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Natural and synthetic rubber / waste – EVA (Ethylene-Vinyl Acetate) composites for sustainable application in the footwear industry

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Abstract

The production of natural and synthetic rubber / waste – EVA (Ethylene-Vinyl Acetate) composites was performed using natural rubber, styrene-butadiene rubber or acrylonitrile-butadiene rubber and 10 – 20 parts per hundred rubber (phr) of waste. Several physical and mechanical properties of the composites were further determined according to the requirements of the footwear sector. Rheometry and aging tests were also performed. The effects observed on the crosslinking formation during vulcanization of each composite were negligible. The flexion, density, hardness and abrasion of all composites, produced at a laboratory (10 – 20 phr) and industrial scale (20 phr), were not significantly affected by the addition of waste. The tear strength and the tensile strength were the most affected properties, namely for the Natural Rubber/Waste – EVA composites, where EVA acted as filler (tear strength > 13 N mm⁻¹, breaking load > 15 MPa). The study confirms the possibility of a sustainable application of EVA– waste in the footwear industry through the production of eco-composites.

Keywords

EVA; Composites; Rubber; Soles.

Abbreviations

CTCP – Portuguese Footwear Technological Centre

EVA – Ethylene–vinyl acetate

MBTS – Mercaptobenzothiazole disulphide

NBR – Acrylonitrile-butadiene rubber

NR – Natural rubber

PEG – Polyethylene glycol

PU – Polyurethane

PVC – Polyvinyl chloride

SBR – Styrene-butadiene rubber

TMTD – Tetra methylthiuram disulphide

VA – Vinyl acetate

1. Introduction

For the production of a shoe around 40 different raw-materials might be used, but traditionally, leather, rubber (natural and synthetic), foam, plastic and textile are employed (Lee and Rahimifard, 2012; Tatàno et al., 2012). In the last decade, the introduction of synthetic materials like polyvinyl chloride (PVC), polyurethane (PU) and ethylene–vinyl acetate (EVA) has been observed. After vulcanization, the molecular structure of the resulting thermosetting plastic waste presents permanent crosslinks which makes it very difficult to recycle (Correia et al., 2011); accordingly, a significant amount of the waste produced relates to such materials. In fact, the use of thermosetting polymers has increased dramatically in the last few decades, which makes the study of recovery options quite relevant, namely considering the integration within the industrial activities due to the high costs associated to waste management (Lima et al., 2010).

EVA is a copolymer formed by the monomers ethylene and vinyl acetate (VA) with relevant resin and rubber properties that led to its use for several applications (Haque and Pracella, 2010; Yin et al., 2006). A large range of articles using EVA are being produced in the footwear industry, including soles and insoles with EVA presenting VA contents varying in general from 18 to 20% (Mills, 2007).

Due to the increasing amount of EVA wastes in this sector, that end up being landfilled, alternative management strategies should be evaluated.

The patent by Borredon et al. (1994) describes the treatment of polymeric materials containing EVA waste (from the footwear industry), previously ground, in an aromatic or halogenated solvent, followed by treatment with ozone. The patent shows that it is possible to break certain chemical bonds of the polymer without damaging the functional groups and therefore reuse the end product in the production of soles by mixing it with other virgin polymers (e.g. SBR). Yang et al. (2012) reports the

application of combustion and pyrolysis processes for the recovery of fibres, fuels and energy from composite waste materials. No studies were however found on the thermal treatment of EVA waste, aiming the recovery of fibres. The use of EVA waste for the production of materials to be used in construction and civil engineering has also been studied. Lima et al. (2010) evaluated the use of construction and demolition waste as well as EVA waste as replacers of the natural coarse aggregate for the production of a more environment-friendly concrete. Mixtures with different aggregate substitution rates were made (including 25 to 50 Vol.% of waste) and both wastes showed good results and enabled the production of lightweight concrete with semi-structural properties.

Due to high associated costs and the need of specialized staff to perform previous referred recovery routes, the physical/mechanical treatments are still the most appealing. The mechanical processing usually involves grinding and or milling EVA waste to obtain relatively uniform small particles of EVA for incorporation in rubber compounds or composites. Moreira and Soares (2002) evaluated the effect of using different amounts of EVA waste in rubber blends with acrylonitrile-butadiene rubber (NBR) and found that EVA waste allowed the reinforcement of the NBR matrix, with the best results being observed using 50 parts per hundred rubber (phr) of EVA waste. Oliveira et al. (2004) evaluated the properties of composites of natural rubber (NR) with EVA waste (up to 60 phr) and the results showed that the introduction of EVA waste presented a minor impact on the mechanical properties of the materials (tensile strength higher than 8 MPa and minimum elongation at break greater than 300 %), showing the potential of recycling the waste within the footwear industry. Stael et al. (2001) evaluated the production of sugar cane bagasse waste – EVA composites by mixing, and after processing the material at 200 °C, 3.5 MPa and 15 min to produce plates. The

results showed that it was possible to adjust the mechanical performance of the composites to reproduce the behaviour of particle boards based on wood materials, indicating the adequacy of using EVA waste also with that purpose.

The adoption of sustainable production approaches in industrial activities can have significant impacts for the environmental, economic and social aspects associated with the company's activities (Alkaya and Demirer, 2014).

Focusing on an environmental point of view, a sustainable recovery option for such waste type would be to use it as raw material within the industrial production process (contributing for a sustainable production), because it allows reducing the waste generation at the source and the environmental impacts of incorrect waste management. On the other hand, sustainability from an economic perspective might also be possible because the reduction of transportation and elimination costs and also of production costs (by lowering raw material costs) can be achieved. In addition, an increased stability of the companies (supported on the environmental and economic gains) can be obtained and additional opportunities can be established, leading to jobs creation, with relevant social impacts.

Most of the previous studies on physical treatment are still restrictive because they focused mostly on experimental laboratory work and on using one elastomer/material for the production of the composites. In agreement, it would be extremely relevant to evaluate the production of the composites using different natural and synthetic materials and also to conduct pilot scale/industrial scale production of the products, to validate the potential for the sustainable recovery in the footwear industry.

Taking into account what was previously referred, the main goals of the present work were to: i) evaluate the production of rubber /waste – EVA composites using 10 and 20 phr of EVA with natural rubber, acrylonitrile-butadiene rubber and styrene-butadiene

rubber; ii) characterize and evaluate the behaviour of the eco-composites taking into account the most important properties for application in the footwear industry; and, iii) select the best conditions, produce three types of soles at an industrial scale and characterize them aiming their future sustainable use by this industry.

2. Experimental

2.1. Materials

The EVA waste used was a crumbled material supplied by the company Procalçado - Producer of Footwear Components, S.A., previously processed in a 2 roll mixing mill (Roca & Guix) (Fig. 1). The three elastomers, natural rubber (NR), acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR), were also supplied by the company Procalçado. The composites were prepared considering the incorporation of 10 and 20 phr of EVA waste in relation to the total amount of virgin elastomer. SBR (grade SBR 1502) and NBR (grade NBR 35 LM) materials were from Kumho petrochemical® and presented a Mooney viscosity between 45 and 50 MU (Mooney Units). NR (grade CSR L) was from Cambodia and presented a Mooney viscosity between 55 and 60 MU. The elastomers were formulated using the chemicals listed in Table 1 (rubber grade). The established references for the elastomers were as follows: SBR – L120, NBR – N383 and NR – L159.

2.2. Composites preparation

The composites were prepared in a two roll mixing mill (Roca & Guix) (Fig. 2A). The calculated amount of EVA waste (10 or 20 phr) was slowly added to the mill

(previously operating during 1 h to stabilize the temperature) according to the following procedure: i) 600 g of elastomer were introduced in the mixing mill with an opening between cylinders of 8 and were subjected to 10 passages (in this study, one passage is considered as being the passage of all the material through the cylinders); ii) 150 g of the virgin material were after mixed with the waste in the mill with an opening between cylinders of 4 and 8 passages were performed; iii) the remaining 450 g were after mixed with the previous mixture at a cylinder opening of 4 and 8 additional passages were performed; iv) finally, the cylinder opening was changed to 8 and 5 passages were performed.

After incorporating the EVA waste, plates (rectangular vulcanized portions) or soles were produced through compression moulding of the mixture using a laboratory press (Brand Roca & Guix), at 165 °C and 180 bar (Fig. 2B). Plates and soles of the virgin materials were also produced for comparison and aging tests were performed using the plates. The materials were further characterized (according to section 2.5).

For the production of soles, considering the good results obtained during the analysis of the plates, only the composites of 20 phr EVA were taken into account. The soles were produced at an industrial scale and, therefore, larger amounts of the mixture were prepared; however, the incorporation was made using a two roll mixing mill (Brand Metalurgica de Benfica, 1.5 m) and a press of higher capacity (Talleres Candela PL-250-BE), similar to those used for the production of plates (Fig. 2).

For all the parameters studied, the samples were identified with the sample identification (ID) number presented in Table 2. In the case of the flexion, tearing strength and tensile strength properties, the identification number includes, in addition, the letter L or T if samples were taken on the longitudinal or transversal direction, respectively.

2.3. Aging tests

In order to evaluate the effect of aging, one plate of each composite including 20 phr of EVA was used. The material was subjected to aging at a temperature of 70 °C (Heraeus Instruments oven) during a period of 24 h and then the physical and mechanical properties were evaluated.

2.4. Rheometry

A rheometry test was conducted before producing the plates in the press, to evaluate if it was necessary to conduct a readjustment of the adopted formulation. For that purpose, a rheometer (Gibitre Rheocheck Oscillating Disk rheometer) was used under the following conditions: $T = 190\text{ °C}$, $t = 3\text{ min}$. After ensuring that the temperature was stable, a sample of 8 – 12 g was analysed in the equipment. Two samples of virgin materials (0 phr, Table 2) and four samples of each composite were analysed.

2.5. Determination of the physical and mechanical properties

2.5.1. Flexion

This property indicates the resistance to successive folding and unfolding movements and it was measured in agreement with BS 5131-2.1:1991. For this property, longitudinal (L) and transversal (T) samples (three replicates) of the plates were taken. In the case of the soles, due to its function, three replicates were also taken, but only in one direction. Results are presented as mean values.

2.5.2. Density

The density test was performed according to ISO 2781, Method B-2008, using a pycnometer, namely to evaluate the uniformity between the various samples. For each plate and sole, two samples were analysed and results are presented as mean values.

2.5.3. Hardness

The hardness affects the comfort of the sole. This property was measured taking into account the procedures employed by the national entity - Portuguese Footwear Technological Centre (CTCP). The equipment used for this measurement was a durometer (Afri Shore A Hardness Tester). The values presented are mean values of five measurements in all cases.

2.5.4. Tear strength

Tear strength (resistance to tearing) is a very relevant parameter considering soles production and it was determined according to EN ISO 20872-2001. The equipment used was a dynamometer (Pegasil ZIPOR, Model Jupiter). In the case of the soles, three replicates were also taken, but only in the transversal direction. Results are presented as mean values.

2.5.5. Tensile strength

This is another important parameter and it was determined in agreement with EN ISO 22654 – 2002. The equipment used was a dynamometer (Pegasil ZIPOR, Model Jupiter). In the case of the soles, three replicates were also taken, but, only in the longitudinal direction. Mean values are presented. The parameters measured were breaking load, elongation and module.

2.5.6. Abrasion

The resistance to friction, by scraping or erosion, was determined according to EN ISO 20871 2001. For that purpose, samples of each composite were placed in a specific equipment (Pegasil ZIPOR, abrasion machine), that consists on a roll with a harsh

surface that while rolling wears the sample that contacts with its surface. The results are presented as mean values and take into account the density results.

3. Results and discussion

3.1. Rheometry

Table 3 shows the rheometry results obtained from the analysis of the plates, for the three composites as well as for the virgin materials.

Comparing with the virgin material (sample 1), it can be seen that for the composites of natural rubber (samples 2 and 3) a sharp drop in viscosity (decreased minimum torque) was observed. This reduction can be attributed to the effect called peptization, caused by the mechanical action of the cylinder through the various passages of the material that affects the molecular chains of the polymer (Hoffman, 1989). Therefore, the decrease should not be due to EVA incorporation but from the breaking of bonds of the elastomer by the mechanical action of the mill. The results for the NBR and SBR composites (5–6 and 8–9 samples, respectively) corroborate this hypothesis since no significant changes were observed which indicates that the EVA incorporation did not affect this property and also that those materials were less susceptible to the mechanical stress caused by the mill, compared to the NR. For the maximum torque (MH), a slight reduction was observed for the NR composite, expressing a reduction in the number of crosslinks formed; the pre- vulcanization time (t_{s5}) and optimal vulcanization time (t'_{90}) showed negligible variation. In the case of the NBR composites, slightly lower values of t_{s5} and t'_{90} were found compared to the virgin material, showing a higher vulcanization rate; the maximum torque was not significantly affected. In what concerns

the SBR composites, the main effects were observed for the Ts5, with a higher pre-vulcanization time required compared to the virgin material; however, similar optimum time and lower maximum torque (MH) were obtained, which indicates that an interaction of the EVA waste occurred, affecting the number of crosslinks formed. Overall, the incorporation of EVA seemed to affect the vulcanization of each composite, and, consequently, the crosslinking formation; the effects were different depending upon the virgin elastomer used. Nevertheless, the changes observed were in general not significant and therefore no readjustment of the formulation was conducted.

3.2. Physical and mechanical properties – laboratory scale samples

The results for the flexion, density and hardness of the composites showed no relevant effects of EVA incorporation that could affect the performance of the material for application in the footwear industry.

The flexion test showed no effect (mostly 0.0 mm / kcicle determined), with all values within the requirements set by CTCP)(0.1 mm / kcicle). The mean density varied between 1.05 g cm^{-3} and $1.17 \pm 0.01 \text{ g cm}^{-3}$, with the highest values being observed for the NBR composites ($1.13 - 1.17 \text{ g cm}^{-3}$) and the lowest values for the NR composites ($1.05 - 1.06 \text{ g cm}^{-3}$). The negligible variations observed for the three composites regarding density indicate uniformity between samples. In what regards hardness, a successive increase of this parameter for each type of composite was observed, by increasing the amount of EVA used. However, the results do not affect in any way the possibility of EVA waste recovery since all samples showed values within the desirable range according to CTCP, of 45 – 80 ShA (Shore A hardness scale). The results varied from 57.0 ± 1.1 to 62.4 ± 1.2 ShA.

Most relevant properties, where variations were observed, will be discussed in more detail from now on.

3.2.1. Tear strength

The results obtained for the longitudinal samples (Fig. 3a) showed a significant decrease on the tearing strength for the NR composites. For the other materials, the introduction of EVA produced no significant changes.

The values obtained were all higher than the minimum according to CTCP, except for specimen 8L (SBR, 10 phr), with the mean value observed being just on the limit.

The analysis of the results obtained for the transversal samples (Fig. 3b) show that, for the NR as well as for the NBR composites, the EVA addition lead to a higher resistance of the material. On the other hand, for the SBR, the addition of EVA led to a small decrease in the tear strength; the aged sample was the only one presenting values below the minimum required. By comparing the results between longitudinal and transversal samples, a very high difference of behaviour is observed. This might be explained by the fact that the anisotropy (variation with the direction in which the measurement is performed) in this test is very critical. One reason for the occurrence of this phenomenon might be the movement of material or molecular orientation when filling the mould (Garcia, 2002; Gurney and Gough, 1947; Lavebratt and Stenberg, 1994). Nevertheless, with the exception of the transversal sample aged (12T), all composites showed results higher than the minimum limit established by CTCP for this property (8 N mm^{-1}).

3.2.2. Tensile strength

The results obtained for the tensile strength show, in all cases, values above the minimum defined as desirable by CTCP (8 MPa). In terms of variations, on the longitudinal samples (Fig. 4a) a small decrease in breaking load with the addition of

EVA for the NBR and NR composites, except for the aged NBR plate, was observed. Oliveira et. al. (2004) also reported a reduction of the breaking load with increasing incorporation of EVA waste. On the other hand, for the SBR composite, the incorporation of 10 phr of EVA resulted on an increase of the resistance, expressed by a higher breaking load. The results for the transversal samples (Fig. 4b) show the same tendencies observed for the longitudinal samples. Regarding the elongation at break (more applied for applications requiring large stretching), all values were well above the minimum elongation (300%) established by the CTCP (between 542% and 782%). Although the differences were not high, the composites showed better results for this property when less waste was used (10 phr); on the other hand, at 20 phr, EVA-waste tended to act as filler (both in transversal and longitudinal samples). The results obtained for the 300% modulus (2.4 – 4.4 MPa) showed the best results for the natural rubber composites, possibly due to the crystallization zones (Hoffman, 1989). For the NBR and SBR composites, the module was very slightly affected. The results obtained by Oliveira et. al. (2004) regarding the breaking load and the elongation at break of natural rubber composites (19.1 – 19.9 MPa and 635 – 650 %) were similar to those obtained in the present work.

3.2.3. Abrasion

The results for the abrasion varied between 137 and 195 mm³, being in agreement with the maximum limit of 250 mm³ established by CTCP. In general, a gradual increase in the abrasion with the incorporation of EVA was found for all composites. Such a result was expected since the method used for EVA incorporation (milling) maintained EVA particles with a significantly large size that allowed their loosening when the composite was subjected to this type of erosion.

3.3. Physical and mechanical properties - analysis of industrial scale samples

The results obtained for the soles regarding the flexion, density, hardness and abrasion showed no relevant effects of EVA incorporation that could affect the performance of the material for application in the footwear industry, in agreement with the results obtained for the plates. The flexion test showed no effect (0.0 mm/kcicle determined in all samples) and the mean density presented a negligible variation, with values for all samples varying between 1.06 g cm^{-3} and 1.14 g cm^{-3} . The hardness of the composites also increased with the amount of EVA incorporated; however, all values were well within the desirable range which is between 45 and 80 ShA. The results varied from 59.0 ± 1.5 to 61.6 ± 1.7 ShA. Regarding the abrasion, the incorporation of EVA seemed to affect the resistance of the material to friction. However, all the results were well below the maximum allowed by the CTCP (250 mm^3), being in the range of $130 - 171 \text{ mm}^3$. The behaviour regarding tear strength and tensile strength will be discussed in more detail from now on.

3.3.1. Tear strength

Results obtained for the tear strength of the soles (Fig. 5) followed the same behaviour previously observed for the plates, with a decrease of the tear strength with EVA incorporation, except for the SBR composite, where an inversion of the behaviour was observed when comparing plates and soles. This different behaviour may be explained by the fact that when the plates are moulded, the flow of the material is even (vertically and horizontally); however, for the soles, when the composite is moulded, the material flow is multidirectional which might lead to entangled polymer chains (Hoffman, 1989). Thus, the complexity and unpredictability of the chains orientation leads to a higher anisotropy, which in this case was more evident in the case of SBR. All values were

higher than the minimum established by CTCP with very good results being obtained regarding the NR composites.

3.3.2. Tensile strength

Results for the tensile strength agree with those obtained for the tear strength, where the NR and NBR composites (samples 2 and 4) presented similar behaviour compared to the plates, in this case with a decrease in the breaking load by EVA addition (Fig. 6). It can be however observed that the virgin NR sole (1) presented a much higher breaking load compared to the plate (1). This high value may result from the mentioned anisotropy, more pronounced in soles. Thus, the sample could have the polymer chains aligned in the direction of the deformation performed leading to this higher value (Hoffman, 1989). Moreover, the unique characteristic of natural rubber to undergo deformation-induced crystallization coupled with the already referred anisotropy might be responsible for the variations observed (Hoffman, 1989). Results for the SBR showed the same inversed trends that might also be explained by the more pronounced anisotropy of the soles.

Also for this parameter, the NR composites showed the best results, since the results obtained for the NBR and SBR composites were extremely close to the minimum limit of 8 MPa (8.24 ± 0.03 MPa and $7.84 \text{ MPa} \pm 0.23$, respectively).

Overall, the results show feasibility of EVA waste incorporation for the sustainable production of footwear components since the production of composites containing 10 – 20 phr showed generally properties within acceptable limits according to CTCP, making feasible the recycling using up to 20 phr. The results obtained for the industrial production of soles agree with those obtained for the plates and confirm that the EVA waste generally acts as filler, worsening some physical/mechanical properties of the

material. As for the virgin materials, the natural rubber composites showed the best properties with values all very safely within the requirements imposed by CTCP.

4. Conclusions

The laboratory and industrial scale studies on the production of natural and synthetic rubber / waste – EVA (Ethylene-Vinyl Acetate) eco-composites showed that, from the physical and mechanical properties analysed, the flexion, density, hardness and abrasion of the composites produced compared to the three virgin materials (natural rubber, styrene-butadiene rubber and nitrile-butadiene rubber) do not jeopardize the performance of the material for application in the footwear industry, taking into account the specifications applied.

Different trends were found for some of the properties in the plates produced in the laboratory compared the soles produced industrially, due to the more pronounced anisotropy of the soles, showing the importance of performing such studies.

From the evaluated parameters, the tensile strength and the tear strength were mostly affected by EVA-waste incorporation. The greater differences, with more evident negative impacts being observed (lower tear strength and breaking load), were found for the NR/Waste-EVA composites, but the final values were much higher than the minimum established by CTCP.

The eco-composites allowed the fulfilment of the requirements imposed for application in the footwear industry; however, generally, EVA waste acted as filler, causing the worsening of some evaluated properties. On the other hand, for the SBR composites, some of the properties exhibited an improvement with the addition of EVA. The

different trends obtained by comparing plates and soles, probably due to anisotropy, led to uncertainties on this matter.

The present study confirms the possibility of using a thermosetting polymer – EVA – derived from the production of footwear as a by-product for the sustainable production of three rubber-EVA composites (using up to 20 parts per hundred rubber).

Acknowledgments

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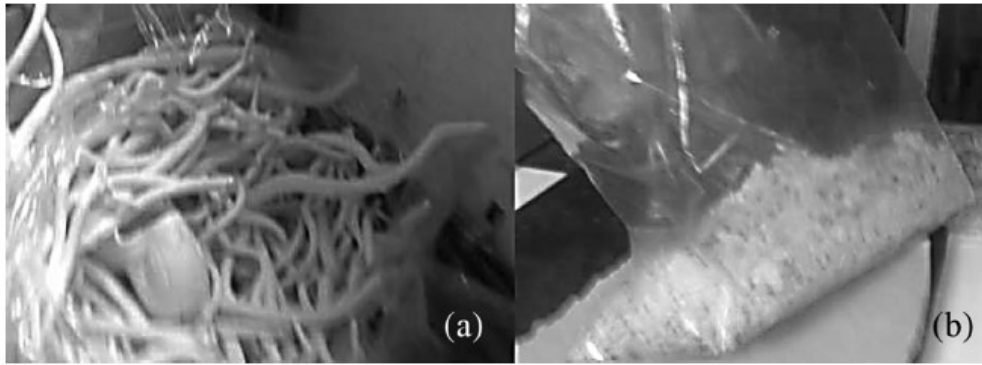


Fig. 1. EVA waste used. (a) EVA waste as-received; (b) EVA – waste after grinding.

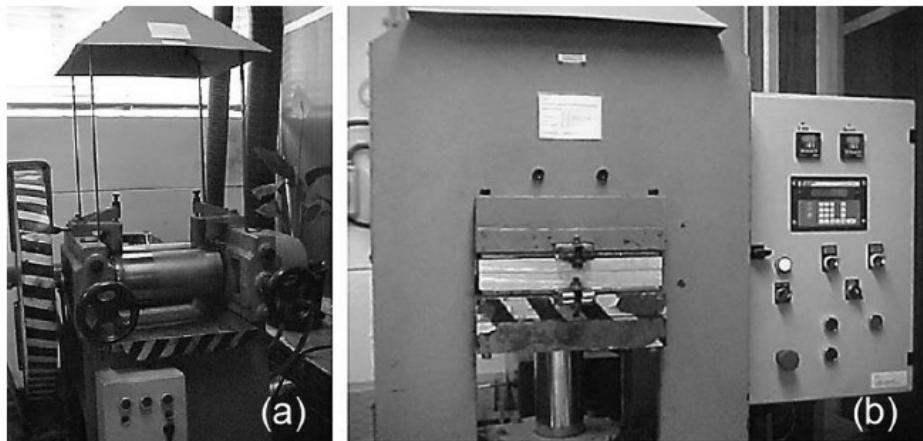


Fig. 2. Composites preparation (plates). (a) Two roll mixing mill; (b) Laboratory press.

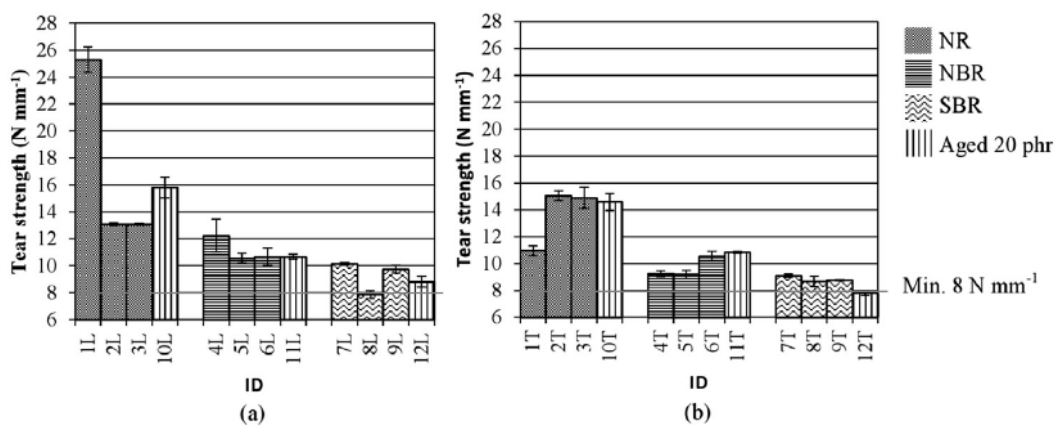


Fig. 3. Tear strength of virgin materials and composites – plates; (a) longitudinal samples; (b) transversal samples; minimum according to CTCP is presented.

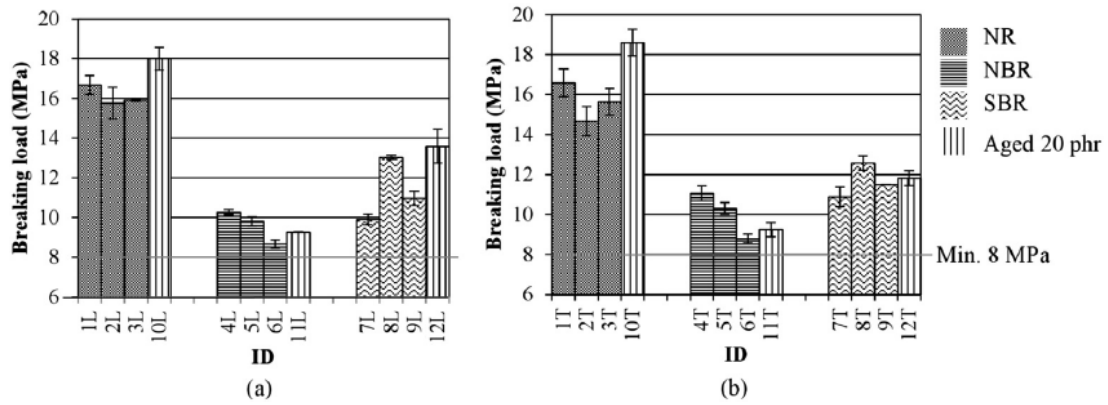


Fig. 4. Breaking load of virgin materials and composites – plates; (a) longitudinal samples; (b) transversal samples; minimum according to CTCP is presented.

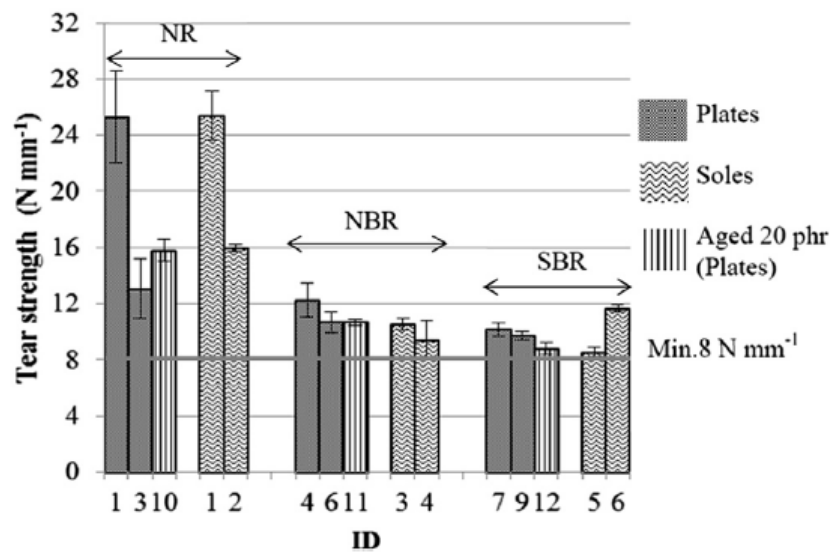


Fig. 5. Tear strength of virgin materials and composites – plates and soles; minimum according to CTCP is presented.

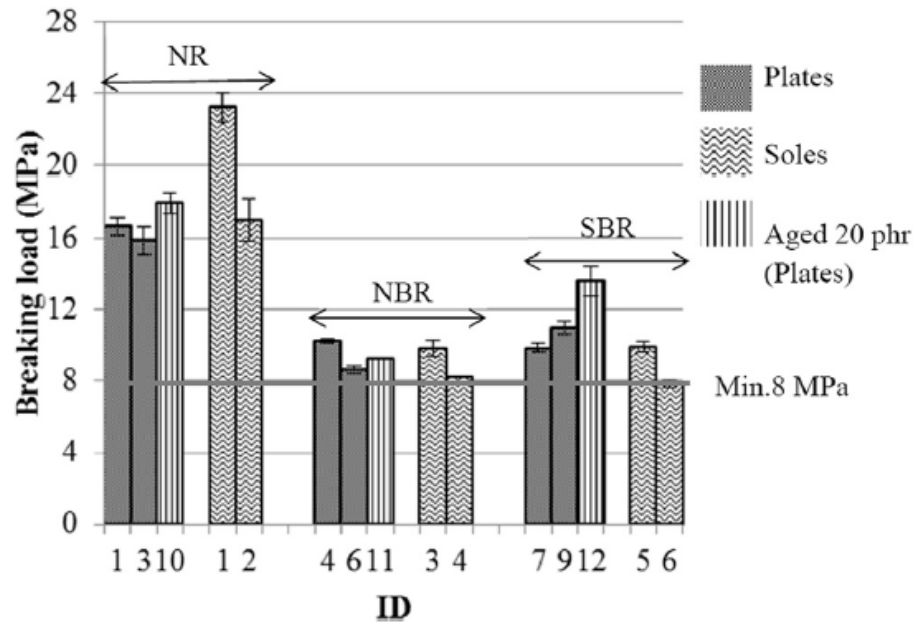


Fig. 6. Breaking load of virgin materials and composites – plates and soles; minimum according to CTCP is presented.

Table 1 Elastomers formulation.

Compound	SBR – L120 (phr)	NBR – N383 (phr)	NR – L159 (phr)
Polymer			
Natural Rubber (NR)	–	–	80
Styrene-butadiene rubber (SBR)	80	–	–
Acrylonitrile-butadiene rubber (NBR)	–	90	–
Butadiene Rubber (BR)	20	10	20
Filler (Silica)	40	50	30
Activator (Polyethylene Glycol - PEG 4000, Stearic acid, Zinc oxide)	10	7	5
Vulcanization agent (sulphur)	1.8	2	1.7
Antioxidant (phenolic), Accelerator (Mercaptobenzothiazole disulphide – MBTS, Tetra methylthiuram disulphide – TMTD), and others.	6	6	5

Table 2
Samples identification.

EVA waste incorporation/elastomers	NR	NBR	SBR	
0 phr	1	4	7	Plates
10 phr	2	5	8	
20 phr	3	6	9	
20 phr for ageing	10	11	12	
0 phr	1	3	5	Soles
20 phr	2	4	6	

Table 3
Rheometry results for the plates (ML – minimum torque, MH – maximum torque; ts5 – pre-vulcanization time (time for the torque to raise 5 units above ML), t'90 – optimum vulcanization time).

Sample ID	ML (lbf.in) $\bar{X} \pm s$	ts5 (s) $\bar{X} \pm s$	t'90 (s) $\bar{X} \pm s$	MH (lbf.in) $\bar{X} \pm s$
1	29.35 \pm 0.05	73 \pm 1	123 \pm 1	61.97 \pm 0.23
2 ^a	16.19	74	121	57.37
3	19.65 \pm 0.02	73 \pm 1	117 \pm 2	56.59 \pm 0.27
4	16.71 \pm 0.15	69	97 \pm 3	51.04 \pm 0.25
5	17.97 \pm 0.16	61	86 \pm 1	49.01 \pm 0.31
6	19.29 \pm 0.28	58	81 \pm 2	48.51 \pm 0.22
7	22.68 \pm 0.35	55 \pm 3	110 \pm 1	69.30 \pm 0.21
8	21.20 \pm 0.15	67 \pm 2	113 \pm 5	63.33 \pm 0.17
9	21.77 \pm 0.47	65 \pm 2	107 \pm 1	60.56 \pm 0.77

^a For this sample, no replication was possible.