THE INFLUENCE OF PROTEIN AND ELASTOMER WASTE MIXTURE ON THE NBR-BASED ELASTOMER COMPOUND

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ABSTRACT. The paper presents the influence of a mixture of elastomeric and protein waste from the footwear industry on the properties of elastomeric compounds based on NBR (butadiene-co-acrylonitrile) rubber, as well as their obtaining and characterization. The mixture of leather and rubber waste was cryogenically ground, in three grinding cycles, and the selected size was 0.35 mm, and the rotation speed of 14,000 rpm. After grinding, the leather and rubber waste mixture was functionalized with potassium oleate at a temperature of 60°C. The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and the mixture of protein and elastomeric waste (in the ratio of 15, 20, 40, 50%) from the footwear industry were processed by mixing on an internal Brabender mixer, tested from a rheological, physical and mechanical point of view (hardness, elasticity and tensile strength) after conditioning for 24 h at room temperature according to the standards in force, but also by FT-IR spectroscopy performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50, equipped with ATR with diamond crystal. Following characterisation, it can be said that they present optimal values that fall within the standards for the footwear industry.

KEY WORDS: elastomer, protein and elastomeric waste, composite, vulcanisate, compound

INFLUENȚA DEȘEULUI PROTEIC ȘI ELASTOMERIC ÎN AMESTEC ASUPRA PROPRIETĂȚILOR COMPOUNDULUI ELASTOMERIC PE BAZĂ DE NBR

REZUMAT. Lucrarea prezintă influența deșeului elastomeric și proteic în amestec, deșeu provenit din industria de încălțăminte, asupra proprietăților compoundurilor elastomerice pe bază de cauciuc NBR (butadien-co-acrilonitrilic) și, de asemenea, obținerea și caracterizarea acestora. Deșeul de piele și cauciuc în amestec a fost măcinat criogenic, în trei cicluri de măcinare, iar dimensiunea selectată a fost cea de 0,35 mm, viteza de rotație fiind de 14.000 rot/min. Deșeul de piele și cauciuc în amestec după măcinare a fost funcționalizat cu oleat de potasiu la temperatura de 60°C. Compoundurile polimerice pe bază de cauciuc butadien-co-acrilonitric (NBR) și deșeu proteic și elastomeric în amestec (în proporție de 15, 20, 40, 50 %), deșeu provenit din industria de încălțăminte, au fost prelucrate prin tehnica amestecării pe un amestecător Brabender intern, testate din punct de vedere reologic, fizico-mecanic (duritate, elasticitate și rezistență la rupere) după condiționare timp de 24 h la temperatura camerei conform standardelor în vigoare, dar și prin spectroscopie FT-IR realizată cu un spectrometru de absorbție moleculară IR cu fascicul dublu, în intervalul 4000-400 cm^{-1}, folosind FT-IR Thermo Nicolet iS 50, dotat cu ATR cu cristal de diamant. În urma caracterizărilor aferente putem spune că acestea prezintă valori optime ce se încadrează în standardele aferente pentru industria de încălțăminte.

CUVINTE CHEIE: elastomer, deșeu proteic și elastomeric, compozit, vulcanizat, compound

L'INFLUENCE DES DÉCHETS PROTÉIQUES ET ÉLASTOMÈRES EN MÉLANGE SUR LES PROPRIÉTÉS DES COMPOSÉS ÉLASTOMÈRES À BASE DE NBR

RÉSUMÉ. L'article présente l'influence des déchets mixtes élastomères et protéiques de l'industrie de la chaussure sur les propriétés des composés élastomères à base de caoutchouc NBR (butadiène-co-acrylonitrile), ainsi que leur obtention et leur caractérisation. Les déchets de cuir et de caoutchouc dans le mélange ont été cryobroyés, en trois cycles de broyage, la taille choisie était de 0,35 mm, et la vitesse de rotation de 14.000 tr/min. Les déchets de cuir et de caoutchouc en mélange après broyage ont été fonctionnalisés avec de l'oléate de potassium à une température de 60°C. Les composés polymères à base de caoutchouc butadiène-co-acrylonitrile (NBR) et de déchets mixtes élastomères et protéiques (dans un rapport de 15, 20, 40, 50%) de l'industrie de la chaussure ont été traités par la technique de mélange sur un mélangeur interne Brabender, testé d'un point de vue rhéologique, physique et mécanique (dureté, élasticité et résistance à la traction) après conditionnement pendant 24h à température ambiante selon les normes en vigueur, mais aussi par spectroscopie FT-IR réalisée avec un spectromètre d'absorption moléculaire IR à double faisceau, dans la gamme 4000-400 cm^{-1}, utilisant le FT-IR Thermo Nicolet iS 50, équipé d'ATR en cristal diamant. En suivant les caractérisations, on peut dire qu'ils présentent des valeurs optimales qui rentrent dans les standards de l'industrie de la chaussure.

MOTS-CLÉS : élastomère, déchets élastomères et protéiques, vulcanisé, composé

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INTRODUCTION

In the last decade, waste management has gained momentum not just at the European level, but at the global level. That is why rubber waste, especially used waste (from the footwear industry and not only) was perceived as a potential source of very valuable raw materials [1]. Recycling and reusing it (reintroducing up to 5 reuse cycles) can contribute to environmental protection – Directive 2008/98/EC [2], and protection of human health by eliminating emissions during the burning of this type of waste, as well as to increasing the turnover of specialized economic agents [3] and at the same time with the help of advanced technologies it is possible to contribute to the improvement of product quality [4]. Also, in December 2015 the European Commission adopted a set of measures related to the Circular Economy in order to achieve the transition to an economy in which resources are used sustainably [3, 5]. At the same time, our country issued a series of regulations and decisions related to waste management. An important Governmental Decision is GD no. 85/2002 – "Introduction of the waste management record and the European waste catalog": "Also, waste means a material that appeared as a result of a biological or technological process and that can no longer be used as such" [6]. Waste recycled, reused and processed by cryogenic grinding to micro or even nanometer sizes can be used, with the help of new advanced technologies, in the industry of processing elastomers, as well as plastomers, in the presence of new materials, which when used can restore predetermined properties [7, 8]. Butadiene-co-acrylonitrile (NBR) elastomers are easy to process due to properties such as high abrasion resistance, high temperature stability from -40 to +108°C (-40 to +226°F) [9-13]. The vulcanisates based on NBR, fillers, plasticizers and other ingredients specific to elastomers also show good resistance to mineral oils, petroleum products, resistance to aging (by adding accelerators and activators) and low gas permeability [14]. Some fillers can be successfully replaced (totally) by cryogenically ground waste (leather and rubber waste mixture from the footwear industry) [12].

The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and protein and elastomeric waste from the footwear industry in a mixture of 15, 20, 40, 50% were processed by the mixing technique, tested in terms of rheological, physical and mechanical properties according to the standards in force, but also by FT-IR spectroscopy. Following characterisation, it can be said that they present optimal values that fall within the standards for the footwear industry [15].

EXPERIMENTAL

Materials

The materials used to obtain elastomeric compound (based on butadiene-co-acrylonitrile and protein and elastomer waste in mixture) were:

1) NBR rubber – butadiene-co-acrylonitrile rubber: content in acrylonitrile – 34%; Mooney viscosity (100%) – 32±3; density – 0.98 g/cm^3; 2) Stearin: white flakes; moisture – 0.5% max; ash – 0.025% max; 3) Zinc oxide microparticles (ZnO): white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; 4) Silicon dioxide (SiO_2): density: 1.9-4.29 g/cm^3, molar mass – 60.1 g/mol; 5) Kaolin: white powder, molecular weight 100.09; 6) Leather and rubber waste mixture; 7) Leather and rubber waste mixture: ground waste functionalized with potassium oleate; 8) Mineral oil; 9) N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm^3, solidification point above 76.5°C, flat granules coloured brown to dark violet; 10) Sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; 11) Tetramethylthiuram disulfide (Th): curing agent, density – 1.40g/cm^3, melting point <146°C, an ultrafast curing accelerator, 12) Diphenylguanidine (D): curing agent, density 1.19 d/cm, Tt>145.

Methods

Preparation of Elastomeric Compounds Based on NBR Rubber and Functionalized Protein and SBR Rubber Waste in Mixture

The vulcanized polymer compounds with the mixture of protein and elastomeric waste were processed by mixing on an internal Brabender mixer, with the possibility to adjust the mixing speed and working temperature, respecting the

order of introduction of the ingredients. After processing, the formulations (Table 1) are tested from a rheological and physical-mechanical point of view [15] (normal state and accelerated aging), in terms of biodegradation [16] and FT-IR spectroscopy [6]. Before being introduced into the formulations, the mixture of leather and rubber waste (15, 20, 40, 50%) was ground using a Retsch ZM 200 cryogenic mill, in three cycles, to different sizes (1 mm initially at 12,000 rpm, then to 0.5 mm at 12,000 rpm), and the selected size was 0.35 mm, at a rate of 14,000 rpm [17]. After grinding, the waste was functionalized with potassium oleate (in a proportion of 25%) at a temperature of 60°C [18].

The initial working temperature on the Brabender mixer is set at 45°C. The NBR elastomer (butadiene-co-acrylonitrile) is introduced for plasticization for 2', at 45 rpm. After plasticizing the NBR, the rest of the ingredients are added and mixed for 4' according to the working recipe, keeping the initial temperature, at 30 rpm. Mixing is continued for 2' for homogenization at temperatures between 80-100°C, 100 rpm. After being obtained in the Brabender mixer, the polymer composites based on NBR rubber and leather and rubber waste in a mixture were rheologically tested, at 165°C, for 24', on a Monsanto Rheometer. Rheological testing is done to determine the optimal vulcanization times by pressing in an electric press (in molds specific to elastomers), where standardized samples (15x15x2 mm) are obtained. Pressing to obtain the samples in standardized molds is done by the compression method between the plates of the electric press at optimal parameters, as follows: pressing temperature – 165°C, 6 minutes pressing time, 10 minutes cooling time and pressure – 300 kN. After that, the samples are left to rest for 24 h at ambient temperature, and then they are subjected to related characterizations according to the standards in force: physical-mechanical testing (normal state and accelerated aging at 70°C, 168 h) and FT-IR spectroscopy analysis [15-19].

Table 1: Polymer composite based on NBR (butadiene-co-acrylonitrile rubber) compounded with non-functionalized/functionalized protein and elastomer waste mixture

Symbol	MU [%]	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
Butadiene-co-acrylonitrile	%	100	100	100	100	100	100
Stearin	%	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	%	6	6	6	6	6	6
Silicon dioxide	%	30	-	20	10	-	-
Kaolin	%	30	30	30	30	30	30
Protein and elastomer waste functionalized with potassium oleate	%	-	-	15	20	40	50
Non-functionalized protein and elastomer waste	%	-	10	-	-	-	-
Mineral oil	%	3	3	3	3	3	3
IPPD 4010	%	1	1	1	1	1	1
Sulfur (S)	%	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethylthiuram disulfide (Th)	%	0.9	1.5	0.9	0.9	0.9	0.9
Diphenyguanidine (D)	%	0.5	0.5	0.5	0.5	0.5	0.5

B_0 – composite without waste

Characterization of Polymeric Compounds

The polymeric compounds were tested in terms of physical-mechanical properties like: hardness, °ShA – ISO 48-4:2018; elasticity %, ISO 4662:2017; tensile strength, N/mm^2 – SR ISO 37-2020, normal condition and accelerating ageing at 70°C and 168 h.

Physical-mechanical characterization was performed and then followed by spectrometric characterization. FT-IR spectral determinations were performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50, equipped with ATR with diamond crystal.

RESULTS AND DISCUSSIONS

Rheological Characterization of Polymeric Compounds Based on NBR Elastomer and Protein and Elastomer Waste in Mixture

Through rheological testing, the optimal times of vulcanization in the electric press are established in order to obtain the samples that are subjected to physical-mechanical testing and FT-IR spectrometry.

In Table 2 are shown the arheological characteristics of mixtures based on NBR rubber compounded with protein and elastomer waste mixture non-functionalized and functionalized with potassium oleate.

Table 2: Rheological characteristics of mixtures based on NBR rubber compounded with protein and elastomer waste mixture

Rheological characteristics at 165°C	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
ML (dNm)	17.3	15.3	19.7	18.1	12.8	15.1
MH (dNm)	46.9	41	45.2	45	34.7	36.8
ΔM = MH-ML (dNm)	29.6	25.7	25.5	26.9	21.9	21.7
t_{s2} (min)	2.91	2.43	2.59	2.38	2.03	1.55
t_{50} (min)	6.38	3.12	3.44	3.18	2.54	2.03
t_{90} (min)	18.61	5.02	5.07	4.67	5.18	4.94

From the recorded rheological characteristics, Figure 1, it can be seen that by replacing the silicon dioxide (active filler) with leather and rubber waste in a non-functionalized/ functionalized mixture (with potassium oleate 25% at a temperature of 60°C), the rheological characteristics are:

1. The maximum and minimum torque, ML and MH, decrease with the increase in the amount of protein waste and rubber in the non-functionalized/functionalized mixture (in different proportions from 15-50%);
2. ΔM = MH-ML – the torque variation decreases with the increase in the percentage of leather and rubber waste in the mixture, which indicates a stiffening of the samples, due to the agglomeration of protein waste fibers;
3. Due to the vulcanization (with vulcanization accelerators), a degradation of the samples is observed by some cross-linking bonds breaking, and the reversion phenomenon that is specific to vulcanized samples is also observed;
4. The optimal vulcanization time (t_{90}) decreases due to the replacement of the active filler with the mixture of protein and elastomeric waste;
5. the scorching time (t_{s2}) also decreases with the decrease in the percentage of leather and rubber waste mixture, or by the total replacement of silicon dioxide with waste functionalized with potassium oleate.

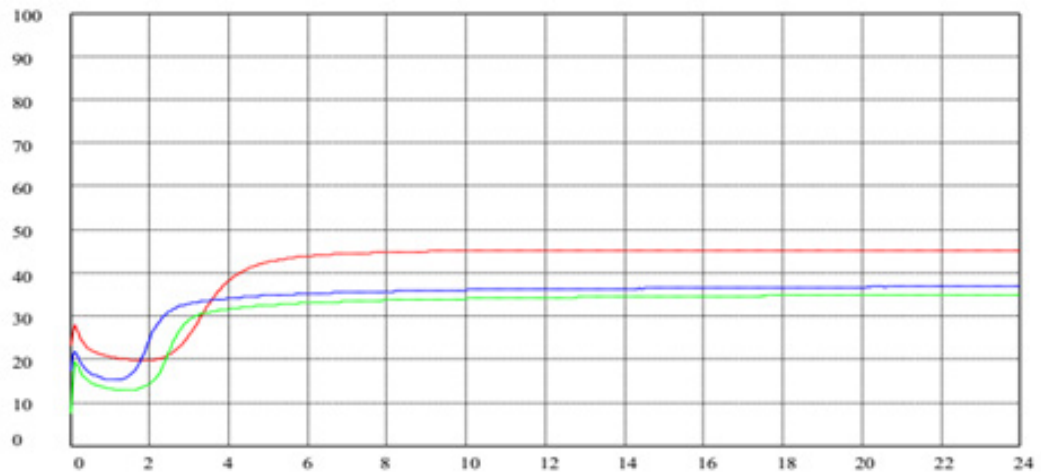

Figure 1. Torque variation expressed in dNm (OY axis) over time expressed in minutes (OX axis) for leather waste samples functionalized with potassium oleate: BCB_1 (red) – 15% waste; BCB_3 (green) – 40% waste; BCB_4 (blue) – 50% waste

Physical-Mechanical Characterization of Polymeric Compounds Based on NBR elastomer and Protein and Elastomer Waste in Mixture

Table 3: Physical-mechanical characterization of polymeric compounds based on NBR elastomer and protein and elastomer waste in mixture non-functionalized/functionalized with potassium oleate

Sample	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
Physical-mechanical characteristics: Normal State						
Hardness, °Sh A	61	62	61	59	58	57
Elasticity, %	18	20	24	24	25	25
Tensile strength, N/mm^2	11.3	5.1	9.5	8.85	3.16	2.67
Physical-mechanical characterization: Accelerated aging at 70°C and 168 h						
Hardness, °Sh A	66	64	63	62	61	60
Elasticity, %	24	22	22	23	24	26
Tensile strength, N/mm^2	14.47	5.6	13.75	8.77	3.25	2.75

Physical-mechanical characterisation was carried out according to standards in force.

As a result of physical-mechanical characterisation, Table 3, it follows that:

1. the hardness of polymeric compounds based on NBR rubber compounded with leather and rubber waste in mixture non-functionalized/functionalized with potassium oleate decreases proportionally with the amount of waste added to the mixture, especially for samples BCB_3 (40% functionalized waste, without active filler) and BCB_4 (the active filler is totally replaced with 50% functionalized waste) by maximum 6-7°Sh A;
2. the elasticity increases in different proportions, between 11-38% compared to the control sample B_0, with the increase in the percentage of non-functionalized/ functionalized waste and with the total replacement of the active filler (SiO_2), especially for the samples in which SiO_2 is totally replaced with protein and rubber waste in functionalized mixture (BCB_3 and BCB_4), indicating that the protein and elastomeric waste reduces the stiffness of the samples;
3. the tensile strength also decreases compared to the control sample (B_0),

especially for sample BCB_4 (compound with 50% waste functionalized with potassium oleate), the sample in which the silicon dioxide is replaced with leather and rubber waste mixture. Tensile strength decreases by approximately 78% compared to sample B_0;

4. after accelerated aging for 168 h at 70°C, hardness increases by 2-3°ShA for samples with 15-20% functionalized waste, as well as for samples in which the active filler is totally replaced with 40-50% waste (samples BCB_3 and BCB_4). In the case of elasticity after the accelerated aging process, a proportional increase by 4-8% compared to the control sample is observed.

Fourier Transformed Infrared Spectroscopy (FT-IR)

The stretching vibration bands of the polymer compounds based on NBR and protein and elastomeric waste in a functionalized mixture with potassium oleate are based on the bands in the reference spectrum of the NBR (butadiene-co-acrylonitrile) elastomer, Figure 2.

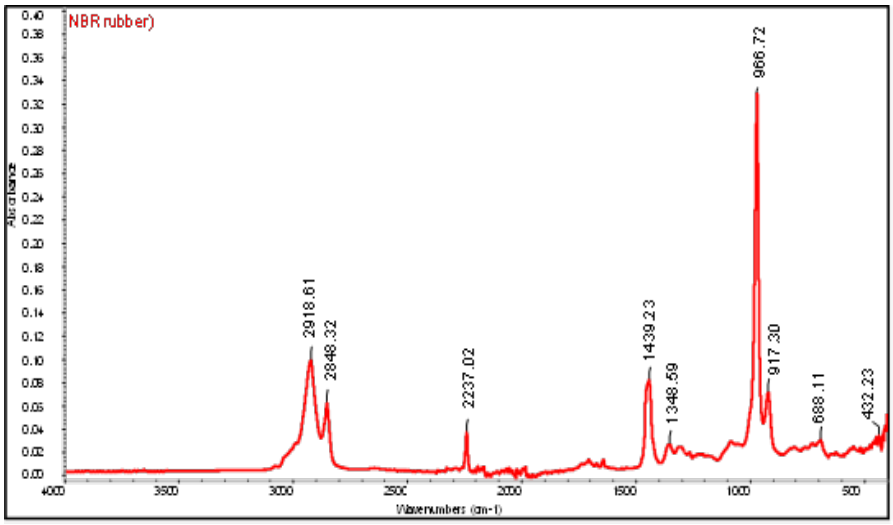

Figure 2. FT-IR spectrum for NBR rubber

The FT-IR spectrum (Figure 2) recorded for butadiene-co-acrylonitrile rubber (NBR) highlights the characteristic bands originating from the nitrile bond as well as the butadiene functional groups. Thus, the band at 2237.02 cm^{-1} confirms the presence of stretching groups of -CN bonds from nitrile as well as the stretching vibration of double bonds from butadiene =C-H at 966.72 cm^{-} [15, 19].

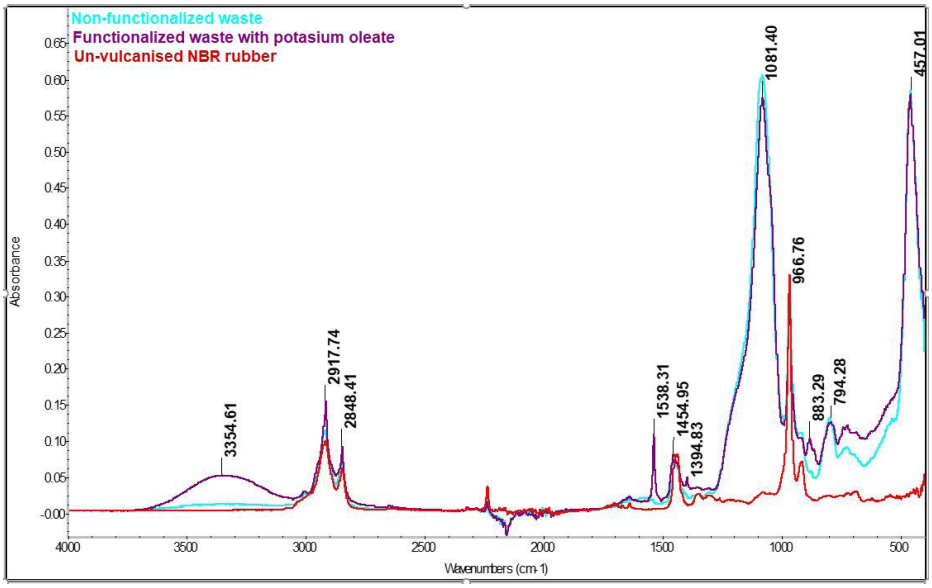

Figure 3. FT-IR spectra from non-functionalized/functionalized waste and un-vulcanized NBR elastomer

In the FTIR spectrum recorded for the butadiene-co-acrylonitrile elastomer (NBR) and unfunctionalized waste and functionalized with potassium oleate, Figure 3, the bands originating from the NBR rubber can be visualized at 2917.74, 2848.41, 1454.95, 966.76 cm^{-1}, and the presence of the silicon dioxide/kaolin at 1081.4, 794.28 and 457.01 cm^{-1}.

The bands showing the presence of potassium oleate can be observed at 1538.31 cm^{-1} and 1394.83 cm^{-1} respectively (associated with the asymmetric and symmetric stretching vibration of COO^- bonds).

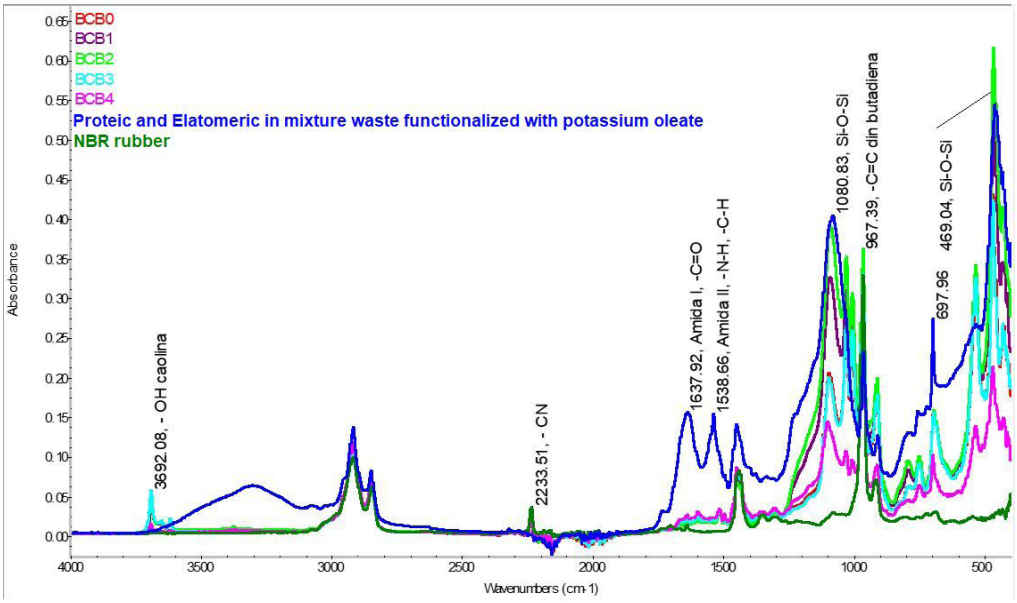

Figure 4. FTIR spectra of composites based on NBR rubber compounded with different amounts of leather and rubber waste non-functionalized/functionalized with potassium oleate

For sample BCB_0 (compound based on NBR rubber compounded with 10% non-functionalized leather and rubber waste) and BCB_1-BCB_4 (samples based on NBR rubber compounded with 15, 20, 40 and 50% protein and elastomeric waste functionalized with oleate potassium), the recorded FT-IR spectra highlight the characteristic bands of the individual components of butadiene-co-acrylonitrile rubber – 966.39 cm^{-1}, leather fibers, kaolin and silicon dioxide – 1080.83 cm^{-1} and 469.04 cm^{-1}. The intensity of the bands originating from the protein fibers is lower because, in addition to the leather fibers, the waste also contains high amounts of elastomer, which decreases the intensity of the bands known as Amide I – 1637.92 cm^{-1} and Amide II – 1538.66 cm^{-1}. For samples BCB_1 and BCB_2, the intensity of the bands obtained from silicon biooxide is higher than in the case of samples BCB_3 and BCB_4. From the recorded spectra it can be seen that the intensity of the bands coming from silicon dioxide and kaolin decreases as SiO_2 is replaced with protein and elastomeric waste in a mixture functionalized with potassium oleate.

CONCLUSION

The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and protein and elastomeric waste from the footwear industry in a mixture of 15, 20, 40, 50% were processed by the mixing technique in an internal Brabender mixer, tested from a rheological point of view to establish the optimal vulcanization times for pressing in the electric press at controlled times, temperatures and pressures, to obtain products with characteristics necessary for use in the footwear industry: plates for soles for general use, but also in the food industry, technical plates, insoles, etc.

The bands of the stretching vibrations of the polymer compounds based on NBR and protein and elastomeric waste in a mixture functionalized with potassium oleate are based on the bands in the reference spectrum of the NBR elastomer. The presence of potassium oleate can be observed at 1538.31 cm^{-1} and 1394.83 cm^{-1}, respectively, associated with the asymmetric and symmetric stretching vibration of COO^- bonds. The recorded FT-IR spectra highlight the characteristic bands of the individual components of the NBR elastomer – 966.39 cm^{-1}, kaolin and silicon dioxide – 1080.83 cm^{-1} and 469.04 cm^{-1}. The intensity of the bands originating from the protein fibers is lower because the waste also contains high amounts of elastomer, which decreases the intensity of the bands known as Amide I – 1637.92 cm^{-1} and Amide II – 1538.66 cm^{-1}.

The physico-mechanical characterisations, normal state and accelerated aging were carried out according to the standards in force for testing elastomers in the footwear industry. Following the physico-mechanical characterisations, it is found that they are strongly influenced by the percentage of leather and rubber waste mixture, especially in the case of samples in which the active filler (silicon dioxide) is totally replaced by the waste (ground in three cycles up to size of 0.35 mm at a rate of 14,000 rpm) functionalized with potassium oleate, 25%, at 60°C, samples BCB_3 and BCB_4 presenting optimal values that fall within the related standards for the footwear industry.

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