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Effect of native starch on processing and vulcanizing properties of rubber blends

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Abstract: *Effect of native starch on processing and vulcanizing properties of rubber blends*. Research and development in the rubber industry in the last decades pay attention to application of biodegradable and natural renewable bio-based fillers such as starch and lignin. Native corn starch as filler in the rubber model blends accelerated crosslinking reaction and improved physical and mechanical properties of vulcanizates.

Keywords: starch, lignin, rubber blends, filler

INTRODUCTION

Fillers belong to important components of rubber blends because they modify rheological properties of raw-rubber blend as well as physical properties of vulcanizates. Research and development in the rubber industry in the last decades pay attention to application of biodegradable and natural renewable bio-based fillers such as starch and lignin[1]. The surfaces of starch contain a large amount of hydroxyl groups as the silica. Starch/plasticizer composites have been suggested for use in elastomer composition for various purposes, including tires[2-4]. Other biopolymers, such as lignin have been tested for use as modifying components in rubber blends as filler with anti-degradation abilities[5], substituent of polymer matrix and also as modifier of some mechanical properties[6].

EXPERIMENTAL

The model blends, consisting of a natural rubber or styrene butadiene rubber polymer (NR or SBR), a bio-filler (native corn starch to 20 phr), and vulcanizing system (ZnO, stearine, CBS, S) were evaluated (the effect on vulcanizing process, physical properties and processing properties) and compared with the real blends consisting of all common rubber blend components. The processing properties were evaluated using Extrusiongraph Brabender L/D = 25; dye Φ = 5 mm.

RESULTS AND DISCUSSION

In our present work the basic exploration of native corn starch as fillers in model as well as in real rubber blends is reported.

Tab. 1 Vulcanizing and viscosity properties of model blends

NR based blends

Starch (phr)	T_{s2} [min]	T_{c90} [min]	M_{max} [dNm]	ML 1+4@100°C
0	3.01	5,65	14,3	31,7
5	2.53	4,74	14,9	32,6
10	2.39	4,67	15,5	32,9
15	2.45	4,66	16,7	34,1
20	2.50	4,64	17,7	34

SBR based blends

Starch (phr)	T_{s2} [min]	T_{c90} [min]	M_{max} [dNm]	ML 1+4@100°C
0	3.13	7,46	16,1	35,5
5	2.51	6,32	18,1	34,5
10	2.56	5,69	18,1	35,9
15	2.51	6,03	20,3	37
20	2.33	5,7	20	38,8

At first we used the model blends consisting of polymer (NR or SBR) native corn starch and vulcanizing system (ZnO, stearine, N-Cyclohexyl-benzothiazole-2-sulphenamide, S). The miscibility, processability and effect on vulcanizing and physical properties were evaluated.

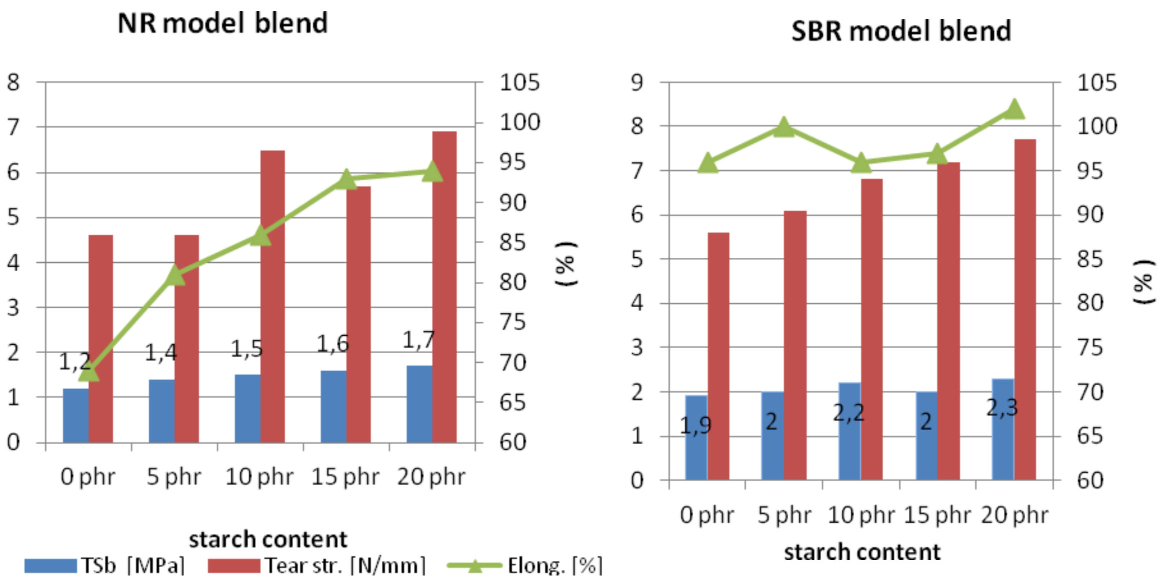

Fig. 1 Physical and mechanical properties of model blends.

It was found that in the model blends the starch as a filler affected the crosslinking reaction. The values of optimum curing time Tc_{90} decreased and values of torque were increased in both rubber blends. The physical properties such as tensile strength, tear strength and elongation were also increased. This is caused by the reinforcing effect of the applied filler into model blends and its principal compatibility with the tested polymers.

Tab. 2 Processing properties of model blends

NR based blends

Starch (phr)	Weight [g/min]	Φ [mm]	M [Nm]	Density [g/cm^3]
0	6.58	8.59	30.0	0,9507
5	7.19	8.26	38.3	0.9634
10	7.75	8.39	40.5	0.9715
15	8.06	8.10	44.6	0.9837
20	8.29	7.88	45.1	0.9876

SBR based blends

Starch (phr)	Weight [g/min]	Φ [mm]	M [Nm]	Density [g/cm^3]
0	5.98	9.28	37.1	0.9659
5	6.01	9.29	32.5	0.9842
10	6.18	9.20	31.5	0.9961
15	6.45	8.93	33.4	1.0101
20	6.24	8.77	33.5	1.0134

The processing properties were also improved. The weight of the extruded material under stead flow was increased and growing of extruded string diameter F was decreased with increasing amount of a bio-filler. Densities of blends with increasing amount of starch filler increased also, because model blends were not filled with any filler.

The corn starch was tested in the real rubber blends. Unmodified native corn starch was applied as substitution of part of silica filler. Measured results showed slight or fairly large effect on observed properties, depending on the proportion of substituted filler or raw rubber. The vulcanizing characteristics such as scorch time Ts2, optimum curing time Tc90 of NR real blend were lower, what means acceleration of crosslinking reaction and achieve the optimum vulcanization took shorter time.

Tab. 3 Vulcanizing and viscosity properties of real blends.

NR based blends

Starch (phr)	T_{s2} [min]	T_{c90} [min]	M_{max} [dNm]	ML 1+4@100°C
0	2.82	6,8	8,7	39,6
5	2.6	5,93	8,6	24,9
10	2.38	5,24	8,1	23,2
15	2.26	5,12	8,4	24,8
20	2.15	4,87	8,2	21,4

SBR based blends

Starch (phr)	T_{s2} [min]	T_{c90} [min]	M_{max} [dNm]	ML 1+4@100°C
0	1.17	1,69	5,1	25,9
5	1.10	1,58	5,23	26,8
10	1.29	1,73	5,52	24,9
15	1.33	2	5,92	24,7
20	1.68	2,68	5,5	23

Contrariwise, the value of Ts2, Tc90 of SBR real blend were higher, what indicates different effect of starch in crosslinking reaction in SBR based blend. ML value of Mooney processing viscosity decreases in both cases.

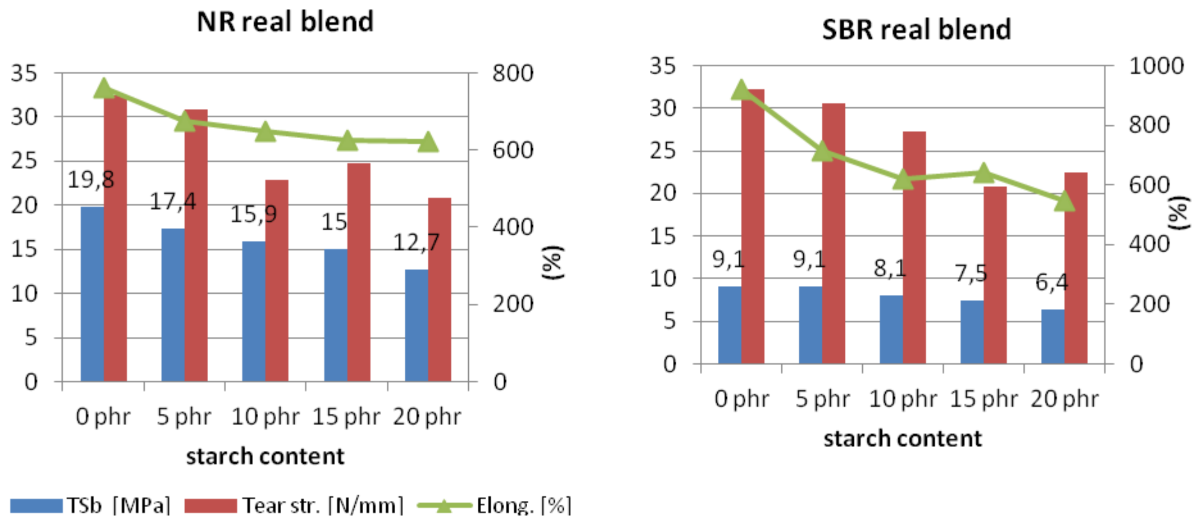

Fig. 2 Physical and mechanical properties of real blends.

The application of the biopolymer to the real rubber blends as substitution of a part of white fillers, caused a decreases of the tensile strength, elongation and tear strength values with the increasing amount of native corn starch. At a lower level of the substitution the declination is not substantial what indicates a practical application especially after modification of the filler.

Biopolymers have the different effect on the vulcanization process depending on their chemical nature and their application in rubber blends must be affiliated with modification of the vulcanization system.

The processing properties of real rubber blends were improved also. The weight of the extruded material under stead flow in case of NR based blend the increase was higher in comparison with SBR blends and growing of extruded string diameter F was decreased with increasing amount of a bio-filler. Also densities of blends with increasing amount of starch filler increased slightly also, because volume weight of corn starch is higher in comparison with substituted fillers.

Tab. 4 Processing properties of real blends

NR based blends

Starch (phr)	Weight [g/min]	Φ [mm]	M [Nm]	Density [g/cm^3]
0	6.58	8.59	30.0	0,9507
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The processing properties were also improved. The weight of the extruded material under stead flow was increased and growing of extruded string diameter F was decreased with

CONCLUSIONS

- native corn starch as filler in the rubber model blends accelerated crosslinking reaction and improved physical and mechanical properties of vulcanizates,
- biopolymer fillers (native corn starch) in the real rubber blends affected vulcanizing parameters and decreased physical and mechanical properties.

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Streszczenie: *Wpływ skrobi naturalnej na przerób i wulkanizację gumy*. Badania w przemyśle gumowym w ostanich dekadach skoncentrowane są na zastosowaniu biodegradowalnych i odnawialnych wypełniaczy takich jak skrobia i lignina. Skrobia kukurydziana jako wypełniacz w mieszankach gumowych przyspiesza sieciowanie i poprawia fizyczne oraz mechaniczne własności wulkanizatów.

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