STUDIES ON NATURAL RUBBER BASED COMPOSITES FILLED WITH PRODUCTS FROM RENEWABLE RESOURCES WITH IMPROVED ADHESION TO ICY SURFACES

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ABSTRACT

Slips and falls on icy surfaces can cause serious injuries of people. The primary risk factor for slipping incidents is undoubtedly the decreased friction coefficient between the shoe sole and the ice or snow surface.

Nowadays environmental protection has been gaining significance and becoming highly important for the various innovation strategies. In rubber industry the concept of environmental protection is more often associated with the maximum use of elastomers and ingredients from renewable sources in the manufacture of rubber products.

The aim of this work is to investigate the possibilities of using elastomers and ingredients from renewable sources - natural rubber, silica obtained by rice husks incineration and microcrystalline cellulose - as fillers and rapeseed oil as a process additive in compositions, intended for the manufacture of soles for winter footwear having an increased coefficient of friction to various types of icy surfaces.

Dynamic mechanical thermal analysis has been used to predict the adhesion of the materials to „dry ice", „wet ice" and melting ice. It has been found that, in all the cases examined, the composites containing natural rubber and a combination of microcrystalline cellulose (20 phr) and silica (40 phr) as fillers are the most suitable for the purpose. The silica used can be both synthetic and from renewable sources. The tribological tests carried out have confirmed these composites under the conditions of „dry ice" and „wet ice" fall into the class of the highest resistance against slip but on melting ice they do not have the necessary degree of resistance. It is believed that the use of a polar elastomer and hydrophobilizing the surface of microcrystalline cellulose particles will solve the problem.

Keywords: elastomers composites, renewable resources, coefficient of friction, icy surfaces.

INTRODUCTION

Slips and falls are quite common on icy surfaces and can cause serious injuries. It is believed that slipping accounts for 16 % of all incidents and 43 % of all fall incidents in the Scandinavian countries [1]. In Finland, for example, as a result of slipping caused by icy or snowy surfaces, nearly 50,000 pedestrians each year receive injuries leading to medical consultation [2]. The primary risk factor for slipping incidents is undoubtedly the decreased friction coefficient between the shoe sole and the surface beneath it. The facts described above indicate a significant public health issue associated with the adhesion of the footwear to the icy surface.

A number of compositions of rubber compounds with increased adhesion to ice and snow have been described in the patent literature. Their ingredients are 5-norbornene at an amount of 5 to 100 phr [3]; 35 to 50 mass % hollow spherical microparticles of at least one alumosilicate which size in the range of 2 to 500 microns [4]; 5 to 50 mass % of a photo-crosslinking liquid polymer resin such as poly(butadiene acrylate)

or poly(butadiene-methacrylate) [5]; 2 to 50 mass % of powdered water soluble microparticles of magnesium sulphate and from 2 to 50 mass % of water-soluble short fibers of polyvinyl alcohol [6]; between 2 and 60 mass % of metallic salts (chlorides, carbonates, sulphates or mixtures thereof) of sodium, potassium, magnesium, calcium whose particle size is between 3 and 600 microns) [7].

A number of authors report that when microcrystalline cellulose is used as a filler the mechanical properties, heat aging resistance, processability, heat up-build and dynamic mechanical properties of the vulcanisates obtained are improved [8, 9].

Literature, however, gives no evidence of elastomeric compositions of enhanced adhesion to icy surfaces which, in addition to elastomers (natural rubber, epoxidized natural rubber), also contain ingredients (e.g. fillers, plasticizers, and the like process additives) from renewable resources, microcrystalline cellulose and silica produced by rice husk incineration.

The aim of the work is to investigate the possibilities of using elastomers and ingredients from renewable resources - natural rubber filled with rice husk silica and microcrystalline cellulose, and rapeseed oil as a technological additive in formulations for the production of soles for winter shoes with improved slip resistance on various types of icy surfaces.

EXPERIMENTAL

Elastomers and ingredients

The natural rubber used was made in Thailand (standard Thailand rubber STR-10), which had Moony viscosity ML 60±7; impurities content of 0.10; ash content less than 0.6 % and index of preserved plasticity over 50. The silica used as filler was obtained by incineration of rice husk implementing a previously developed technology [10]. The filler had the following characteristics: specific surface area (BET) 38 $m^2 g^{-1}$; pour density 0.49 g cm^{-3}; heat loss 0.7 % (2 h at 105°C according to BDS EN ISO 787-2/1999) and pH of an aqueous solution 9.5 (according to BDS EN ISO-787-9/1999).

Standard silica Ultrasil 7000 GR from Evonik, Germany was also used. It had specific surface area (BET) 175 $m^2 g^{-1}$; pour density 0.55 g cm^{-3}; heat loss 5.5 % (2 h at 105 °C); pH of an aqueous solution 6.5.

Carbon black N550 (made in Russia) having the following characteristics: particle size 50 - 65 nm; specific surface area 45 - 60 $m^2 g^{-1}$; Oil number 96 - 100 ml/100g; pH = 7 - 9, was used as a pigment.

Microcrystalline cellulose (Aldrich, USA) had the following characteristics: particle size ranging from 5 to 30 μm; pH = 5 ± 7.5; water-soluble substances not exceeding 0.24 %; loss on drying $\leq$ 5 % (for 3 h at 105°C).

We used the following compatibilizers:

- bis(triethoxysilylpropyl)tetrasulfide (TESPT) - silane Si 69® - a bifunctional sulfur-containing organosilane from Evonik Industries, finding application in rubber industry in combination with light fillers comprising silanol groups. The sulfur content of TESPT was about 22.5 %. TESPT was a yellowish liquid with a molecular mass of 532 g mol^{-1} and density of 1.1 g cm^{-3} (It was used in the silica-containing compounds).

- 3-thiocyanato-propyl triethoxysilane (Si - 264, also manufactured by Evonik Industries), a liquid with a sulfur content of 12.5 %, an average molecular mass of 263 g mol^{-1} and a density of 1.0 g cm^{-3} (It was used in the compounds containing microcrystalline cellulose).

The other ingredients used to manufacture the rubber compounds were the standard ones for rubber industry and the following abbreviations are used for them: Anti-aging agent - polymerized 2,2,4-tri methyl-1,2dihydroquinoline (TMQ) ; Anti-aging agent -Dimethylbutyl-phenyl-p-phenylenediamine (6PPD); Accelerator - N-tert-butyl-2-benzothiazyl sulfenamide (TBBS); Retardant - N-Phenyl-N-(trichloromethylthio)-benzenesulfonamide (Vulkalent E/C).

Characterization of the fillers used

The TEM investigations were performed on a TEM JEOL 2100 instrument at an accelerating voltage of 200 kV. The specimens were prepared by grinding and dispersing them in ethanol by ultrasonic treatment for 6 min. The suspensions were dripped on standard holey carbon/Cu grids.

Composition of the rubber compounds used

The formulations of the rubber compounds used to manufacture footwear soles of improved slip resistance against icy surfaces are shown in Table 1.

Preparation and vulcanization of the rubber compounds

The compounds were prepared on an open two-roll laboratory mill (rolls Length/Diameter 320x160 mm,

Table 1. Formulations of the natural rubber based compounds (in phr).

Ingredients	MCC-1	MCC-2	MCC-3
1. Natural rubber STR-10	100	100	100
2. Microcrystalline cellulose	60	30	20
3. Silica from rice husk	-	30	-
4. Silica Ultrasil 7000 GR	-	-	40
5. Carbon black N 550	5	5	5
6. Si-264	6	3	2
7. TESPT	-	3	4
8. Rapeseed oil	25	25	25
9. Zinc oxide	3	3	3
10. Stearic acid	2	2	2
11. TMQ	1.5	1.5	1.5
12. 6PPD	1.5	1.5	1.5
13. TBBS	1.5	1.5	1.5
14. Diphenylguanidine	0.5	0.5	0.5
15. Vulkalent E/C	0.3	0.3	0.3
16. Sulfur	1.6	1.6	1.6

friction 1.17 and speed of the slower rotating roll 25 min^{-1}). The rubber compounds were vulcanized in the form of 400x400 mm plates on an electrically hydraulic vulcanization press at 150°C, at 10 MPa and for a time determined by the vulcanization isotherms of the compounds taken on a MDR 2000, AlphaTechnology vulcameter.

Characterization of the rubber compounds and vulcanizates based on them

The compounds and vulcanizates were characterized as follows:

- Vulcanization characteristics, determined according to ISO 3417: 2002;

- Physicomechanical properties (Modules 100 and 300, tensile strength, elongation at break, residual elongation), according to ISO 37: 2002 and EN 12 803;

- Shore A hardness according to ISO 7619:2001

- Dynamic characteristics, the tangent of the mechanical loss angle (tanδ) at a frequency of 5 Hz, 64 μm deformation, in the temperature range of -80°C to + 80°C, in particular at -10°C, -4°C, and -1°C, heating rate 3°C/min. The size of the samples tested was as follows: width 10 mm, length 25 mm, thickness 2 mm.

A Rheometric Scientific dynamic mechanical thermal analyzer was used.

- Wear resistance, according to EN 12 770;

- Bending resistance, according to BSS 5658-72;

- Tribological characteristics, the static and dynamic coefficient of friction were determined using a laboratory apparatus and methods.

A functional scheme of the device used is presented in Fig. 1. The tribological system consists of a tested sample (1) and contrabody (2). The sample of a certain size was fixed into a holder (3) (sledge) which was attached to the dynamometer (6) and a micrometric screw (5) by means of a non-elastic thread. The lower surface of the holder (3) was set at 2 mm over the contact surface between the sample (1) and contrabody (2).

Measurements of the static friction force (To) using the shown device (Fig. 1) were carried out in the following order: the sample (1) was fixed into the holder (3) and a given load P was determined with the help of the loads (4). The scale of the dynamometer (6) was reset and a tangential force F was set over the sample holder (3) smoothly through the non-elastic thread by a slow movement of the micrometer screw (10 μm s^{-1}). The
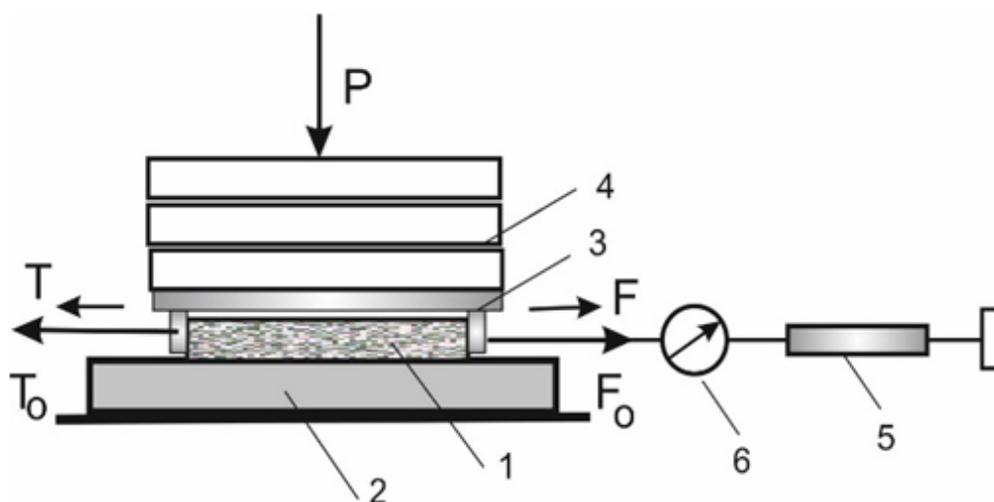
Fig. 1. Functional scheme of laboratory device for studying static and kinetic friction at a slow sliding rate: 1 - sample; 2 - contrabody; 3 - sample holder; 4 - loads; 5 - micrometer screw; 6 - dynamometer.

value of the force F was measured on the dynamometer scale (6) tilled in N. The maximum value of the force Fo was indicated by the dynamometer scale via a recoded movement of its pointer, then followed a decrease of force F value. The rate of static friction force To was equal to the maximum deviation of the dynamometer pointer, the dynamic frictional force T was equal to the dynamometer reading when moving the sample (1). Fig. 2 presents a photograph of the laboratory device for measuring the static and dynamic friction force placed into a cryogenic chamber for the purpose of determining the coefficient of friction at low temperatures.

A small parallelepiped ice block was used as a contrabody. The icy surface was evened via treatment with

Fig. 2. Photograph of the tribological tester placed into a cryogenic camera.

liquid sandpaper STRUERSP180. The samples tested were evacuated into the camera for 30 min prior to the measurements. For each experiment the measurements were performed triple and the average value was taken into account.

The static friction coefficient μ_0 dynamic (kinetic) friction coefficient μ and the jump of the friction coefficient $\Delta\mu$ (i.e. the difference between the static and dynamic friction coefficients) were calculated according to equations (1- 4).

$$\mu_o = T_o / P \tag{1}$$

$$\mu = T / P \tag{2}$$

where P is the load, i.e. N=P, and T is the friction power.

The difference between the static friction power and the dynamic friction power

$$\Delta T = T_o - T \tag{3}$$

is called "jump" of friction during the transition static state– movement.

$$\Delta\mu = \mu_o - \mu \tag{4}$$

The measurements were carried out at -10°C (corresponding to the so called "dry ice"); -4°C (corresponding to the so called "wet ice") and -1°C (corresponding to the so called melting ice, i.e. ice covered by a layer of water).
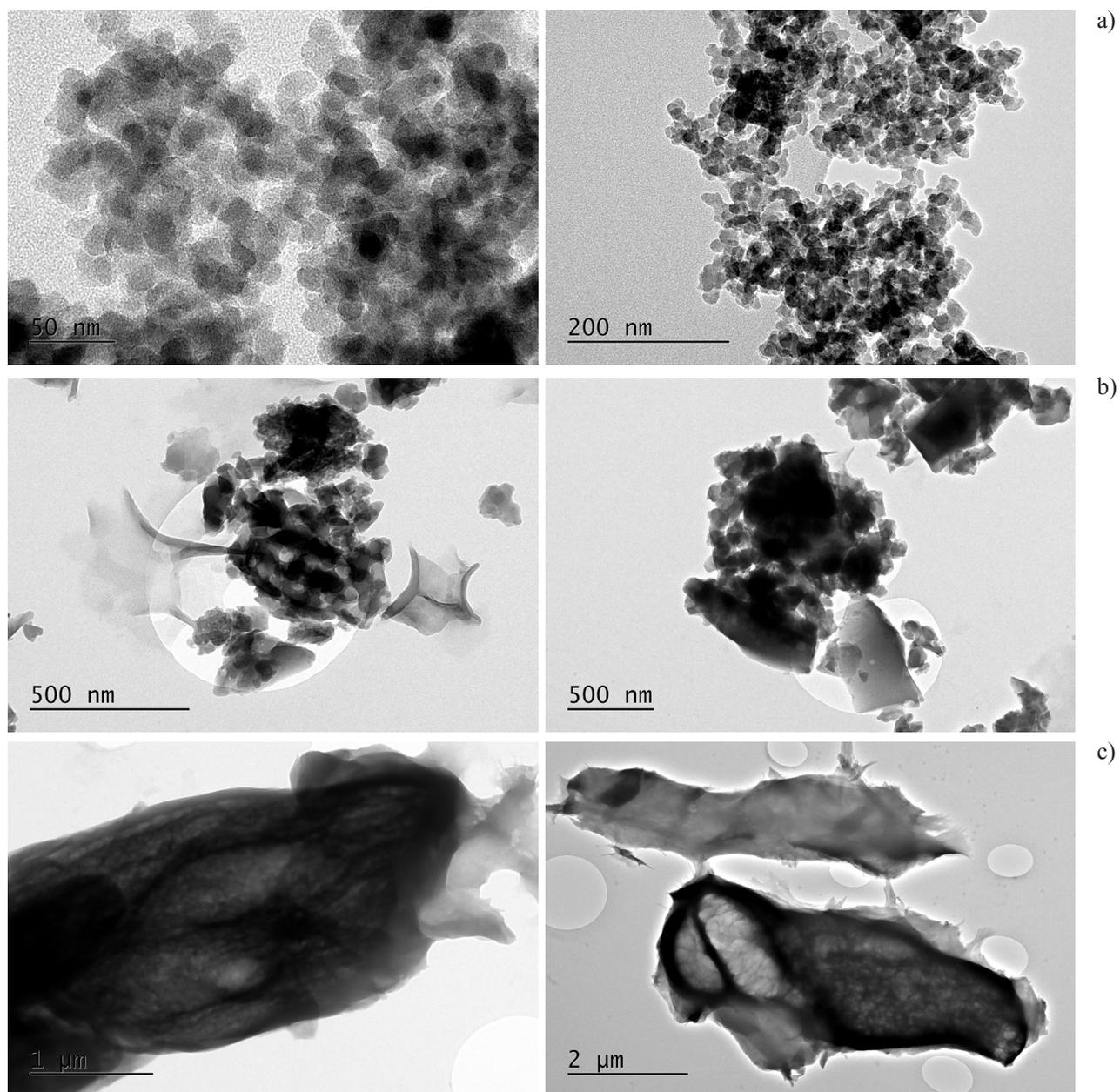
Fig. 3. TEM micrographs of: a) synthetic silica Ultrasil 7000 GR; b) silica obtained by rice husk incineration; c) micro-crystalline cellulose.

RESULTS AND DISCUSSION
Characterization of the fillers used

Fig. 3 presents TEM images of the fillers used. As seen, there is a large difference in the size and shape of the fillers elementary particles. In the first case (Ultrasil 7000 GR) the particles are approximately spherical in shape and size about 20 nm (Fig. 3a). Those of silica obtained by rice husk incineration are of irregular shape and have dimensions in the range of 200 - 500 nm (Fig. 3b). In the case of microcrystal cellulose the particles are mostly rod-shaped and even larger (5 - 7 microns) (Fig. 3c).

Vulcanization characteristics

The vulcanization characteristics of the studied rubber compounds are summarized in Table 2. The results summarized show that the vulcanization characteristics of the composites tested vary considerably depending on the chemical nature of the filler used. The lowest values for all parameters are of the composites containing only microcrystalline cellulose (MCC-1). With the introduction of silica, the values of all vulcanization characteristics increase significantly. The effect for the composition containing standard silica is more pro-

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Table 2. Vulcanization characteristics of rubber compounds comprising elastomers and filler from renewable sources.

	MCC-1	MCC-2	MCC-3
ML, dNm	0.1	0.3	1.0
MH, dNm	10.2	13.4	17.5
ΔM=MH-ML	10.1	13.1	16.5
T_{s1}, min:sec	3:15	3:49	4:40
T_{s2}, min:sec	3:27	4:05	5:05
T_{50}, min:sec	3:58	5:04	6:30
T_{90}, min:sec	6:29	9:48	12:13

Legend: ML minimum torque correlates with the effective viscosity of the mixture; MH - maximum torque correlates with the hardness of the compounds ΔM = MH-ML correlated with the density of the vulcanization network; Ts1- scorch till one torque unit rise above the minimum, correlates with the resistance to premature vulcanization; Ts2 time till the beginning of the vulcanization process (increase of the torque by 2 units), correlated with the resistance to premature vulcanization; T50 - time to run 50 % of the vulcanization process; T90 - time to run 90 % of the vulcanization process (optimum vulcanization time).

nounced, if compared to that of the compound containing the same amount of silica from rice husk. The observed effects can be explained by the fact that microcrystalline cellulose is a softer filler, with a plasticizing effect. It is apparently less active and not compatible enough technologically and thermodynamically, if compared to silica (microcrystalline cellulose is hydrophilic, while the rubber matrix is hydrophobic). Silica adsorbs the accelerators on its surface, thereby retards the vulcanization process, what is particularly well pronounced in the case of standard silica, which has a higher specific surface area. Its adsorption effects are better than that of the filler obtained from rice husk incineration.

Physicomechanical characteristics

The physicochemical characteristics of vulcanizates containing elastomers and ingredients from renewable resources are summarized in Table 3. Some values recommended in literature for manufacturing footwear soles are also given for comparison.

As known, at the smaller size of the filler particles and higher specific surface area the reinforcing efficiency improves [13], as well as all the physical and mechanical parameters what is evidenced by the results shown in Table 3 and by our TEM studies described above (Fig. 3). It is also seen that, the combination of microcrystalline cellulose also guarantees the recommended

Table 3. Physicomechanical properties of vulcanizates containing ingredients from renewable sources.

	MCC-1	MCC-2	MCC-3	Recommended values [11, 12]
Modulus at 100% elongation, M_{100}, MPa	0.6	1.2	1.2	
Modulus at 300% elongation, M_{300}, MPa	1.4	3.8	4.6	-
Tensile strength, σ, MPa	5.6	12.3	15.3	Min 8 [23]
Relative elongation, ε_1, %	640	600	590	Min 300 [23]
Residual elongation, ε_2, %	22	27	35	-
Shore A hardness, equivalents	52	59	63	60-88 [23]
Wear resistance, mm^3	350	195	164	Max 150 [23]
Tear resistance, N/mm	3.0	9.8	22.5	Min 8 [23]
Fatigue failure resistance, cycles	> 60000	> 60000	> 60000	Min 40 000 [24]

physic-mechanical performance, which is much more appropriate when using standard silica (MCC-3). The low reinforcing efficiency of microcrystalline cellulose alone (MCC-1), is also due to its hydrophilic surface, which has poor compatibility with the hydrophobic rubber matrix, apart from the low specific surface area and large particle size. Obviously, microcrystalline cellulose needs additional surface modification in order to be made hydrophobic, hence to improve its compatibility with the natural rubber matrix and the physic-mechanical characteristics of the vulcanizates that contain it, respectively.

Bending resistance

All composites tested were subjected to experiments to determine their „flexural strength" index as described in [12]. All composites withstood over 60,000 cycles of bending to 180° without any cracking. According to the standard, samples must withstand at least 40 000 cycles without cracks, so it is obvious that they meet the requirements.

Predicting the adhesion to ice and snow taking into account DMTA, etc. analyses data

The dynamic mechanical thermal analysis allows to define the complex dynamic modulus E*, the storage modulus E′ and the losses modulus E″ of a rubber material by the reaction of the material against the impact of oscillating force causing a sinusoidal load. The relationship between them can be represented by the equation $E^* = E' + jE''$. Thus the ability of the composite to store energy (the storage modulus expresses the elastic component of the complex dynamic modulus) and its ability to lose energy (the loss modulus expresses the plastic component of the complex dynamic modulus) [14]. Their ratio $tg\delta = E''/E'$, the so called tangent of mechanical loss angle, is of particular importance. Its importance is due to a definitely established fact [15] that, the tangent of mechanical loss angle of the rubber material from which the sample is made at low temperatures correlates well with its adhesion to ice and snow (the higher the tangent, the higher the adhesion).

Fig. 4 summarizes the data from the tangent of mechanical loss angle of the investigated rubber composites at -10°C, -4°C and -1°C, correlating with "dry ice", "wet ice" and melting ice, respectively.

As seen from the presented results, at all the temperatures studied the composites containing microcrystalline cellulose in a combination with standard silica
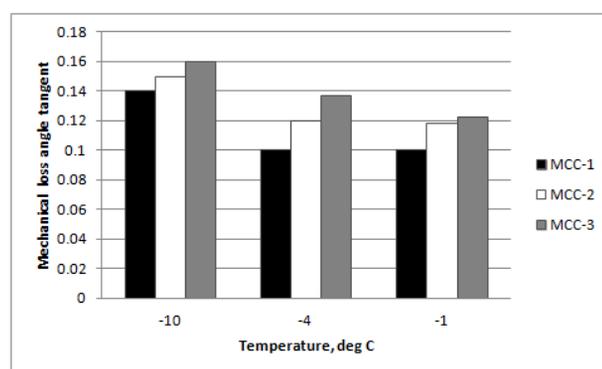

Fig. 4. Tangent of mechanical loss angle of the rubber composites studied at -10°C ("dry ice"); -4°C ("wet ice") and -1°C (melting ice).

(MCC-3) have the highest tangent of mechanical loss angle, the highest predicted adhesion to icy surfaces, respectively. The composites containing rice husk silica (MCC-2) have a bit lower adhesion. The lowest adhesion values are for the composites containing only microcrystalline cellulose (MCC-1). It is also seen that, as the temperature increases, the tangent of mechanical loss angle decreases, i.e. adhesion to the surface weakens. This fact should be taken into account when choosing a composite for soles manufacturing, since at higher temperatures the tangent of mechanical loss angle should be as low as possible so that to ensure slip resistance against all kinds of icy surfaces ("dry ice", "wet ice", melting ice). In the cases we have studied, that turned to be the composite containing a combination of microcrystalline cellulose and silica from rice husk incineration.

Tribological measurements of the coefficient of the static and kinetic (dynamic) friction

Figs. 5 - 7 present the coefficient of the static and kinetic (dynamic) friction of the composites tested, as well as the difference between them (the so called "jump") at temperatures corresponding to "dry ice", "wet ice" and melting ice.

The coefficients of static and dynamic friction of our composites measured tribologically under conditions closest to the real ones confirm the results about the tangent of mechanical loss angle obtained by DMTA. It has been confirmed that, composites filled with the combination of microcrystalline cellulose and silica are the most suitable for soles making because they have the highest values of the static and dynamic friction coefficients and the greatest difference between them,
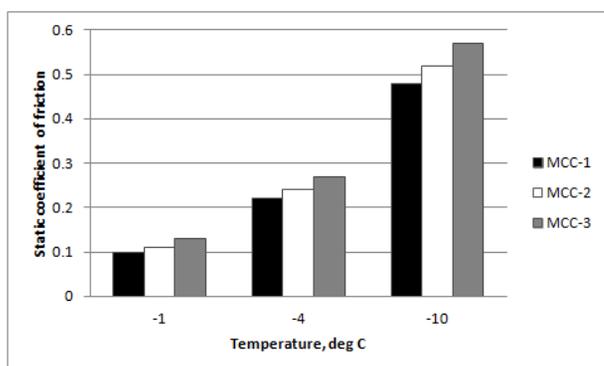
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Fig. 5. Coefficient of the static friction of the composites tested at temperatures corresponding to "dry ice", "wet ice" and melting ice.
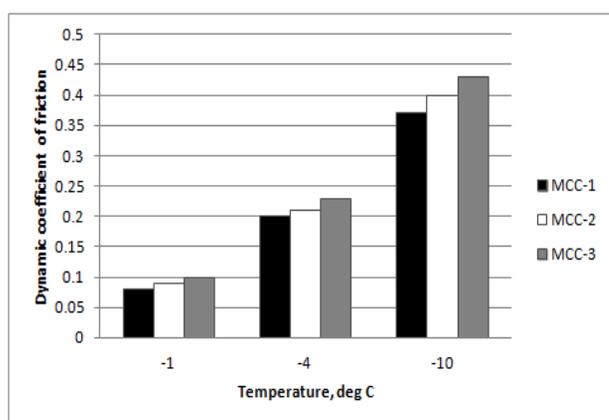

Fig. 6. Coefficient of the kinetic (dynamic) friction of the composites tested at temperatures corresponding to "dry ice", "wet ice" and melting ice.
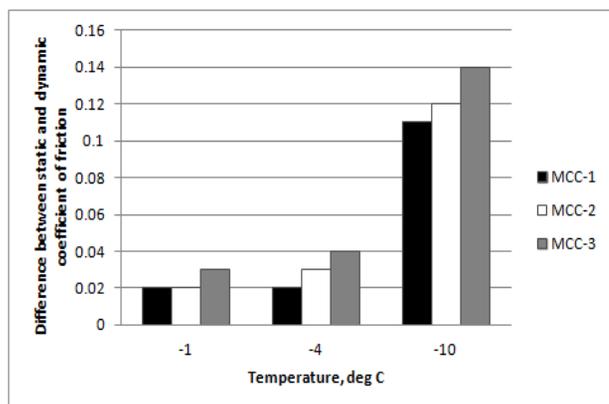

Fig. 7. Difference between the values for the coefficient of the static and kinetic (dynamic) friction of the composites tested (the so called "jump") at temperatures corresponding to "dry ice", "wet ice" and melting ice.

Table 4. Classification of the adhesion class depending on the kinetic coefficient of friction.

Kinetic coefficient of friction	Degree of slip resistance
> 0.30	highly stable
0.20-0.29	stable
0.15-0.19	unstable
0.05-0.14	slipping
< 0.05	highly slipping

what guarantees high slip resistance. The composites containing standard silica have some advantage over those containing silica from rice husks.

The following classification of the coefficients of kinetic friction and the class of adhesion (to ice)/slip is given in the specialized literature [16, 17] (Table 4).

The comparison of the values of the kinetic friction coefficients obtained tribologically with those in the specialized literature recommended for similar applications (Table 4) show that, the composites containing a combination of microcrystalline cellulose and silica (with the predominance of the standard to that obtained by rice husk incineration) under the conditions of "dry ice" and "wet ice", fall into the highest classes - "very stable" or "stable" against slipping. However, under the conditions of melting ice (-1°C) they do not guarantee the required kinetic friction coefficients and fall into the "slipping" class. Since it is assumed that under the conditions of melting ice there is a layer of water which presence reduces the friction coefficient, it is obvious that adjustments should be made to the composition of the rubber compound, so that the friction coefficient under these conditions get higher. Such steps may be replacement of non-polar natural rubber with much more polarized epoxidized natural rubber (at 25 % or 50 % of epoxidation); as well as surface modification of the microcrystalline cellulose particles in order to convert them from highly hydrophilic into hydrophobic. That will be the subject of future research.

CONCLUSIONS

Versatile variants of rubber composites containing elastomers and ingredients from renewable sources (natural rubber, microcrystalline cellulose, silica produced by rice husk incineration, rapeseed oil) have

been studied with regard to manufacturing footwear soles with enhanced slip resistance on various types of icy surfaces. The compounds and vulcanisates have been characterized with respect to the parameters recommended in the specialized literature on footwear soles based on elastomers and their compliance with literature data is shown. Dynamic mechanical thermal analysis has been used to predict the adhesion of the materials to "dry ice", "wet ice" and melting ice. It has been found that, in all the cases examined, the composites containing natural rubber and microcrystalline cellulose-silica as fillers are the most suitable for the purpose. The silica used can be both synthetic and from renewable sources. The tribological tests carried out have confirmed that the composites containing the combination of microcrystalline cellulose-standard silica (at a 1:2 ratio) under the conditions of "dry ice" and "wet ice" fall into the class of the highest resistance against slip but on melting ice they do not have the necessary degree of resistance. It is believed that the use of a polar elastomer and hydrophobilizing the surface of microcrystalline cellulose particles will solve the problem. The developed composites for manufacturing footwear soles comprise chiefly elastomers and ingredients from renewable sources (elastomers, fillers, process additives), which depending on the specific composition, are in the range of 60 - 89 % of all products used. The results show that those materials can be used to improve the slip resistance on icy surfaces.

Acknowledgements

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