PHYSICAL-MECHANICAL PROPERTIES OF IONOMERS BASED ON MALEATED ETHYLENE PROPYLENE DIENE TERPOLYMER

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The action of zinc oxide, ionic/non-ionic plasticizers and fillers on the physical-mechanical characteristics of ionomers (ionic thermoplastic elastomers) based on maleinized ethylene propylene terpolymers was investigated. The blend characteristics are dependent on the levels and types of components of blend. The optimum compositions are selected according to the application areas of the concerned blend.

Keywords: ionic thermoplastic elastomers, maleated ethylene propylene diene terpolymer, physical-mechanical characteristics

1. Introduction

Ionomers or ionic thermoplastic elastomers are another class of polymers that exhibit activated multiple self-healing. Ionomers have up to 20 mol.% of ionic species incorporated into the polymeric structure, creating interactions or aggregates [1] that have a profound effect upon their mechanical [2-3] and physical properties [4]. These aggregates consist of several ion pairs known as multiplets [5-8] which form regions of restricted mobility or "physical crosslinking" sites. Above a threshold concentration of ionic species, these regions of restricted mobility overlap, creating multi-phase structures and morphologies [6]. It is the reversible nature of this physical crosslinking, however, that underpins this self-healing phenomenon and can be broadly understood in terms of the model proposed by Tadano et al. [9]. An ionomer is considered to be a two-phase system of ordered ionic clusters dispersed within a continuous semicrystalline polymer matrix. As the temperature is increased, the polymer exhibits an order-to-disorder transition as a result of which the ionic clusters, although persisting, lose order and strength. As the temperature is increased further, the semi-crystalline polymer matrix melts, even though the disordered

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clusters remain and continue to provide increased melt strength [10]. These transformations play a vital role in the self-healing process immediately after impact, as the thermal energy of impact dissipates, because their reversibility ensures rapid solidification while reordering of the ionic clusters and physical crosslinks follows more slowly. However, it is in fact the mechanical and viscoelastic properties arising from the variety of different morphologies which controls the self healing process. There are a few studies [11-15] 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 physical-mechanical properties which take place in the 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 [16].

A formulation of ionic thermoplastic elastomer compound consists generally of a neutralized ionomer, ionic plasticizer, non-ionic plasticizer, filler, antioxidants, other polymers, etc. [17].

This paper presents the development and physical-mechanical characteristics of an ionomer composition based on maleated ethylene propylene diene terpolymer (EPDM-g-MA). The extent of zinc oxide, the ionic / non-ionic plasticizers and fillers which influence the characteristics of the resulting products was determined with the purpose of selecting the optimum compositions of ionic thermoplastic elastomer based on EPDM-g-AM according to the application areas. All the laboratory prepared compounds were tested for the physical-mechanical characteristics.

2. Experimental

EPDM-g-MA elastomers exhibit the peculiar features of EPDM elastomers, but they can react with divalent metal oxides salts leading to crosslinking by ionic bonds. In this paper EPDM-g-MA elastomer Royaltul 485 containing 0.5% MA having semicrystalline structure and as neutralizing agents of the ionic groups - zinc oxide in the presence of stearic acid were used. The reaction between EPDM-g-AM and ZnO is presented in Fig. 1.

In addition to EPDM-g-MA, zinc oxide and stearic acid, the compositions also contain the following elements: ionic plasticizer (zinc stearate), nonionic plasticizer (paraffin oil), fillers (precipitated silica Perkasil, chalk and carbon black HAF) and antioxidant (Irganox 1010 - pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)).

Thermoplastic compositions were prepared by melt blending technique, on a laboratory electrically heated roller mill equipped with a cooling system. The ingredients were weighed according to the processing formulations (see Tables 1

and 2).

The blend constituents were added in the following sequence: roll binding of EPDM-g-AM (5 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^{o}C.

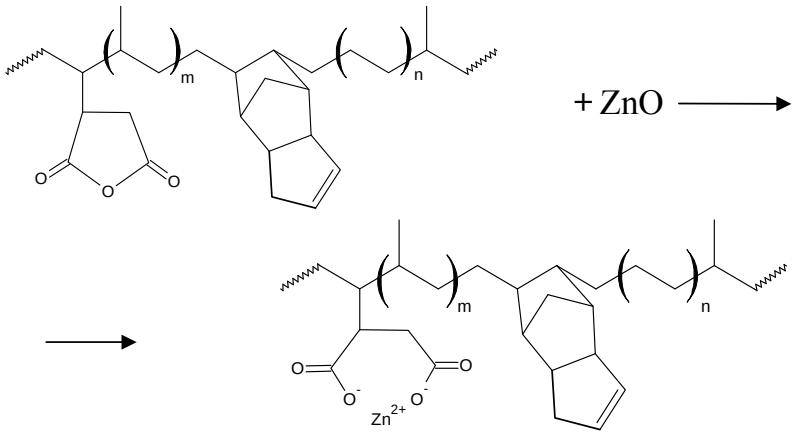

Fig. 1. Reaction between EPDM-g-AM with ZnO leading to the crosslinking by ionic bonds

Plates for the physical-mechanical tests were obtained by compression molding into 2x150x150 mm sheets on a laboratory electrical press at a temperature of 160^{o}C and pressure of 150 MPa for 10 minutes. The molded samples were stored away from light, at room temperature.

Tensile strength and tearing strength tests were carried out with a Schoppler strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2005, respectively angular test pieces (type II) in according to SR EN 12771/2003. Hardness was measured by using a hardener tester according to ISO 7619-1/2004 using 6 mm thick samples. Elasticity was evaluated with a Schob test machine using 6 mm thick samples, according to ISO 46662/1986. Residual elongation is the elongation of a specimen measured 1 minute after rupture in a tensile test. It was calculated using the formula 1:

$$\text{Residual elongation (\%)} = [(L-L_0)/L_0] \times 100 \quad (1)$$

where: L_0 is the initial length between two marks and L is the length between the marks 1 minute after the sample broke in a tensile test.

The densities of elastomer samples were determined by hydrostatic weighing method, according to SR ISO 2781/2010. By this method, the volume of a solid sample is determined by comparing the weight of the sample in air to the weight of the sample immersed in a liquid of known density. The volume of the sample is equal to the difference in the two weights divided by the density of the liquid.

Table 1

Formulations of rubber blends based on EPDM-g-MA Royaltuf 485

Ingredients/Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
EPDM-g-AM Royaltuf 485, g	100	100	100	100	100	100	100
Zinc oxide, g	-	5	10	20	20	20	20
Stearic acid, g	-	0.5	1	2	2	2	2
Zinc stearate, g	-	-	-	-	20	40	60
Precipitated silica Perkasil, g	-	-	-	-	30	30	30
Paraffin oil Texpar 22, g	-	-	-	-	-	10	10
Antioxidant Irganox 1010, g	1	1	1	1	1	1	1

Table 2

Formulations of rubber blends based on EPDM-g-MA Royaltuf 485

Ingredients/Sample	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
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 Perkasil, g	30	60	90	60	30	30	60	-	-	30
Chalk, g	-	-	-	30	60	30	-	60	30	-
Carbon black HAF, g						30	30	30	60	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

Determining abrasion resistance was done according to STAS 6699/1989, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasivepaper. A wearing tester with abrasive cloth and abrasive based on normal electro-corundum on dressed cloth substrate with granulation of 212–80 μm (PE 80) according to STAS 1469-83, whose abrasiveness must be of 180–220 mg control rubber. The samples used

were obtained from rolled blends and pressed by cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.
Accelerated ageing trial was done according to SR ISO 188/2007 using the hot air circulation oven method. Similar samples to those used for tensile testing and for hardness determination were used. Test duration was of 7 days and temperature of 70±1ºC. The results were compared with those from samples not subjected to ageing.

3. Results and discussion

The physical-mechanical properties of rubber blends based on EPDM-g-MA Royaltuf 485 obtained is presented in Table 3 and Table 4.

Table 3

Characteristics of rubber blends based on EPDM-g-MA Royaltuf 485

Characteristics/Sample	1	2	3	4	5	6	7
Hardness, ºShA	71	73	74	74	83	76	84
Elasticity, %	46	40	40	42	34	38	30
100% Modulus, N/mm^2	1.9	1.9	2	2.2	3.7	2	3.5
300% Modulus, N/mm^2	2.5	2.7	2.9	3.2	6.7	3	5.5
500% Modulus, N/mm^2	3.6	4	4.9	5.8	11.4	5.1	8.6
Tensile strength, N/mm^2	7.2	7.3	14.3	15.3	12.9	9.7	9.5
Elongation at break, %	764	700	727	700	567	740	567
Residual elongation, %	172	163	148	156	115	151	131
Tear strength, N/mm	34.5	39	40	44	63	41	52

Analyzing blends 1-4 it is noticed that upon increasing the amount of ZnO introduced in blends, due to the property of carboxyl groups on the macromolecular chain to react with oxides of bivalent metals (see Fig. 1), ionic crosslinks are formed, similar to sulfur bridges in cured rubber. This ionic crosslinking has led to an increase in hardness (from 71 to 74°ShA), an increase in modulus, tensile strength and tear strength. Blend 4 exhibited the best characteristics.

As a result of introducing some ingredients in blends such as plasticizers and fillers, a decrease of tensile strength and elasticity and hardness increase can be noticed (see blend 4 compared to blends 5-17).

Adding the nonionic plasticizer Paraffin oil Texpar 22 (see blends 5 and 8) has led to a decrease in hardness, modulus, tensile strength and tear strength because 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 [17].

With the increase of ionic plasticizer amount – zinc stearate in the blend (see blends 5-7) an increase in hardness, modulus tear strength is noticed because 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.

Table 4

Characteristics of rubber blends based on EPDM-g-MA Royaltuf 485

Characteristics/Sample	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Hardness, ºShA	74	89	93	87	81	81	84	82	82	86
Elasticity, %	34	28	30	34	34	30	30	32	28	30
100% Modulus, N/mm^2	2.1	3.6	5.7	3.7	3.1	3.6	4.6	2.8	3.5	4
300% Modulus, N/mm^2	3.7	-	-	-	4.8	6	8.4	5.5	6.6	7.5
500% Modulus, N/mm^2	6.7	-	-	-	-	-	-	7.2	-	-
Tensile strength, N/mm^2	8.2	4.1	5.7	3.7	5.5	8	9.4	7.8	8.4	8.3
Elongation at break, %	580	167	153	193	433	500	406	593	473	447
Residual elongation, %	61	32	16	13	44	55	36	66	60	68
Tear strength, N/mm	43	41	55	42.5	44	48.5	62	54	62	63
Specific weight, g/cm~~3~~	1.11	1.18	1.24	1.26	1.27	1.26	1.24	1.28	1.24	1.24
Resistance to abrasion, mm~~3~~	135	190	240	231	205	175	137	194	155	145
Resistance to accelerated ageing 70Cx168h										
Hardness variation, ºShA	-2	-1	+2	+2	-2	-5	-1	-5	-3	-2
Tensile strength variation, %	+15	+2	+18	+18	+16	+20	+15	-19	+4	+11

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 the latter. The appearance of these bonds determines a reinforcing effect of rubber composition and the improving of modulus, tear strength or of tensile strength [18]. For obtained blends it was noticed that when the precipitated silica filler increases (see blends 8-10) there is an increase in hardness, 100% modulus, and tear strength, as well as a decrease in elongation at break and residual elongation. Comparing blend 10, which contains an amount of 90 phr precipitated silica filler (parts per 100 rubber parts), with blends 11-17 which contain 90 phr fillers, it is noticed that their physical-mechanical properties have similar values, but an increased hardness can be noticed in blends with a higher precipitated silica or HAF blends, indicating that the precipitated silica or HAF induces a higher reinforcing effect than chalk because they are active fillers. Blends containing HAF have good values for resistance to abrasion, tensile strength and tear strength. Optimal properties were obtained for blends 14 and 17 which only contain HAF active filler and precipitated silica.

4. Conclusions

In this paper the action of the ionic/non-ionic plasticizers and fillers on the characteristics of ionic thermoplastic elastomers based on maleinized ethylene propylene terpolymers was investigated. The blend characteristics are dependent on the levels and types of components of blend. The optimum compositions are selected according to the application areas of the concerned blend. EPDM-g-AM based ionic thermoplastic elastomer compositions can be used for hard gaskets and joints, footwear elements, flexible membranes, hoses, flexible gaskets and joints, etc.

R E F E R E N C E S

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