THE PLASTICIZER ACTION ON THE PHYSICO-MECHANICAL CRARACTERISTICS OF THERMOPLASTIC IONIC ELASTOMERS BASED ON MALEINIZED ETHYLENE-PROPYLENE TERPOLYMER

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În acest studiu s-a realizat determinarea influenței plastifianților ionici şi neionici asupra caracteristicilor elastomerilor termoplastici ionici pe bază de elastomer etilen propilen terpolimer maleinizat. S-au utilizat două tipuri de elastomer etilen propilen terpolimer maleinizat care conțin cantități diferite de anhidridă maleică (0.5% respectiv 1% anhidridă maleică). Ca plastifiant ionic s-a utilizat stearatul de zinc, iar ca plastifiant neionic s-a introdus uleiul parafinic. S-a observat că plastifiantul ionic prezintă caracteristicile unei şarje, conducând la creşterea durității şi scăderea elasticității, a modulului de elasticitate, a rezistenței la rupere şi rezistenței la sfâşiere. Plastifiantul neionic a solvatat lanțurile neionizabile ale elastomerilor conducând la creşterea elasticității şi a alungirii la rupere şi la o scădere a durității, rezistenței la rupere şi rezistenței la sfâşiere. Proprietățile amestecurilor depind de concentrațiile de plastifianți ionici şi neionici. Valorile optime ale acestor concentrații se aleg în funcție de domeniul de utilizare a amestecului respectiv.

In this work the influence of the ionic and non-ionic plasticizers on the characteristics of thermoplastic ionic elastomers based on maleinized ethylene-propylene-diene terpolymer elastomer has been determined. Two kinds of maleinized ethylene-propylene terpolymer elastomers containing different maleic anhydride percentages (0.5 % and 1 %) were investigated. Zinc stearate and paraffin oil were used as ionic plasticizer and non-ionic plasticizer, respecivelly. The ionic plasiticizer has shown filler characteristics leading to an increased hardness and decreased elasticity, elasticity modulus, tensile strength and tear strength. The non-ionic plasticizer has solvated non-ionizable elastomer chains leading to increased elasticity and elongation at break and decreased hardness, tensile strength and tear strength. Blend characteristics are dependent on the ionic and non-ionic plasticizer levels. The best plasticizer levels are selected according to the application field of the concerned blend.

Keywords: thermoplastic ionic elastomers, maleinized EPDM, ionic plasticizer, non-ionic plasticizer, physico-mechanical characteristics.

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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 % [1-3].

The ionic elastomer compounds resemble highly with the traditional rubber compounds but there are some differences. Because the former are thermoplastic, there is no curing stage and, therefore, no sulphur and vulcanization accelerators or peroxides are added. Another significant difference is the use of an ionizing agent - *ionic plasticizer* in preparing ionic thermoplastic elatomers. 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 [4-7]; at room temperature it behaves 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.

A formulation of ionic thermoplastic elastomer compound consists generally of: a neutralized ionomer, ionic plasticizer, non-ionic plasticizer, filler, other polymers, antioxidants, etc [8-9].

Non-ionic plasticizers play the role of solvating 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 application 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 characteristics, etc.
- Enlarging the application field because of their lower costs.

In this work 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 investigated.

The compounds of ionic thermoplastic elastomers can be used in many applications [10-17], such as: hose and footwear manufacture, modifier for polymer materials, adhesive preparation, manufacture of impermeable thin flexible membranes, etc.

1. Experimental

In preparing the ionic thermoplastic elastomers the following raw and auxiliary materials were used:

– Two types of EPDM elastomers with various levels of maleic anhydride: 0.5 % and 1 %;
– Neutralizing agent: zinc oxide;
– Ionic plasticizer: zinc stearate;
– Non-ionic plasticizer: paraffin oil;
– Filler: precipitated silica, HAF carbon black;
– Antioxidant.

Paraffin oil at levels of 10 -50 phr (parts per100 parts elastomer) and zinc stearate at levels of 20 - 40 phr (parts per 100 parts elastomer) were used in plasticizing the macromolecular chains and ionic groups, respectively.

The main work stages in preparing rubber blends were the following:

♦ Testing the raw materials;
♦ Ingredient weigh feeding;
♦ Ingredient mixing was performed on a Brabender plasticorder. The process variables were: temperature: 170^{o}C, rotational speed: 100 rpm, mixing time: 20 min. The elastomers and ingredients were added in the mixer in the following sequence:

1. elastomer
2. neutralizer
3. filler + plasticizers (ionic and non-ionic)

The blends were homogenized on an electrically heated laboratory roller mill. The optimum process variables were: temperature: 140-160^{o}C and friction coefficient: 1:1.1.

Samples used in tests for physico-mechanical characterization were made by means of an laboratory electrical press at a temperature of 170^{o}C.

Tests were performed according to the standards in force (SR ISO 769/2001, SR ISO 37/1997, SR ISO 34-1/2000, 1817/2000).

2. Results and discutions

The prepared blends have shown different physico-mechanical characteristics according to the levels of the added plasticizer:

1) Hardness – Fig. 1 shows that adding the plasticizer (paraffin oil) for polymer chains has resulted in a decreased hardness (by 12^{o}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^{o}C) and at the room temperature it acts like a filler (increases by 1^{o}ShA up to 11^{o}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.

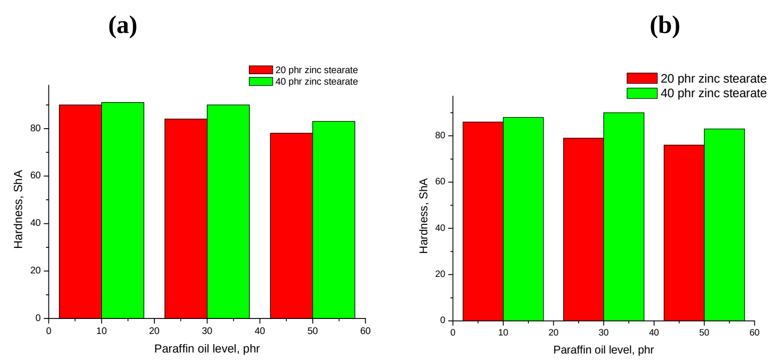

Fig. 1 - Changes in the hardness according to the added plasticizer amounts.
(a) for EPDM blends with 0.5 % maleic anhydride
(b) for EPDM blends with 1.0 % maleic anhydride

2) Elasticity – Fig. 2 shows an increase in elasticity with the increase in the amount of paraffin oil added to the blends; 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.

(a) **(b)**

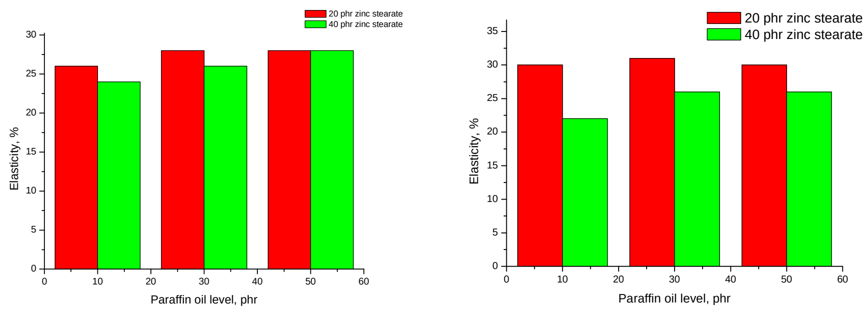

Fig. 2 - Changes in the elasticity according to the added plasticizer amounts.
(a) for EPDM blends with 0.5 % maleic anhydride
(b) for EPDM blends with 1.0 % maleic anhydride

<u>3) Tensile strength and elasticity modulus</u> – as can be seen in Figs. 3-4, 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.

(a) **(b)**

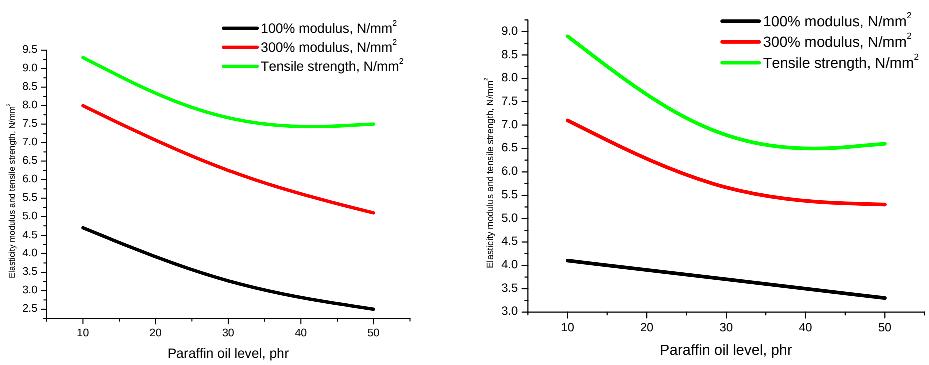

Fig. 3 – Changes in the elasticity modulus and tensile strength according to the added amount paraffin oil to the blends of EPDM with 0.5 % maleic anhydride
(a) for the blends with 20 phr zinc stearate
(c) for the blends with 40 phr zinc stearate

(a) **(b)**

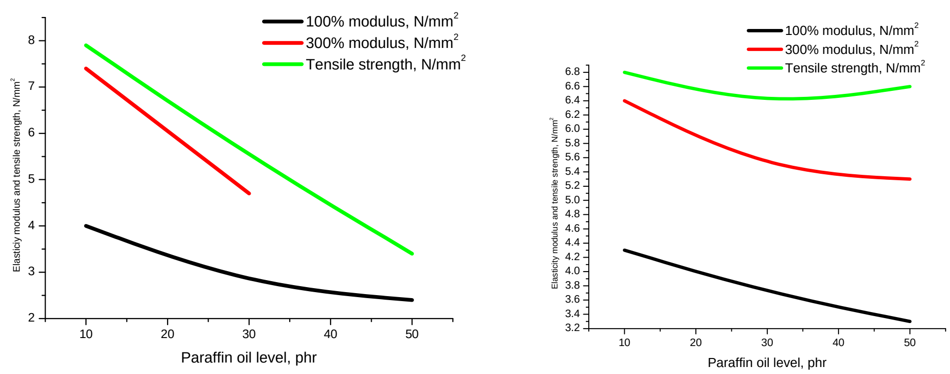

Fig. 4 – Changes in the elasticity modulus and tensile strength according to the added amount paraffin oil to the blends of EPDM with 1.0 % maleic anhydride
(a) for the blends with 20 phr zinc stearate
(b) for the blends with 40 phr zinc stearate

4) 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. 5). It decreases with high plasticizer levels.

(a) **(b)**

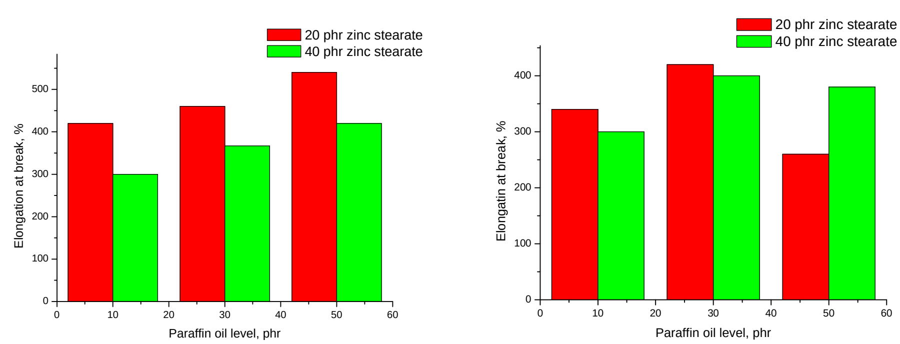

Fig. 5 - Changes in the elongation at break according to the added plasticizer amounts.
(a) for EPDM blends with 0.5 % maleic anhydride
(b) for EPDM blends with 1.0 % maleic anhydride

5) Tear strength - decreases wit the added paraffin oil and also with the increase in zinc stearate level (Fig. 6).

(a) (b)

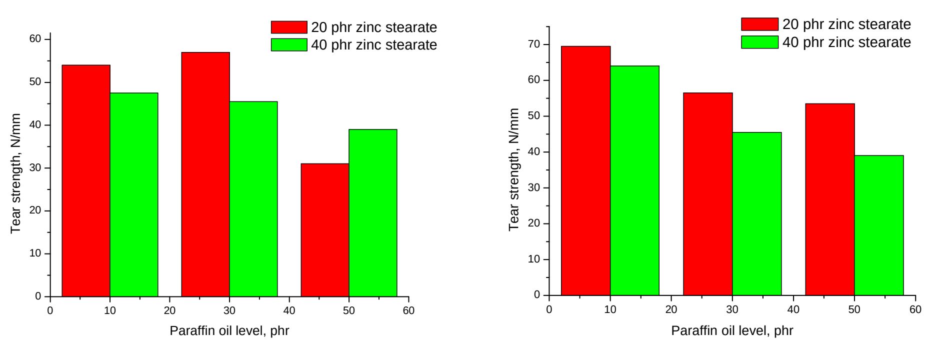

Fig. 6 - Changes in the tear strength according to the added plasticizer amounts.
(a) for EPDM blends with 0.5 % maleic anhydride
(b) for EPDM blends with 1.0 % maleic anhydride

Conclusions

In this work the action of the ionic and non-ionic plasticizers on the characteristics of ionic thermoplastic elastomers based on maleinized ethylene propylene terpolymers was investigated. Two types of maleinized ethylene propylene terpolymer elastomers with various levels (0.5 and 1.0) of maleic anhydride were used. Zinc sterate and paraffine oil were used as ionic plasticizer and non-ionic plasticizer, respectively. 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-ionizable elastomer chains leading to some increase in elasticity and elongation at break and decrease in hardness, tensile strength and tear strength.

The blend characteristics are dependent on the ionic and non-ionic levels. The best levels are selected according to the application fields of the concerned blend. Thus, the hard blends can be used for hard gaskets and joints, footwear elements, etc.; soft blends can be used for flexible membranes, hoses, flexible gaskets and joints, etc.

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