Novel Approaches of Using of Spirulina Platensis in Natural Rubber Based Composites

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ABSTRACT: The aim of this work was to investigate the influence of Spirulina (*Spirulina platensis)* as a natural filler on the curing characterization, morphology and mechanical, thermomechanical and thermal properties of natural rubber (NR) based composites. Spirulina was introduced into NR mixture in amount of 0 phr, 10 phr and 30 phr. The vulcanization process was carried out at the determined process condition by using hydraulic press at optimum vulcanization time (t_{90}). It was noticed that Spirulina affected on the reduction of t_{90}, and scorch time (t_2) of the NR mixtures. Obtained vulcanizates were subjected to the number of tests e.g. scanning electron microscopy analysis, mechanical dynamical analysis, tensile test, hardness, and thermogravimetry. Generally, it was found that Spirulina added in amount of 10 phr NR positively influenced on tensile strength (TS_b), storage modulus and hardness of obtained composites.

KEYWORDS: Spirulina, algae, natural rubber, composites, DMA

1 INTRODUCTION

Algae are photosynthetic organisms related to plants that grow in water and produce energy from carbon dioxide and sunlight. They occur in the large scale in the nature and can be divided into type depends on the color, size or function. Algae might be a future potential source of renewable energy and a base for oleochemicals. There are known type of algae which can generate many times more oil per acre than other plants used for biofuels, such as corn or soybean [1-3]. Nowadays widely known the applications of algae are the food (especially animal and fish food supplement) and pharmacy sector [4, 5]. Literature indicates that algae can be used in many branch of industry e.g. bio-based polyols or bio-plastic production as well [6, 7] or preparation of the silver nanoparticles (by using cyanobacterium) [8, 9] and copper oxide nanoparticles [10]. The grown interest of algae is caused by its advantages like fast reproduction cycles with high consumption of waste CO_2, good resistance to high UV radiation doses and better effectiveness of energy conversion to biomass due to low demands on other metabolic functions [11].

One of the most commonly known and used algae is *Spirulina platensis*. This blue green algae belong to the cyanobacterium class and Spirulina genus. The chemical composition of Spirulina is a complex of many different chemical compounds such as fatty acids, vitamins, amino acids or antioxidant pigments such as carotenoid. Ramasamy and Gopalakrishnan by using GC-MS technique have investigated extract of Spirulina in four different (polar and non-polar) solvent: Ethanol, hexane, chloroform and dichloromethane. Among identified compounds were found: Heneicosane; octadecane; triacontane; heptadecane; phytol pentacosane, hexacosane, heptacosane; heptadecane; n-hexadecanoic acid; nonacosane; heneicosane, dotriacontane, heptacosane; pentacosane; 1-(2-methylpropenyl) aziridine. The occurrence of phenolic compound in plant is well documented and these compounds play important role with antioxidant activity in biological system. In the rubber industry phenolic compounds are potential antioxidants and can be used to avoid oxidizing of the elastomers [12]. The chemical composition of the large number of microalgae and cyanobacterial extracts and extracellular products reveal antibacterial or antifungal activity. The volatile compound and crude solvent extract of algae species has ability to inhibit the growth of the bacteria [4, 13].

Algae feedstock is the base for various monomers and bioplastics production including hybrid plastics such cellulose-based plastics, poly-lactic acid (PLA), bio-polyethylene [1, 11]. Up to now there is no information about materials based on natural rubber filled with algae, especially with Spirulina. Taking into account all prior mentioned advantages of Spirulina this work is focused on the evaluation of the Spirulina as a filler at the natural rubber composites and their influence on utilitarian composites properties. Effect of the Spirulina addition on the curing characteristic morphology, selected mechanical (static and dynamic conditions) and thermal stability of prepared natural rubber based composites was studied.

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2 EXPERIMENTAL

2.1 Materials

Natural rubber (NR), cis-1,4 polyisoprene (density ~0,93 g/cm^3) was purchased from Słupskie Zakłady Wyrobów Gumowych "Guma Pomorska" Company, (Słupsk, Poland), steric acid (density~0,93 g/cm^3, melting temperature: 69°C) and zink oxide (density ~5,61 g/cm^3, melting temperature: 1870°C) were purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland); tetramethylthiuram disulfide used as an accelerator T (M_n=240,4 g/mol, density ~1,29 g/cm^3, melting temperature ~ 140°C) and stabilizer IPPD N-isopropyl-N'-phenyl-p-phenylenediamine (M_n=226,32 g/mol, density ~1,17 g/cm^3, melting temperature: 70°C) were provided by Brenntag Sp. z o. o. (Gdynia, Poland). Spirulina (the size of particles were ranged from 14 μm to 134 μm) was purchase from Intenson Europe Sp. z o.o. (Karczew, Poland).

2.2 Natural Rubber Based Composites Preparation

The rubber mixtures containing 0 phr, 10 phr, and 30 phr (parts per 100 parts of natural rubber) of Spirulina (microalgae) were prepared and coded as V0 (vulcanizate without filler), S10 (natural rubber based composites containing 10 phr of Spirulina) and S30 (natural rubber based composites containing 30 phr of Spirulina). Prior used Spirulina have been dried at 70°C for 24 h in the laboratory oven, while the natural rubber was annealed at 60°C for 1 h. The rubber mixtures were produced by using the Buzuluk mixing mill (open roll machine) according the formulation given in Table 1. Next, vulcanization was performed using the hydraulic press ZUP Nysa, type: N512-40/1.8, at determined conditions of pressure (ca. 5 MPa), temperature 140°C and determined optimum vulcanization time (t_{90}). Obtained natural rubber based composites containing Spirulina were compared to natural rubber vulcanizate without filler (V0) and NR based composites filled with 30 phr of chalk (coded as K30).

2.3 Methods

2.3.1 Curing characterization
Vulcanization process was characterized according to PN-ISO 3417 at 140°C, using a Monsanto R100S (USA) rheometer with oscillating rotor. Oscillation angle was 3° and torque range 0-100 dNm. Based on obtained data, cure rate index (CRI) values were calculated in accordance with the equation:

$$CRI = \frac{100}{(t_{90} - t_2)}$$

where,
-t_{90} is optimum vulcanization time (min),
-t_2 is scorch time (min).

Table 1 Formulation of natural rubber mixture based composites.

COMPONENT	CONTENT (PHR)
NATURAL RUBBER	100
STERIC ACID	3
ZINK DIOXIDE	5
STABILIZER IPPD	1,5
ACCELERATOR T	0,5
SPIRULINA	0/10/30
SULFUR	2
MINERAL OIL	2

2.3.2 SEM
Scanning electron microscopy was performed by using Quanta FEG scanning electron microscope equipped with the Everhart-Thornley detector (ETD). The cross section of samples coated with gold was analyzed. Measurements were taken with applying a high vacuum 10,00 kV at a magnification of 250 and 1000.

2.3.3 DMA
Dynamic mechanical analysis of natural rubber based composites was conduct by using a DMA Q800 Analyzer. Measurements were taken under the nitrogen atmosphere in the temperature range from -100°C to 100°C. An operating frequency was 10 Hz and a heating rate 4 °C/min. Dimensions of the samples were ca. 18×10×2 mm (length×width×thickness). Storage modulus, loss modulus and glass transition temperature (as a peaks maximum at E' and tanδ in the function of temperature) were determined.

2.3.4 Tensile test
The tensile strength (TS_b) and elongation at break (E_b) were measured by using standard testing machine, a Zwick Z020 according to the EN ISO 527-1:1996 and EN ISO 527-2:1996 standards. The dumbbell-shaped samples of standard dimensions were prepared and tested at a rate of 300 mm per minute. The measurements were performed at room temperature.

2.3.5 Hardness

Hardness was measured according to the PN-EN ISO 868:2005 standard. The circular samples were placed on a flat surface, and 10 measurements were taken per sample by applying a Shore a durometer for 3 s.

3 RESULTS AND DISCUSSION

3.1 Curing Characteristic

Curing characteristic of rubber mixture allowed to determine two significant parameters to further vulcanization process such as: The scorch time (t_2) and optimum vulcanization time (t_{90}). Both of them have a huge impact on the storage and processing of natural rubber materials. Based on mentioned data, the curing rate index (CRI) can be calculated. Each prepared sample prior vulcanization process has been tested in the mean of vulcametric measurements. Based on the measurement additionally minimum torque (ML) and maximum torque (MH) were determined. The results have been shown in Table 2.

Table 2. Curing characteristics of NR based composites.

Parameter	Symbols of the samples			
	V0	S10	S30	K30
CRI (min^{-1})	33.9	33.2	34.8	49.0
t_2 (min)	5.46	5.45	3.94	7.15
t_{90} (min)	8.41	8.36	6.81	9.19
ML(dNm)	0.67	0.27	0.48	0.48
MH(dNm)	19.62	10.58	15.07	4.78
ΔM (dNm)	18.95	10.31	14.59	4.30

The natural rubber based composites containing 10 phr and 30 phr of Spirulina displayed the curing characteristics which were similar to those of the vulcanized sample without the filler content. The increasing of Spirulina amount caused insignificant increased of CRI. It was found that Spirulina leads to decrease the optimum vulcanization time regardless of the Spirulina content. The natural rubber based composites containing 30 phr of Spirulina has shorter t_{90} ca. 2 min what is an additional economic benefit.
The torque minimal value (ML) which is related with initial viscosity and processing properties of rubber mixtures depends on the amount and type of the filler. Based on obtained data it was found that natural rubber mixtures containing 30 phr of Spirulina and 30 phr of chalk (commonly used filler) characterized by similar values like the same higher initial viscosity. As a higher is ML value thereby higher possibility to create the aggregation by the fillers dispersed in to polymer matrix. The lowest value of ML was recorded for sample S10, which contributed to the good dispersion of the Spirulina into natural rubber matrix and the same good mechanical characteristic of this material.

The MH value corresponds with stiffness and shear modulus of vulcanized samples [14]. The maximal torque values (MH) strongly depend on the filler type and amount. The MH value of the sample with the 30 phr of Spirulina is quite lower to the based rubber vulcanizate sample (V0). Decreasing of the MH values of the rubber based composites containing Spirulina might indicate on the additional plasticization effect caused by the Spirulina filler (because of fatty acid content). Taking into account the amount of Spirulina, the sample coded S30 has a higher MH than in the case of S10, despite the plasticizing resulted of the filler could be the effect of aggregates formation.

ΔM attribute to the crosslinking density. Based on the result presented in Table 2 it can be conclude that the vulcanizates without the filler, V0 should be characterized by the higher cross link density. The presence of crosslinks in the rubber phase limits the flow and mobility of rubber chains [15] and lead to achieving by the samples maximal torque values.

3.2 SEM Analysis

In order to investigate the morphology of prepared natural rubber based composites, filler distribution in the matrix and adhesion between them scanning electron microscopy (SEM) has been used. Natural rubber based matrix (V0) and composites sample filled with 30 phr of chalk and sample filled with 30 phr of Spirulina have been tested and presented in the Figures 1(A), 1(B), and 1(C), respectively. Analyzing Figure 1 it was observed good interaction between both, Spirulina and the chalk and the natural rubber matrix. Smooth matrix surface in either case suggests that the process of crosslinking was efficiency done. Based on the SEM images it can be statement that in the case of Spirulina addition (Figure 1(C)) there is a good compatibility of the composite matrix and filler (no gaps on the boundary NR-Spirulina) but also Spirulina particles tendency to aggregates creation because of strong interaction between filler particles.
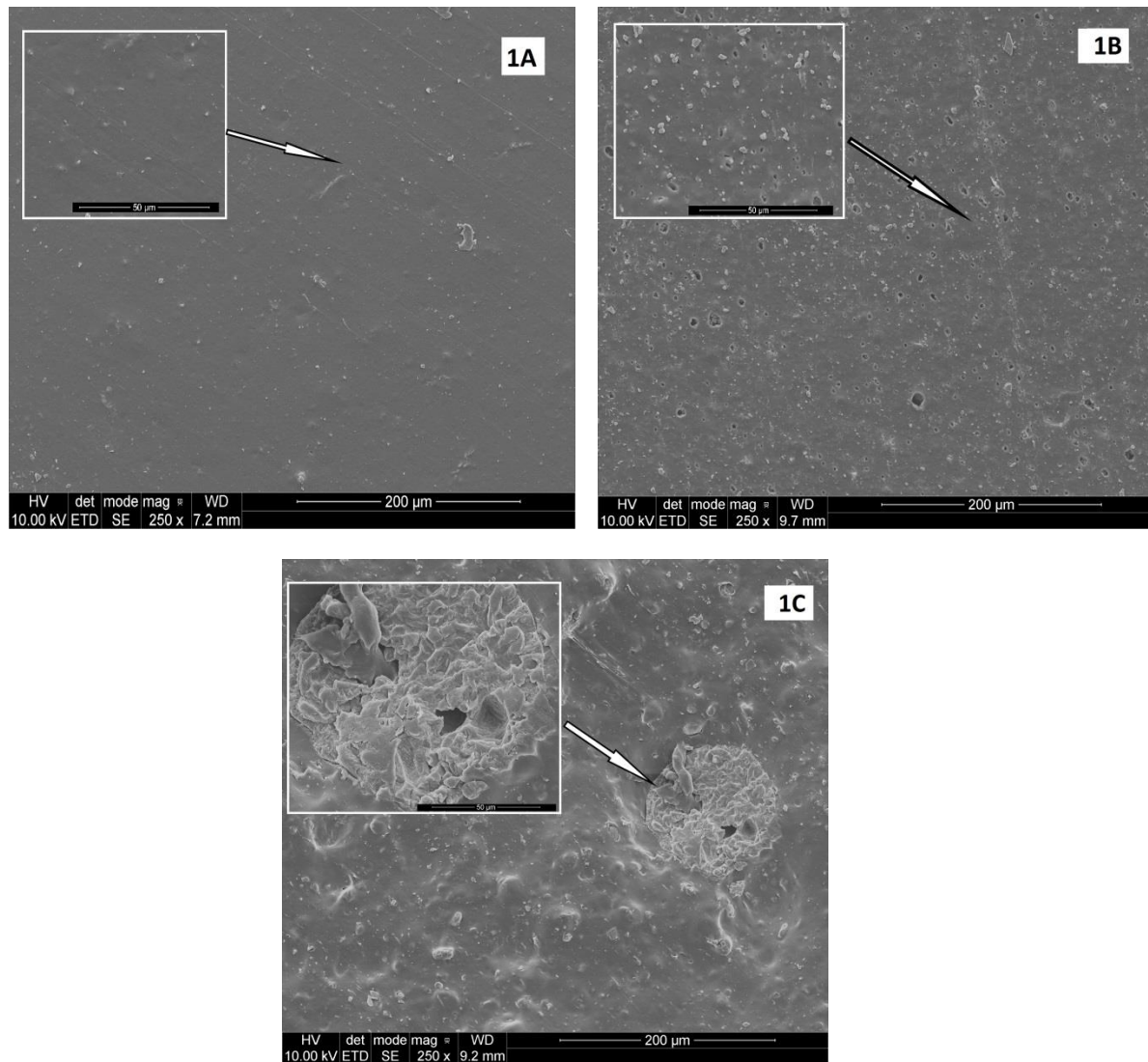
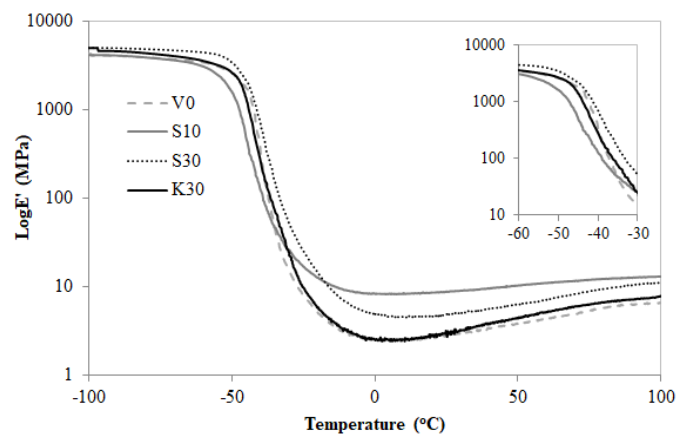**Figure 1** SEM images of natural rubber based matrix (V0) and its composites containing chalk (30K) and Spirulina (30S).

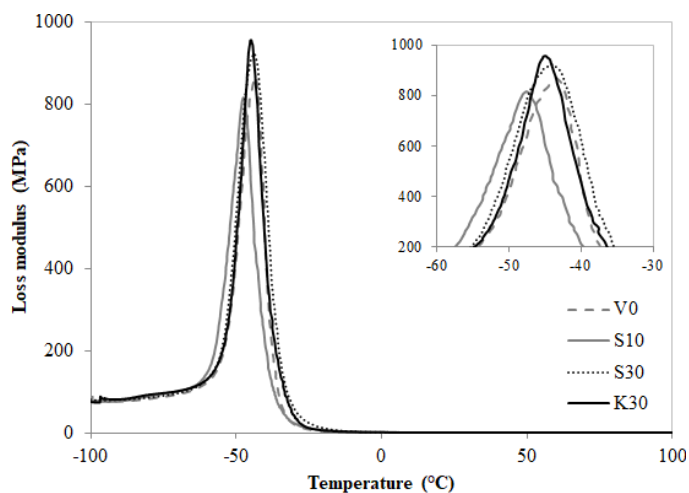**Figure 2** The storage modulus (E') as a function of temperature for natural rubber based composites.

Figure 3 The loss modulus (E'') as a function of temperature for natural rubber based composites.
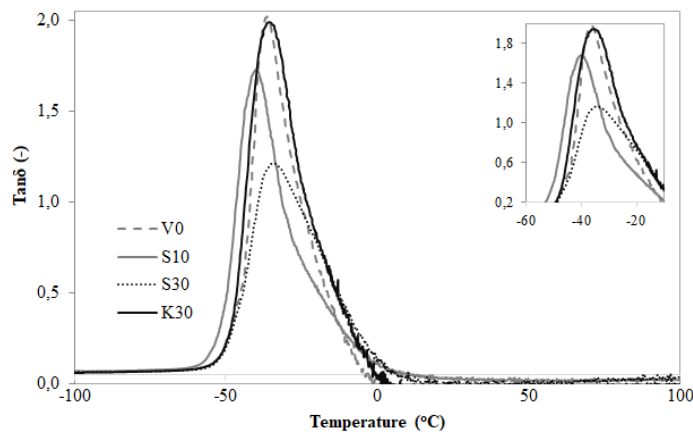

Figure 4 The loss factor (tanδ) as a function of temperature for natural rubber based composites.
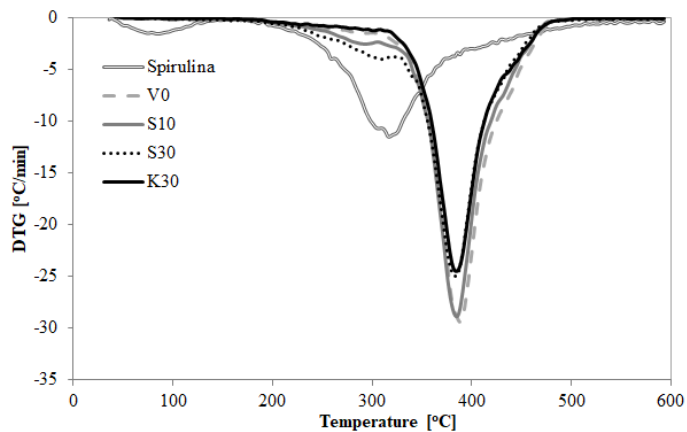

Figure 5 DTG as a function of temperature for natural rubber based composites and Spirulina.
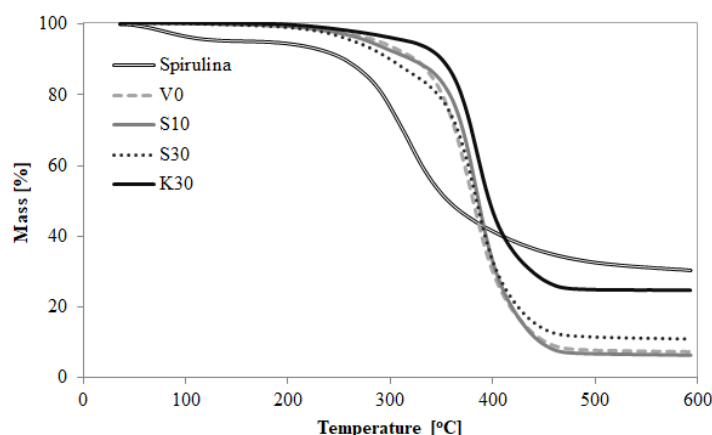
Figure 6 Mass as a function of temperature for natural rubber based composites and Spirulina.

3.3 DMA Analysis

The storage modulus (E'), loss modulus (E'') and loss factor (tanδ) as a function of the temperature have been shown in Figures 2-4. In Figure 2 the Log E' *vs.* temperature curves of the vulcanizates is presented. At the lowest temperature range from -100°C to ca.-60°C is assigned the glassy region of natural rubber based composites. In that region, the curve indicates the linear following (typical behavior for the 1, 4-cis-polizoprene macromolecules) and the maximum recorded value is attributed to the material stiffness and cross-linking density [14, 16 -17]. For composites S10 and S30 the alfa transition displayed at the temperature range ca. from -50°C, while for vulcanizate V0 and composite K30 at ca. -45°C.

The intercoperation of Spirulina and natural rubber based matrix was analysis at the range of room temperature (T=25°C). It can be easily noticed that between natural rubber based matrix and Spirulina the strong interaction occurred. What is more, the optimum level of Spirulina content to maintain privilege interaction between Spirulina and matrix is 10 phr. Higher addition of Spirulina caused stronger interaction between filler particles than between matrix and filler what can be observed in logE' decreasing, regardless NR-based composites containing Spirulina are characterized by higher storage modulus in comparison to V0 and K30.

The effect of Spirulina additive in the natural rubber based composites on the loss modulus was presented in Figure 3. Well-shaped single peaks have been registered for each obtained vulcanizates and those peaks displayed similar characteristic. A slight loss modulus decreasing is observed in the case of the

sample S10 (Figure 3), that indicates on more energy irreversible lost by the vulcanizate and consequent of higher stiffens of this material. Generally, the loss modulus values ranged from 800 MPa to 950 MPa.

According to the Figure 4 the glass temperatures (T_g) as a temperature at the maximum value of tanδ have been determined. The glass temperature registered for samples V0 and K30 is ca. -36°C while for the natural rubber based composites containing Spirulina is slightly shifted to the lower values (up to ca. -42°C for sample coded S30). Decreasing of the Tg can be related with increasing of the polymer chain mobility because of the fatty acids occurring in the structure of Spirulina and thereby plasticization effect.

Loss factor of rubber based composites indicated on the different damping properties of obtained materials. The tanδ is changed from 1.1 to 2.0 (Figure 4). The lowest values of tanδ were registered for natural rubber based composites containing Spirulina. Moreover, increasing of Spirulina content in rubber matrix causes decreasing in tanδ and damping ability [18]. Taking into account that generally chalk (inert filler) is added into natural rubber matrix to reduce the price of final product without the decreasing the mechanical properties is confirmed.

3.4 Mechanical Properties as a Tensile Properties and Hardness

The results of tensile test (tensile strength, TS_b and elongation at break, E_b) and hardness were given in Table 3. Spirulina as a filler of natural rubber composites caused decreasing of tensile strength of vulcanizates about 3 MPa and 7 MPa in comparison to the vulcanizates without filler (coded V0). Decreasing of TS_b can be result of tendency to the aggregation of Spirulina filler. Based on curing characterization and

DMA analysis this assumption could be very likely. The insignificant decreasing in E_b was noted as well.

The vulcanizate sample, V0 and natural rubber composite filled with chalk are characterized by the highest and similar tensile strength. Taking into account hardness, implementation of Spirulina as a filler due to increasing of this property. Hardness increase with increasing Spirulina amount in the natural rubber matrix what indicated on good interaction between filler and matrix.

Table 3 Tensile strength, elongation at break and hardness of the natural rubber based composites containing Spirulina or chalk.

Property	Symbols of the samples			
	V0	S10	S30	K30
TS_b (MPa)	18.72±0.7	15.65±1.0	11.2±0.7	16.98±1.0
E_b (%)	741±54	710±18	733±17	811±18
Hardness (ºShA)	37.7±0.2	40.2±0.5	45.3±0.4	46.1±0.1

3.5 Thermogravimetry (TGA)

Thermal properties of obtained materials have been examined by using thermogravimetry analysis. Mass loss and DTG as a function of temperature are presented in the Figure 5 and Figure 6. To better understand the thermal decomposition process of the composites, the TGA characteristic of Spirulina filler was conducted as well.

Spirulina decomposed in one main step at ca. 316°C. Spirulina is highly hygroscopic filler, what is visible as an additional decomposition step on the DTG *vs.* temperature curve, around 100°C assigned peak is caused by water evaporation (Figure 6). The thermal decomposition of the natural rubber based composites containing Spirulina occurred in two main steps. The first step at ca. 311°C is correlated with thermal decomposition of Spirulina, broad peak indicated on complex structure of Spirulina. The second at the higher temperature ca. 386°C with the natural rubber matrix decomposition. The vulcanizate sample without filler, V0 and filled with chalk has degraded in one main step with maximum decomposition rate at temperature ca. 386 °C and 388 °C, respectively [16, 19]. The vulcanizate containing chalk decomposed in about 70% with the high content of inorganic filler residue.

The rate of the thermal degradation depends on the Spirulina content. It was found that the addition of Spirulina in 30 phr caused improvement in thermal stability by the decreasing of decomposition rate (Figure 6) in comparison to the sample without filler content. What is more, the DTG value for this sample (S30) is almost the same as for composite containing chalk (K30).

4 CONCLUSION

Spirulina platensis up to 30 phr was successfully utilized as an active filler in natural rubber based composites. Based on the vulcametric measurements it was found that the addition of Spirulina caused decreasing of time vulcanization what is a benefit. SEM analysis showed good adhesion between Spirulina and natural rubber matrix what is a consequence of theirs the good compatibility. The glass temperature of prepared composites is in the range from -42°C to -36°C. Increasing of Spirulina amount in NR matrix caused a slight increase in storage modulus and loss factor changes in comparison to the vulcanizate without filler. Natural rubber based composites containing 10 phr of Spirulina are characterized by good mechanical properties. Higher content of Spirulina in the natural rubber matrix resulted in filler aggregation formation. Positive results indicate on possibility and therefore the need to expanding using of Spirulina additive in different practice materials. The beginning of the thermal decomposition of NR based composites containing Spirulina occurred at the same temperature range as NR based composites filled with chalk, but with the lower composition rate.

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