the following: improving the processing and applications of long chain polymers; lowering the polymer processing temperature under their decay temperature; plasticizers decrease the intermolecular polymer forces, like the temperature does; changing the finished product characteristics, enabling the polymers to be used in specific fields requiring conditions which cannot be met by the unplasticized polymers. Plasticizers increase generally the polymer characteristics, such as flexibility, elongation, resistance to low temperatures but also can lower some characteristics like the tensile strength, the dielectric properties, etc.; enlarging the application field because of their lower costs.

The action of the ionic plasticizer (zinc stearate) and non-ionic plasticizer (paraffin oil) on the ionic thermoplastic elastomer characteristics based on the maleinized ethylene propylene terpolymer rubber was discussed in order to select some optimum compositions for applications.

The prepared blends have shown different physico-mechanical characteristics according to the levels of the added plasticizer. Zinc stearate was used as plasticizer agent in concentrations of 20 and 40 phr, respectively and as nonionic plasticizer, paraffin oil in concentration of 10-50 phr.
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Figure 10 shows that adding the plasticizer (paraffin oil) for polymer chains has resulted in a decreased hardness (by 12°ShA) but adding the ionic plasticizer (zinc stearate) has resulted in an increased hardness as the last one plasticizes the ionic groups at a temperature above the its melting point (128°C) and at the room temperature it acts like a filler (increases by 1°ShA up to 11°ShA). Hardness changes as a result of adding zinc stearate are more marked with the blend containing EPDM and 1 % maleic anhydride because of the enlarged ionic ranges.

An increase in elasticity with the increase in the amount of paraffin oil added to the blends was found out (Fig. 11); but the elasticity decreases as the amount of the added ionic plasticizer is increased and this decrease is more marked with blends containing EPDM and 1 % maleic anhydride. The blends containing EPDM and 1 % maleic anhydride show a higher elasticity with the decreasing in crystalline phase to the favour of amorphous phase.

Fig. 10. Changes in hardness according to the added plasticizer amounts: (a) for blends with Royaltuf 485; (b) for blends with Royaltuf 498

Fig. 11. Changes in elasticity according to the added plasticizer amounts: (a) for blends with Royaltuf 485; (b) for blends with Royaltuf 498
As can be seen in Figs. 12 and 13, paraffin oil solvates the non-ionic ranges leading to a decrease in elasticity modulus and tensile strength and this decrease is less marked with blends containing higher levels of zinc stearate. Increasing the zinc stearate levels in blends has resulted in an insignificant decrease in the elasticity modulus and tensile strength.

Elongation at break increases as the amount of paraffin oil added to the blends is increased and decreases as the amount of zinc stearate added to the blends is increased (Fig. 14). It decreases with high plasticizer levels.

**Fig. 12.** Changes in elasticity modulus and tensile strength according to the added amount paraffin oil to the blends of EPDM with 0.5 % maleic anhydride. (a) for the blends with 20 phr zinc stearate; (b) for the blends with 40 phr zinc stearate

**Fig. 13.** Changes in elasticity modulus and tensile strength according to the added amount paraffin oil to the blends of EPDM with 1.0 % maleic anhydride. (a) for the blends with 20 phr zinc stearate; (b) for the blends with 40 phr zinc stearate
Fig. 14. Changes in elongation at break according to the added plasticizer amounts. (a) for blends with Royaltuf 485; (b) for blends with Royaltuf 498

Tear strength decreases with the added paraffin oil and also with the increase in zinc stearate level (Fig. 15).

The ionic plasticizer has shown filler characteristics leading to some increase in hardness and decrease in elasticity, elasticity modulus, tensile strength and tear strength. Non-ionic plasticizer has solvated non-ionicizable elastomer chains leading to some increase in elasticity and elongation at break and decrease in hardness, tensile strength and tear strength.

Fig. 15. Changes in tear strength according to the added plasticizer amounts. (a) for blends with Royaltuf 485; (b) for blends with Royaltuf 498;

6. Influence of polyolefins on the properties of ionic thermoplastic elastomer compositions

Some characteristics of the compositions based on EPDM-g-MA can be improved by adding other polymers in system. The choosing of polymer type must be made as a function of its miscibility with the thermoplastic elastomer present already in composition. The selection of polymers to obtain blends with enhanced properties takes into account the following
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criteria: structure, solubility, crystallinity degree, superficial tension, etc. (Datta & Lohse, 1996, Utracki, 1998). According to these criteria polymers such as polypropylene, polyethylene (PE), maleated polyethylene (PE-g-MA), HDPE were selected to be used in compositions based on EPDM-g-MA.

Upon analyzing physico-mechanical characteristics of resulting blends, the following are noticed:

- Hardness increases with polyolefin quantity (Fig. 16), and elasticity decreases with the increase of HDPE quantity (Fig. 17). This indicates the fact that with a polyolefin quantity of about 80 phr it has the tendency of becoming a continuous phase and imprints surface properties on the blend.
- 100% modulus (Fig. 18), 300% modulus (Fig. 19) and tear strength (Fig. 20) increase significantly with the increase of polyolefin quantity in the blend, suggesting a good miscibility (link formation) of HDPE with EPDM-g-MA and the properties of the blend are additive.
- Tensile strength (Fig. 21) and elongation at break (Fig. 22) vary unevenly upon the increase of polyolefin amount in blends, but their values are good.
- Residual elongation (Fig. 23) significantly increases as the HDPE quantity introduced in the blends increases, indicating that the obtained blends have both characteristics specific to plastic materials, namely “neck” formation, and properties specific to elastomers (good recovery after applying a force), their share depending on the ratio between the elastomer and polyolefin existing in the blend.

Fig. 16. Hardness versus the HDPE level

Fig. 17. Elasticity versus the HDPE level
Fig. 18. 100% modulus versus the HDPE level

Fig. 19. 300% modulus versus the HDPE level

Fig. 20. Dependence of tear strength on HDPE level

Fig. 21. Dependence of tensile strength on HDPE level
From the results obtained it was noticed that by increasing the quantity of HDPE introduced in EPDM-g-MA blends, hardness, modulus and tear strength increase and elasticity and residual elongation decrease. These effects prove that the properties of polymer blends depend on the characteristics of component polymers and on their molar fractions. The blend containing 80 phr polyethylene was selected, as it had the best values of hardness, modulus, tear strength and good values of tensile strength, elongation at break and elasticity (Zuga & Cincu, 2006c). This blend was used to make ionic thermoplastic elastomer granules in the laboratory extruder-granulator.

![Fig. 22. Elongation at break versus HDPE level](image1)

![Fig. 23. Residual elongation versus HDPE level](image2)

7. Nanocomposites based on maleated ethylene propylene diene monomer and clay

In the last decades, polymer/layered clay nanocomposites (PCN) have attracted considerable attention in both basic research and industry exploitation because they possess a combination of properties that are not available in any of the single components. These systems exhibited improvements in mechanical properties, thermal stability, gas barrier properties, flame retardance, chemical and dimension stability (Stelescu et al, 2010). The clay mineral most used in elastomers/clay nanocomposites is montmorillonite, which have a layered structure consisting of two silicate tetrahedral sheets with an edge shared octahedral sheet of either aluminium or magnesium hydroxide (Ahmadi et al., 2005; Lowe et al., 2011). In order to obtain a nanoscale dispersion of clays in a polymer matrix, the silicates must be pretreated with alkylammonium ions to produce an organoclay (Tjong et al., 2002).
If the organomodified clay particles are dispersed in a polymer matrix three different types of structures can be found in nanocomposites: intercalated, flocculated and exfoliated. In the intercalated structures the polymer chains have penetrated into the layered structure maintaining the well-order multilayered nature. The flocculated structure is similar to the intercalated one, but the intercalated silicate layers sometimes flocculated because of the hydroxylated edge-edge interactions. The exfoliated structures of the silicate nanolayers are randomly dispersed throughout the polymer matrix. The exfoliated structures will determine enhanced properties of nanocomposites due to their higher phase homogeneity as compared to intercalated ones (Kang et al., 2007; Ray et al., 2003). XRD at small angles ($2\theta < 10^\circ$) and transmission electron microscopy (TEM) are effective methods to investigate these structures present in nanocomposites. XRD data reveal some peaks whose position is related to the basal spacing $d_{001}$ and its broadness can give information about the distribution of spacings. In the exfoliated structures the interlayer spacing can be of the order of the gyration radius of the polymer and no peaks in their region are present due to the large $d$-spacings (10 nm) (Kang et al., 2007; Cole, 2008). Transmission electron microscopy gives the possibility to obtain data on the delaminated layers or intercalated stacks. The intercalation/exfoliation of layered clays is determined by compatibility of components, polymer diffusivity and processing conditions.

Polymer/clay nanocomposites can be obtained by different methods, such as solution intercalation, in-situ intercalation polymerization and polymer melt intercalation. The melt compounding method is more advantageous due to its compatibility with current industrial polymer processing procedures and its environmental benefit determined by the lack of solvents (Kawasumi et al., 1997; Vaia & Giannelis, 1997). The properties of nanocomposites obtained by melt blending technique can be controlled by various parameters: molecular architecture of the alkylammonium cation used in ionic exchange, the presence of additives during silicate modification, processing temperature, the type and the content of compatibilizer and polymer viscosity (Reichert et al., 2000).

Because ethylene propylene diene terpolymer is a widely used material, EPDM/clay composites should be of great application potential. The homogeneous dispersion of silicate clay in polymer matrix occurs with difficulty because EPDM does not include polar groups in the polymer chain. In this case the modification of EPDM with maleic anhydride or the use of a compatibilizing agent can assure a good dispersability of organoclay in EPDM matrix.

The EPDM-g-MA compositions were prepared by melt blending method using a Plasti-Corder Brabender equipment at a temperature of 190 °C for 12 min as mix time. The organoclay (OMMT) was montmorillonite intercalated by octadecyltrimethylamine (Nanomer 128E). The other compounding ingredients such as zinc oxide, stearic acid, zinc stearate and antioxidant (Irganox 1010) were also utilized in formulations. PP-g-MA (1 % MA) was applied as compatibilizing agent (Stelescu et al., 2010). Three compositions containing EPDM-g-MA were prepared according to tab. 7. The compositions contain also compounding ingredients such as zinc oxide (10 g), stearic acid (1 g), zinc stearate (20 g) and Irganox 1010 (2 g). The resultant composites were homogenized on an electrically operated laboratory roller mill at 155-165°C. The test specimens for physico-mechanical measurements were obtained by pressing in an electrical press at 170°C for 5 min and pressure of 150 MPa.
Table 7. EPDM-g-MA compositions

| Sample                  | 2θ (°) | d (nm) |
|-------------------------|--------|--------|
| OMMT                    |        |        |
|                         | 3.81   | 2.32   |
|                         | 5.65   | 1.56   |
|                         | 19.86  | 0.45   |
|                         | 26.74  | 0.33   |
| EPDM-g-MA/OMMT          |        |        |
|                         | 2.24   | 3.94   |
|                         | 4.61   | 1.92   |
|                         | 21.55  | 0.41   |
|                         | 23.82  | 0.37   |
| EPDM-g-MA/OMMT/PP-g-MA  |        |        |
|                         | 2.24   | 3.94   |
|                         | 4.72   | 1.87   |
|                         | 17.02  | 0.52   |
|                         | 21.53  | 0.41   |

Table 8. Diffraction pattern characteristics of composites (according to Stelescu et al., 2010)

X-ray diffractometry is a powerful method to study the dispersion of organoclay in polymer matrix. It permits the precise determination of silicate layer spacing and monitors the intercalation behavior of polymer chains. X-ray diffractograms were collected from a Bruker A8 Advance diffractometer with Ni-filtered Cu-Kα radiation (λ = 0.1541 nm) operating a tube voltage of 40 kV and a tube current of 35 mA. The diffractograms were scanned in 2θ range from 1°-30° at a rate of 1°/min. The interlayer spacing (d001-spacing) was evaluated by the Braag equation: λ = 2d sin θ, where θ is the diffraction angle, λ is the x-ray wavelength and d is the interlayer spacing. The modified organoclay shows two 2θ peaks at 3.81° and 5.65° which correspond to a basal spacing of 2.32 and 1.56 nm, respectively (Fig. 24). For the nanocomposites EPDM-g-MA/OMMT and EPDM-g-MA/OMMT/PP-g-MA a high increase in d-spacing of the layered silicate was observed (Tab. 8) and the corresponding diffraction peak is shifted to lower 2θ angles namely 2.24°. The shift of the sharp diffraction peak of organoclay from 2θ = 3.81° to lower diffraction angles in our composites suggests that EPDM-g-MA has been able to intercalate into the gallery space of layered silicate, expanding the basal spacing of organoclay to 3.94 nm, which can clearly confirm the nanocomposite formation. The basal spacing increase in nanocomposites can be also influenced by the presence of hydrogen bondings between the maleic anhydride groups and the oxygen of silicate. The greater polarity of the EPDM-g-MA facilitates the interdiffusion of the polymer chains into the gallery spaces of the organoclay leading to a better dispersion of the nanoclay in polymer matrix. As given in Fig. 24, the EPDM-g-MA/PP-g-MA nanocomposite exhibits a diffraction peak at the same 2θ with the same basal spacing relating to sample EPDM-g-MA (Tab. 8). It can be observed that the intensity of 2θ diffractive peak at 2.24° is practically the same for nanocomposites EPDM-g-MA/OMMT and EPDM-g-MA/OMMT/PP-g-MA, a slight decrease was found out for the peak at about 4.72° for the composition containing compatibilizer PP-g-MA. The X-ray diffractogram of
EPDM-g-MA sample shows a wide diffraction maximum centered at $\theta = 20.65^\circ$ due to amorphous phase. For the studied composites a diffraction peak appeared at around $\theta = 6.54^\circ$. This peak at small diffraction angle can be determined by the presence in composites of some diffraction centers formed by the aggregation tendency of ionic species leading to the formation of some microphases enriched in ions within polymer matrix and it can be attributed to interaggregated interface, the distances between ionic aggregates being Braag spaces while other authors assigned this peak to intraaggregated phase (Zuga, M.D. & Cincu, C., 2006b; 2006c).

Fig. 24. X-ray diffraction patterns of organo clay (1) and EPDM nanocomposites: 2-EPDM-gMA/OMMT; 3-EPDM-g-MA/OMMT/PP-g-MA

The evolution of the weight loss of our composites with temperature is depicted in Fig. 25. Thermogravimetric analysis (TGA) was conducted on MOM Derivatograph at a heating rate of 10°C/min. The samples were heated in the temperature range from room to 750°C in air. The modified organoclay exhibits two stage of decomposition, the first corresponds to the elimination of absorbed free and interlayer water. In the second stage the degradation of organic material occurs starting at 220°C. The temperature at which the weight loss was 5% can be considered the initial decomposition temperature ($T_d$).
Tab. 9 summarized the thermal analysis data such as temperature at 5% weight loss, decomposition temperature at maximum weight loss rate ($T_{\text{max}}$), weight loss determined at the end decomposition ($R$). The three composites exhibit a very sharp weight loss of about 83% between 250 and 490°C, followed by a second short stage with maximum temperature near 510-530°C. As it can be noticed, the thermal stability of composition containing nanoclay and compatibilizer was increased slightly compared to initial sample EPDM-g-MA. Also, the char residue has higher values in the first two compositions (EPDM-g-MA/OMMT and EPDM-g-MA/OMMT/PP-g-MA). The thermal stability of EPDM-g-MA composites did not enhance as much, compared to the simple sample EPDM-g-MA. This small increase in thermal stability can be attributed to the clay nanolayers which can proceed as barriers to reduce the permeability of volatile degradation products from polymer matrix (Hsueh & Chen, 2003; Ahmadi et al., 2005). From Table 8 it can see that the organoclay practically does not decompose during processing or characterization of these materials.

| Sample          | $T_{5\%}$ (°C) | $T_{\text{max}}$ (°C) | $R$ (%) | $T_{m}$ (°C) | $\Delta H_f$ (J/g) | $T_c$ (°C) |
|-----------------|----------------|-----------------------|--------|--------------|-------------------|------------|
| EPDM-g-MA       | 350            | 475                   | 10.08  | 119.01       | 20.57             | 76.41      |
| EPDM-g-MA/OMMT  | 340            | 460                   | 13.31  | 120.52       | 22.07             | 74.02      |
| EPDM-g-MA/OMMT/PP-g-MA | 335          | 455                   | 13.91  | 120.17       | 16.45             | 74.64      |
| PP-g-AM         |                |                       |        | 162.34       | 11.84             | 108.97     |

Table 9. Thermal characteristics of composites (according to Stelescu et al., 2010)
DSC determinations were utilized to characterize melting and crystallization behavior of composites based on EPDM-g-MA. Dynamic scanning calorimetry (DSC) measurements were performed on Perkin Elmer Pyris Diamond calorimeter, at a heating rate of 15°C/min. Figures 26 and 27 depict the DSC cooling and reheating melt thermograms of composites under study. Some of representative data from DSC scans are presented in Table 8 such as melting peak temperature ($T_m$), heat of fusion ($\Delta H_f$), crystallization temperature ($T_c$). The melting process of EPDM-g-AM (nano)composites shows a broad endotherm peak between 65 and 130°C (Fig. 26).

Fig. 26. DSC thermograms of composites 1-EPDM-g-MA; 2-EPDM-g-MA/OMMT; 3-EPDM-g-MA/OMMT/PP-g-MA(according to Stelescu et al., 2010)

![DSC thermograms](image)

Fig. 27. DSC crystallization properties of composites 1-EPDM-g-MA; 2-EPDM-g-MA/OMMT; 3-EPDM-g-MA/OMMT/PP-g-MA.(according to Stelescu et al., 2010)

![DSC crystallization properties](image)
The melting temperatures for the first stage were found to be almost the same for all samples. The small decrease of melting temperature with the introduction of PP-g-MA as well as the decrease of exothermic signal intensities can be due to the decrease of maleated polypropylene crystallization in composition in the presence of EPDM-g-MA. Therefore PP-gAM retards the crystallization of PP. Especially as the incorporation of OMMT in composite (sample EPDM-g-MA/OMMT) determines the increase of $T_m$ and of the fusion heat (Table 9) suggesting a supplementary nucleation increase due to the nanoclay presence. The crystallization temperature of PP-g-MA was around 118°C and this signal is shifted to 109°C after addition of OMMT and EPDM-g-MA in composition due to the limitation of chain mobility determined by the formation of hydrogen bonds between maleated EPDM and OMMT.

The mechanical properties of EPDM-g-MA (nano) composites under different OMMT loadings are presented in figures 28-33. Significant improvement in hardness, tensile strength, modulus and tear strength is clearly noticed for EPDM-g-MA/OMMT/PP-g-MA nanocomposites containing compatibilizer with the increasing of OMMT content. Only the elasticity decreases with the increase of OMMT level in composites (fig.30). The modulus and tensile strength increase rapidly with the increase of nanoclay loading (figs. 29 and 31) compared to that of MA sample. The enhancement in modulus and tensile strength shows that a better dispersion of layered silicate in polymer matrix in the presence of PP-g-MA as compatibilizer occurs and that the properties of the resulting polymer blends are additive. The tensile strength and elongation at break reach a maximum at about 2.5 phr of OMMT and then decrease (figs. 31 and 32), taking into account high nanoclay level and the ability of EPDM-g-MA to accept high loadings of clay diminishes. However, tensile strength and elongation at break of the uncompatibilized sample (EPDM-g-MA) show a minimum at 5 phr of OMMT content. This fact can be attributed to the decrease of ductility while the stiffness become higher by reinforcing effect of OMMT layered silicate. Tear strength and hardness exhibit a remarkable increase with increasing nanoclay level (figs. 28 and 33).

![Fig. 28. Dependence of hardness on nanoclay content](www.intechopen.com)
Fig. 29. Dependence of modulus 100% on nanoclay loading

Fig. 30. Dependence of elasticity on nanoclay level

Fig. 31. Tensile strength as a function of nanoclay content
This increase is due to the fact that the OMMT clay behaves as a reinforcing agent for the polymer matrix leading to the enhanced hardness.

8. Conclusions

The results confirm that the ionic thermoplastic elastomers based on EPDM-g-MA have properties similar to EPDM-based vulcanized rubber blends, and in addition, they can be easily processed using methods specific for thermoplastic materials, thus removing the vulcanization stage involving high power expenditure and release of noxious compounds determining improved characteristics (higher values for elasticity, ageing resistance, abrasive resistance, acid and alkali fastness) of the resulting materials.

Ionic thermoplastic elastomer granules can be used in various areas, due to specific properties such as resistance to water and diluted or concentrated acid and base solutions, resistance to accelerated aging, abrasion resistance or resistance to repeated bending.
The potential users of the new rubber materials will be economic operators processing rubber and plastics, footwear and car component manufactures etc. They can be used in the manufacture of a large range of products like as hoses, gaskets, rubber shoes, protective equipment etc.

9. References

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