THE EFFECT OF FILLER ON CHARACTERISTICS OF SOME ETHYLENE VINYL ACETATE COPOLYMER COMPOSITES

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In this research work, the influence of the amount and type of filler on characteristics of some ethylene vinyl acetate copolymer (EVA) composites was studied. Materials used in the study were: ethylene vinyl acetate copolymers Elvax 260 (27.8% wt% vinyl acetate content), four types of filler (precipitated silica Ultrasil VN3, carbon black HAF, precipitated kaolin and precipitated chalk) and other ingredients (zinc oxide, acid stearic, polyethylene glycol, antioxidant, dibenzoyl peroxide Perkadox 14-40B, polyfunctional monomer). The blends were prepared by means of blending technique, on an electrically heated laboratory roller mill at 70±5°C, friction 1:1.1 and total blending time 6-14'. Samples were crosslinked using two methods: by classic method in the presence of peroxides and by electron beam irradiation. The minimum torque and maximum torque increased with increasing filler content, and the highest values were obtained for the mixtures containing precipitated silica. Increasing the filler content tended to increase the hardness, 100% modulus, tear strength and tensile strength of the composites. The best results were obtained by adding active fillers - precipitated silica and carbon black - to samples crosslinked with peroxides, as well as by electron beam irradiation.

Keywords: ethylene vinyl acetate copolymer, filler, accelerated electrons, physical-mechanical characteristics, curing characteristics

INTRODUCTION

The importance of fillers in the rubber compounds is well known. Fillers can be classified into black and non-black. Soon after carbon black was discovered to be an active filler in rubber, at the beginning of this century, it became one of the most important components in the manufacture of rubber products, with a consumption second only to rubber itself. Non-black fillers are classified as: fillers used mainly to reduce cost, semi-reinforcing fillers and reinforcing fillers used to achieve high, performance in non-black products (Evans, 2001).

Fillers are widely used to enhance the performance of rubbers and other polymeric materials. Filler characteristics such as size and shape of particles and aggregates, chemical nature and porosity of surface, dispersibility and tendency to agglomerate and form secondary filler networks determine its effect on rubber compounds. Surface activity relates to the compatibility of the filler with a specific elastomer and the ability of the elastomer to adhere to the filler. If the size of the filler particle greatly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Fillers with particle size greater than 10,000 nm are therefore generally avoided because they can reduce performance rather than extend or reinforce it. Fillers with particle size between 1,000 and 10,000 nm are used primarily as diluents and usually have no significant effect, positive or negative, on rubber properties. Semi-reinforcing fillers range from 100 to 1000 nm. The truly

reinforcing fillers (active fillers), which range from 10 nm to 100 nm, can significantly improve rubber properties (Evans, 2001; Franta, 1989).

In this research work, the influence of the amount and type of filler on characteristics of some ethylene vinyl acetate copolymer (EVA) composites was studied. Four types of filler used in the study were: precipitated silica (average particle size: 10-100 nm, surface area 40-170 m^2/g), carbon black HAF (average particle size: 20- 36 nm, surface area 80 m^2/g), precipitated kaolin (average particle size: 200-500 nm, surface area 45-130 m^2/g) and precipitated calcium carbonate (average particle size: 40-700 nm, surface area 8-74 m^2/g). It is noticed that precipitated kaolin and precipitated calcium carbonate are semi-reinforcing fillers ranging from 100 to 1000 nm and precipitated silica and carbon black HAF are reinforcing fillers, which range from 10 nm to 100 nm and may significantly improve rubber properties (Evans, 2001; Franta, 1989).

Samples were crosslinked using two methods: by classic method in the presence of peroxides, and by electron beam irradiation. The radiation induced grafting and crosslinking of polymers are new techniques applied in modifying polymers. Use of radiations as power source is justified by the limited classic resources, on the one hand, and a number of specific benefits, on the other hand, such as: (1) removing the curing agents, (2) obtaining new high purity materials, (3) a fast process which enables an accurate monitoring, (4) an effective and uniform curing of the whole rubber body because of the high penetrating ability of radiation, (5) lack of wastes (Manaila *et al.*, 2008; Manaila *et al.*, 2007; Craciun, 2013).

Research papers have been published suggesting that appropriate polyfunctional monomers (PFMs), also called coagents, added in polymer matrix, could be used to obtain desired physical properties of the blend at lower irradiation doses. Coagents are multifunctional organic molecules which are highly reactive towards free radicals. Previous studies (Stelescu *et al.*, 2013; Stelescu *et al.*, 2012) show that the most efficient PFMs in the EVA case were polyfunctional monomer triallylcyanurate (TAC).

EXPERIMENTAL

Materials

Materials used in the study: (1) EVA copolymer Elvax 260 (27.8% wt% VA content, flow index (MFI) 5.5 g/10 min at 190°C and 2.16 kg load), (2) dibenzoyl peroxide Perkadox 14-40B (1.60 g/cm^3 density, 3.8% active oxygen content, 40% peroxide content, pH 7) and polyfunctional monomer triallylcyanurate Luvomaxx TAC DL 70 (TAC) (26% percentage of ash, density 1.34 g/cm^3, 30% active synthetic silica). as vulcanizing agents, (3) four types of filler: precipitated silica Ultrasil VN3, carbon black HAF, precipitated kaolin and precipitated chalk, (4) other ingredients (zinc oxide, stearic acid, polyethylene glycol, antioxidant Irganox 1010 - pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate).

Sample Preparation

EVA compounds which were filled with different dosage of precipitated silica Ultrasil VN3, carbon black HAF, precipitated kaolin and precipitated chalk were prepared by means of blending technique, on an electrically heated laboratory roller mill. For preparation of polymeric composites, the blend constituents were added in the following sequences and amounts: 100 parts EVA roll binding (2'), embedding 3 phr (parts to 100 parts rubber) PEG 4000, 1 phr Irganox 1010 antioxidant, 5 phr zinc oxide,

0.5 phr stearic acid (2'), adding 10, 30, and 50 phr fillers, respectively (2–4'), embedding 3 phr TAC and homogenization of blends and removing from the roll in the form of sheet (2-4'). Process variables: temperature 70±5°C, friction 1:1.1 and total blending time 6-12'. Plates required for physico-mechanical tests have been made by compression molded, using a electrically heated hydraulic press, at a temperature of 160°C, pressure of 150 MPa, to obtain sheets of dimension 150x150x2 mm^3. Samples were crosslinked using two methods: by classic method in the presence of peroxides and by electron beam irradiation. In samples crosslinked using the classic method, 8 phr dibenzoyl peroxide Perkadox 14-40B was added as vulcanizing agent and all cure times were adjusted to bring the respective cures to T_{90} for each sample—the vulcanization time was measured by means of Monsanto Rheometer (see Tables 1-2). For samples crosslinked by electron beam irradiation, plates have been made by compression molding for 5'. Then, the samples were packed in a polyethylene film and were irradiated at 100 kGy in the ILU-6M cavity electron accelerator.

Laboratory Tests

The cure characteristics of the compounds were determined by an oscillating disk rheometer (Monsanto), at 160°C and 30 min, according to the SR ISO 3417/1997. Delta torque or extent of crosslinking is the maximum torque (MH) minus the minimum torque (ML). Scorch time (t_{s2}) is taken as the time to reach 2% of the delta torque above minimum. Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum. The cure rate index (CRI) of the recipe was calculated according to the following formula:

$$\mathrm{CRI} = 100/(t_{90} - t_{s2}) \tag{2}$$

The cure rate index is a measure of the rate of vulcanization based on the difference between optimum vulcanization time, t_{90} and incipient scorch time, t_{s2}.

Mechanical properties of the vulcanizates were measured on a Schopper tensile tester with a nominal rate of the traverse of the moving grip of 460 mm/min. Modulus at 100% strain, tensile strength, and elongation at break tests were carried out according to the conditions described in ISO 37/2012, on dumb-bell shaped specimens of Type 2. Residual elongation is the elongation of a specimen measured 1 min after rupture in a tensile test. It was calculated using the formula:

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

where L_0 is the initial length between two marks and L is the length between the marks 1 min after the sample broke in a tensile test. Tearing strength tests were carried out using angular test pieces (type II) according to SR EN 12771/2003. Hardness of the vulcanized materials was measured using the Shore A scale with vulcanized samples of 6-mm thickness, by using a hardener tester according to ISO 7619-1/2011. Elasticity was evaluated with a Schoob test machine using 6-mm thick samples, according to ISO 4662/2009. All measurements were taken several times and the resulting values were averaged on three to five measurements.

RESULTS AND DISCUSSION

Cure Characteristics of the Blends

Tables 1 and 2 present the results of rheological measurements. For every measured sample, ML, MH, optimum curing time (T90), shorter time (t_{min}), scorch time (t_{s2}) and CRI were determined by reading the variables on the curing curves obtained with the

Monsanto rheometer. It is found that in blends filled with reinforced (active) fillers such as carbon black and precipitated silica (Table 1), upon increasing the amount of filler, an increase of MH, M90 and CRI and a decrease of curing time, t_{90}, occur. In blends where semi-reinforced fillers were added (Table 2), it is found that upon increasing the amount of filler, a slight decrease of t_{90} and a slight increase of CRI occur.

Table 1. Rheometric characteristics of samples filled reinforcing fillers: precipitated silica and carbon black

Rheometric characteristics/ filler type and amount	Control	Precipitated silica			Carbon black		
		10 phr	30 phr	50 phr	10 phr	30 phr	50 phr
The minimum torque ML (dNm)	1	0.2	13.0	21.2	0	11.8	13
The maximum torque MH (dNm)	35	40.5	54.1	70	38	41.8	48
Delta torque ΔM (dNm)	34	40.3	41.1	48.8	38	30	35
M90 (dNm)	31.6	36.5	50	65.9	34.2	38.8	44.5
Curing time, t_{90} (min)	21'45''	20'45''	19'30''	19'15''	21'30''	20'	19'30"
Shorter time, t_{min} (min)	45''	1'	40''	35''	1'	1'	40''
Scorch time, t_{s2} (min)	2'45''	2'30''	1'20''	1'15''	2'45''	2'30''	2'30''
Cure Rate Index, CRI (min^{-1})	5.26	5.48	5.50	5.55	5.48	5.71	5.88

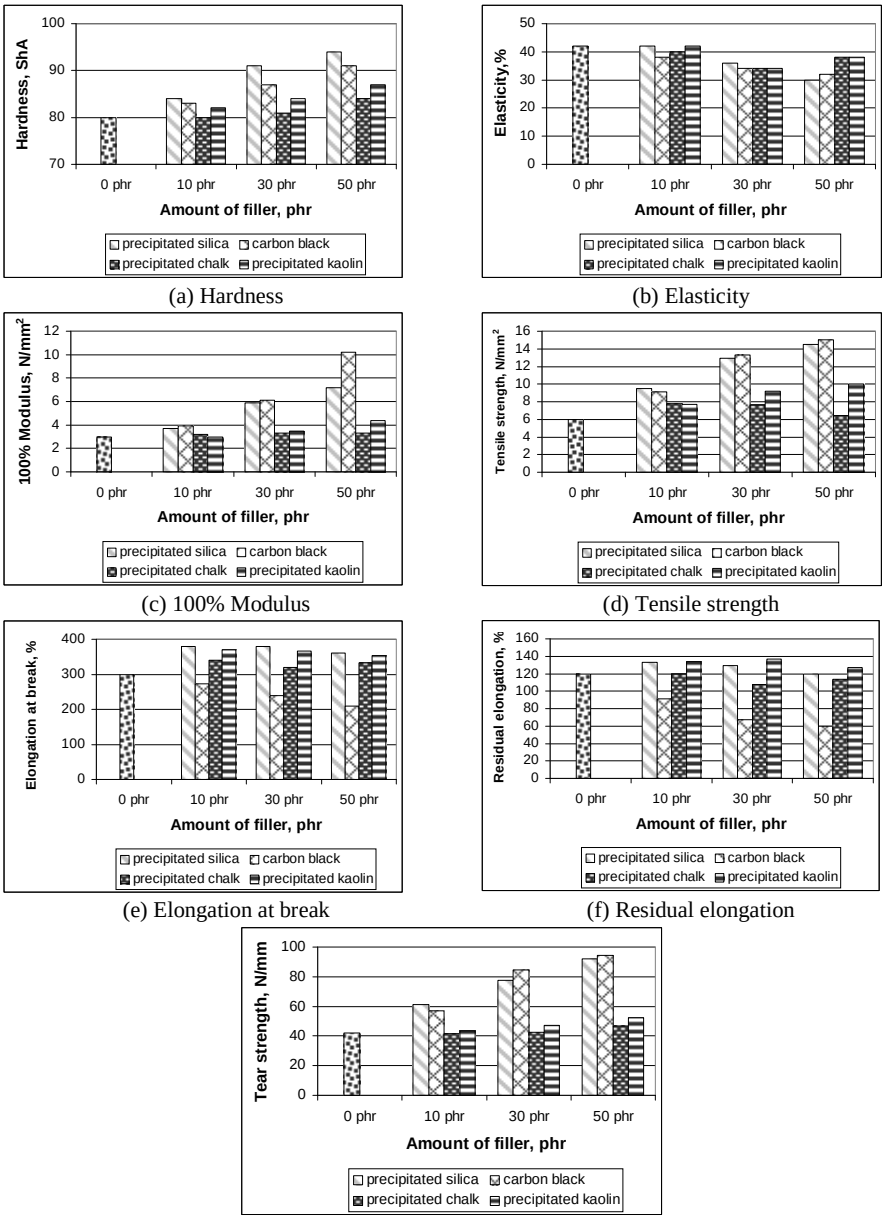
Table 2. Rheometric characteristics of samples filled with semi-reinforcing fillers: precipitated chalk and precipitated kaolin

Rheometric characteristics / filler type and amount	Precipitated chalk			Precipitated kaolin		
	10 phr	30 phr	50 phr	10 phr	30 phr	50 phr
The minimum torque ML (dNm)	27	28	21.8	9.5	10	10
The maximum torque MH (dNm)	47	49	45	38	42	46
M90 (dNm)	45	46.9	42.7	35.15	38.8	42.4
Delta torque ΔM (dNm)	20	21	23.2	28.5	32	36
Curing time, t_{90} (min)	21'15''	20'30''	20'30''	21'15''	20'45''	20'15''
Shorter time, t_{min} (min)	1'	40''	45''	45''	1'	1'
Scorch time, t_{s2} (min)	2'15''	2'	2'15''	2'15''	2'	2'
Cure Rate Index, CRI (min^{-1})	5.26	5.40	5.48	5.26	5.33	5.48

Physico-Mechanical Characteristics of the Blends

In Figure 1 are presented the results of the variations of physical-mechanical properties with the increase of the filler amount in composites and in Table 3 are presented physical-mechanical characteristics of samples filled with 50 phr precipitated silica and 50 phr carbon black respectively, crosslinked by irradiation with 100 kGy. From the obtained results, it is noticed that for blends filled with reinforced (active) fillers such as carbon black and precipitated silica and crosslinked using the classic method (Figure 1), upon increasing the amount of filler, an increase in hardness, 100% modulus, tensile strength and tear strength, and a decrease of elasticity occur. Comparing characteristics of the control blend with those of blends containing 50 phr active fillers, significant improvements of hardness, 100% modulus, tensile strength, and tear strength characteristics were found by adding carbon black and precipitated silica fillers, respectively, both by crosslinking using the classic method (Figure 1), and by crosslinking

by electron beam irradiation at a dose of 100 kGy (Table 3). In blends containing semi-reinforced fillers, upon increasing the amount of filler, only a slight improvement of hardness, 100% modulus, tensile strength, elongation at break and tear strength is noticed.



(a) Hardness (b) Elasticity

(c) 100% Modulus (d) Tensile strength

(e) Elongation at break (f) Residual elongation

(g) Tear strength

Figure 1. The variations of mechanical properties with the increase of the filler amount in composites

Table 3. Physical-mechanical characteristics of samples filled with reinforcing fillers: precipitated silica and carbon black, crosslinked by irradiation with 100 kGy

Physical-mechanic characteristics / filler type and EB dose	Control	Precipitated silica	Carbon black
Hardness, °ShA	86	96	91
Elongation, %	37	38	30
100 % Modulus, N/mm^2	4.1	10.6	9.5
Tensile strength, N/mm^2	14.6	15.8	14.6
Elongation at break, %	390	240	333
Residual elongation,%	175	79	127
Tear strength, N/mm	60	105	86

CONCLUSIONS

As a result of this study, it is found that in blends based on EVA filled with reinforced (active) fillers such as carbon black and precipitated silica, upon increasing the amount of filler, an increase in MH, M90, CRI, hardness, 100% modulus, tensile strength and tear strength as well as a decrease in curing time, t_{90}, and elasticity occur. In EVA blends where semi-reinforced fillers were added, it is found that upon increasing the amount of filler, a slight increase in t_{90} and a slight decrease of CRI, hardness, 100% modulus, tensile strength, elongation at break and tear strength occur. The best results were obtained by adding active fillers - precipitated silica and carbon black - to samples crosslinked with peroxides, as well as by electron beam irradiation.

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