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Article

Synergistic effect of mica, glass frit and melamine cyanurate for improving fire resistance of styrene-butadiene rubber composites destined for ceramizable coatings

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Abstract: Synergistic effect of different fillers is widely utilized in polymer technology. The combination of various types of fillers is used to improve various properties of polymer composites. In this paper a synergistic effect of flame retardants was tested for the improvement of ceramizable composites performance. The composites were based of styrene-butadiene rubber (SBR) used as polymer matrix. Three different types of flame retardants were tested for synergistic effect: Mica (phlogopite) high aspect-ratio platelets along with low softening point temperature glass frit (featuring ceramization effect) and melamine cyanurate, a commonly used flame retardant promoting carbonaceous char. In order to characterize the properties of the composites, combustibility, viscoelastic properties and mechanical properties before and after ceramization were tested. The results obtained show that the synergistic effect of ceramization promoting fillers and melamine cyanurate is especially visible with respect to the flame retardant properties resulting in a significant improvement of fire resistance of the composites.

Keywords: composite; ceramization; ceramification; styrene-butadiene rubber; melamine cyanurate; mica; flame retardancy; coating; glass frit

1. Introduction

Ceramizable (ceramifiable) polymer composites were originally designed and developed for cable coatings ensuring integration of an electric installation in case of a fire-hazard [1-3]. Such approach resulted in a significant enhancement in evacuation techniques and fire-fighting systems. For example, allowing for the development of fireproof elevators ensuring effective evacuation possibilities, especially for disabled or elderly people [4]. Moreover, in recent years the area of ceramizable composites utilization expanded covering fireproof window sealing system [5], coatings for steel construction elements [6] and innovative ablative materials for spacecraft applications [7] starting to compete with much more popular now intumescent coatings [8].

Ceramizable polymer composites are a type of smart materials changing their structure and properties when exposed to fire and elevated temperature. They exhibit high elasticity and easy processing before ceramization and transform into a continuous and stiff ceramic structure after ceramization. From a morphological point of view they are dispersion composites consisting of polymer matrix and a mix of dispersed fillers that initiate the ceramization process. The polymer

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matrix burns and decomposes at elevated temperature while the fillers interact forming a continuous ceramic structure.

There are several mechanisms of ceramization: 1. Addition of a low softening point temperature glass frit that acts as a binding agent for other thermally stable fillers [9-11]; 2. Sintering of filler particles accompanied by silicone rubber matrix covalently bonded to their surface [12]; 3. In-situ formation of calcium silicates from calcium-based fillers and the silica formed after silicone matrix burning [1]; 4. Silicon oxycarbide phase formation from cross-linking of silicone rubber adsorbed on nano-filler surface or catalyzed by platinum compounds [13]; 5. In-situ ceramic structure formation from reactions between the products of thermal decomposition of silicone rubber, ammonium polyphosphate, aluminium hydroxide and mica [14]; 6. Controlled arrangement of mineral fillers inside the polymer matrix [15]. A specific type of a secondary filler may be incorporated/ used in order to improve the properties of the ceramic structure, for example, triggering the formation of a nano-porous phase [16] or enhancing its compression strength [17].

Silicone rubber was originally chosen as a ceramizable composites matrix because amorphous silica is the product of its burning which improves the properties of the ceramic phase. However, silicone rubber exhibits also some limitations like relatively low mechanical properties, high price and low filler loading. Therefore, alternative polymer matrices are tested for ceramizable composites applications, such as: acrylonitrile-butadiene rubber (NBR) [18], ethylene-propylene-diene rubber (EPDM) [19-21], poly(vinyl acetate) [22], polyurethane [23], polyester [24], polyethylene [25], and boron phenolic resin [26-28]. However, their applicability for ceramizable composites still remains limited. The most promising replacement for silicone rubber nowadays seems to be the poly(ethylene-co-vinyl acetate) copolymer (EVA) ensuring good mechanical properties both before and after ceramization [29-32]. The positive effects of EVA application as a matrix for ceramizable composites resulted also in using it as a blend with silicone rubber [33]. However, the use of silicone rubber alone is still very prospective [34, 35]. In our previous work we proved that the application of styrene-butadiene rubber (SBR) as a polymer matrix for ceramizable composites is also very promising [36]. Based on the available literature [37-39] one can state that thermal stability of SBR is comparable to the one of silicone rubber [40, 41]. Moreover, in the presence of oxygen SBR degrades with two-stage kinetics [38], first occurring in the temperature range of 390-520 °C and subsequently between 620-720 °C. The first stage most probably corresponds with the thermal degradation of linear rubber macromolecules and the simultaneous cross-linking (maybe even carbonization) leading to the formation of a thermally stable residue that decomposes thermooxidatively in the second stage. The highly cross-linked structure formed during thermal degradation plays most likely a significant role in maintaining a coherent, self-supporting structure of the ceramizable composites in the temperature range where the elastic SBR matrix is gone but the new ceramic structure is not fully formed yet [36]. For this reason, SBR rubbers emerge as very prospective matrix materials for ceramizable composites.

In the current work we test the effect of the melamine cyanurate (MCA) addition on the properties of SBR based ceramizable composites. MCA has proved itself an effective rubber flame retardant [42] and has been already successfully applied for enhancing flame retardancy of EVA based ceramizable composites [31].

2. Materials and Methods

2.1. Materials

Styrene-butadiene rubber (trade name KER 1500) was used as the polymer matrix. It was synthesized by emulsion method (e-SBR) and purchased from Synthos S.A., Oswiecim, Poland. The rubber contains 22–25 wt.% of bonded styrene, 5.0–7.5 wt.% of organic acids, max. 0.7 wt.% of volatile matters, max. 0.4 wt. % of soaps and max. 0.4 wt.% of total ash. Its viscosity (ML 1+4; 100 °C) ranges 45÷55 °ML. The ceramization promoting glass frit “A 4015” of chemical composition (wt. %): 4 Li_2O - 16 Na_2O - 37 B_2O_3 - 43 SiO_2 and softening point temperature of 540 °C was originated from Reimbold & Strick GmbH, Cologne, Germany. Mica (phlogopite) “PW30” (specific surface area of 2.8 m^2/g), produced by LKAB Minerals GmbH (Lulea, Sweden) was used as a temperature resistant mineral filler. Melamine cyanurate (MCA), trade name Budit 315, was originated from Brenntag Polska, Kędzierzyn-Koźle, Poland. The cross-linking system – sulphur, accelerator (N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)), activators (stearic acid, ZnO) and antioxidant (2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)) – were purchased from Torimex-Chemicals Ltd. Sp. z o. o., Konstantynów Łódzki, Poland.

2.2. Preparation of the samples

The composite mixes (Table 1) were prepared with a laboratory two-roll mill (the rolls length – 200 mm; diameter 150 mm; Bridge, UK), working with rotation speed of the slower roll of 18 rpm (revolutions per minute) and the faster roll 20 rpm (friction – 1.1). Kinetics of vulcanization of the composite mixes were tested by means of rheometer Alpha Technologies MDR2000 according to PN-ISO 37:1998 standard. According to the results obtained, (Table 2 and Figure 1) the samples were shaped and vulcanized in steel molds by a laboratory press at 160 °C and under 10 MPa of pressure.

Table 1. Composition (in phr – parts per hundred parts of rubber) of the ceramizable composites mixes.

Ingredients	**Composition of the samples**					
	Cyan_1	**Cyan_2**	**Cyan_3**	**Cyan_4**	**Cyan_5**	**Cyan_6**
SBR	100	100	100	100	100	100
Mica	-	200	-	200	200	175
Glass frit	-	-	100	100	100	75
MCA	50	50	50	25	50	100
Curatives	10	10	10	10	10	10

Table 2. Vulcanization parameters of the ceramizable composites mixes.

Vulcanization parameter	**Composite mixes**					
	Cyan_1	**Cyan_2**	**Cyan_3**	**Cyan_4**	**Cyan_5**	**Cyan_6**
Scorch time (t_{05})	5′ 30″	3′ 45″	2′ 0″	1′ 00″	2′ 15″	1′ 0″
Torque at t_{05} (dNm)	2.1	5.2	3.3	10.2	26.3	8.9
Optimum curing time (t_{90})	12′ 45″	9′ 0″	9′ 30″	6′ 45″	6′ 15″	6′ 30″
Torque at t_{90} (dNm)	15.8	24.0	26.5	41.8	57.2	37.9

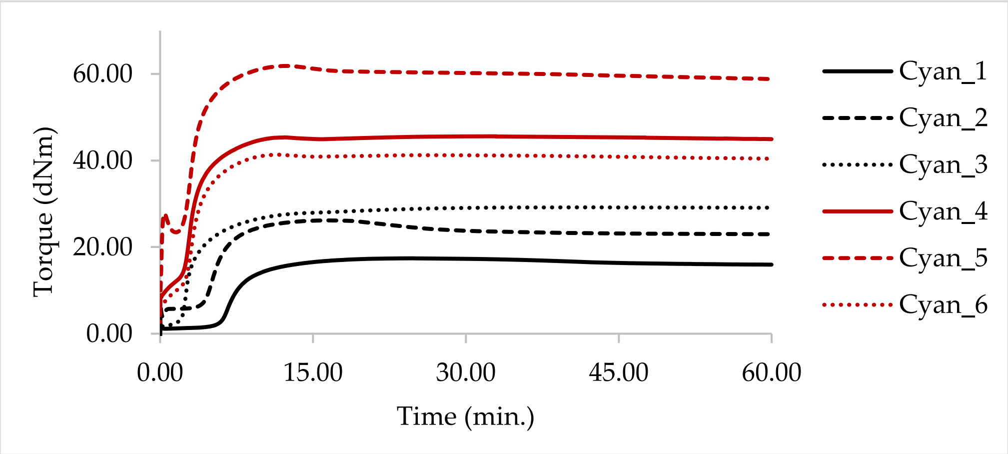

Figure 1. Vulcanization kinetics of the composite mixes measured 24 hours after preparation

The incorporation of the fillers into the e-SBR rubber matrix resulted in a significant decrease of scorch time and optimum vulcanization time. The chemical structure of the melamine, containing three

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amine groups, indicates its possible vulcanization-acceleration feature. The application of only 50 phr of MCA resulted in a scorch time value of 5′ 30″. Surprisingly, the incorporation of additional mineral fillers (mica, glass frit) decreased this value very significantly. This is most probably the effect of a better distribution of MCA in the rubber matrix in the presence of additional mineral fillers. The incorporation of mineral fillers increases the share forces during mixing resulting in better dispersion of MCA. Moreover, it is possible that some MCA molecules adsorb on the filler surface which additionally enhances their dispersion and distribution in the e-SBR rubber matrix. This phenomenon may pose a threat on the processability of the composite mixes causing premature vulcanization.

Increase of the torque value stabilizes on a plateau for all of the composites showing no signs of reversion during one hour of testing.

2.3. Techniques

Viscoelastic properties measurements were made by MonTech RPA 3000 rheometer according to the ASTM D6204 standard Part A for low strain and Part B for high strain. The measurements were made at 100 °C temperature and growing frequencies: 0.1 Hz, 0.2 Hz, 0.4 Hz, 0.6 Hz, 0.8 Hz, 1 Hz, 2 Hz, 5 Hz, 10 Hz, 15 Hz, 20 Hz, 30 Hz, 40 Hz and 50 Hz (10 cycles for each frequency) twice for each composite: low strain 7 % and high strain 100 %. In the third viscoelastic measurement the samples were firstly vulcanized in the rheometer at 160 °C temperature, afterwards cooled dawn to 100 °C and tested at constant frequency 10 Hz, whereas the strain amplitude was changing: 0.1%, 0.2%, 0.4%, 0.6%, 0.8%, 1%, 2 %, 4%, 6%, 8%, 10%, 20%, 40%, 60%, 80% and 90% (10 cycles for each strain).

Mechanical properties of the vulcanizates were tested by Zwick/Roell 1435 testing machine – before and after ceramization, and Zwick/Roell hardness tester (Germany) – before ceramization.

Combustibility of the composite vulcanizates was determined by cone calorimeter (Fire Testing Technology Ltd., East Grinstead, UK). Samples with dimensions of 100 mm x 100 mm x 2 mm were placed horizontally in relation to the IR heating source of 35 kW/m^2. The oxygen index test was performed on home-made device in accordance with the PN-EN ISO 4589-2:2017-06 standard.

Ceramization of the composite vulcanizates was performed in a laboratory furnace FCF 2.5SM (Czylok, Poland). Cylindrical samples (diameter – 16 mm, height – 8 mm) of the composites were heated in 3 different conditions: (1) 1100 – from room temperature to 1100 °C in 30 minutes (heating rate 35 °C/min), (2) 950 – from room temperature to 950 °C in 120 minutes (heating rate 7,5 °C/min), (3) 550-1000 – from room temperature to 550 °C in 53 minutes (heating rate 10 °C/min), 10 minutes of isothermal conditions at 550 °C and at the end heating from 550 °C to 1000 °C in 27 minutes (heating rate 16 °C/min) – total time 90 minutes.

3. Results and discussion

3.1. Viscoelastic behaviour of composites

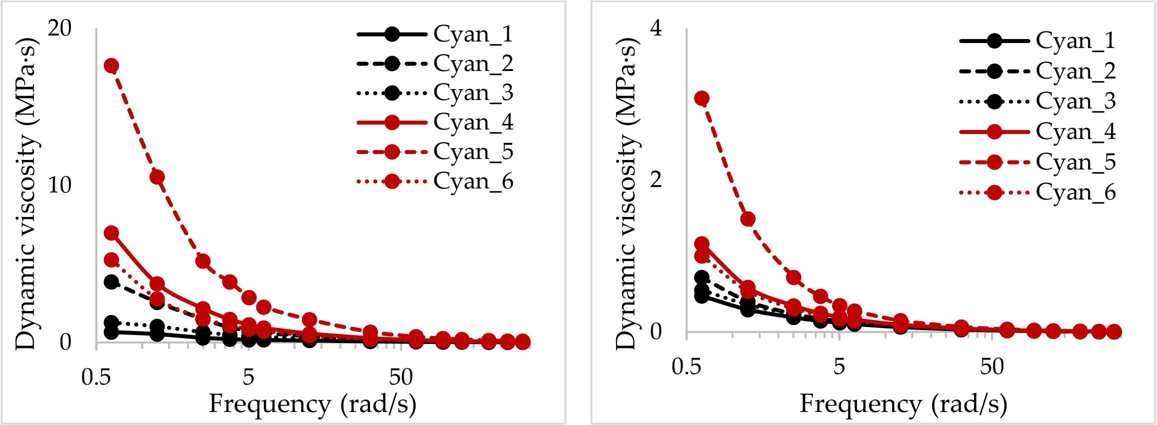
The complex dynamic viscosity η* which is measured by oscillating rheometer is analogous to the viscosity η_{app} measured by a capillary rheometer [43-46]. The complex dynamic viscosity η* is calculated from parameters obtained from RPA (rubber process analyzer) as follows:

The complex shear modulus (G*) relation to storage shear modulus (G′) and loss shear modulus (G″) is presented by the equation (1):

$$\boldsymbol{G}^{*} = \sqrt{(\boldsymbol{G}')^{2} + (\boldsymbol{G}'')^{2}} \quad (1)$$

The complex dynamic viscosity (η*) relation to complex shear modulus (G*) is given by equation (2): ω – frequency (Hz).

$$\boldsymbol{\eta}^{*} = \frac{\boldsymbol{G}^{*}}{\boldsymbol{\omega}} \quad (2)$$



(**a**) (**b**)

Figure 2. RPA dynamic complex viscosity versus frequency for the ceramizable composites: low strain 7% (a), high strain 100% (b).

Table 3. Viscoelastic properties of uncured composites at chosen frequencies: storage shear modulus (G′), loss shear modulus (G″) and complex dynamic viscosity (η*).

Composite	**Frequency (rad/s)**	**Low strain (7%)**			**High strain (100%)**		
		G′ (kPa)	**G″ (kPa)**	**η* (Pa·s)**	**G′ (kPa)**	**G″ (kPa)**	**η* (Pa·s)**
Cyan_1	0.628	59.0	30.5	664373	33.2	33.7	473315
	5.024	110.5	88.8	177198	69.1	67.1	120421
	94.2	405.4	173.4	29392	160.3	129.8	13753
	314	555.8	185.9	11722	168.1	112.8	4048
Cyan_2	0.628	347.1	166.7	3851019	55.1	50.0	717635
	5.024	417.3	298.8	761623	78.5	79.8	139899
	94.2	1021.4	630.0	80004	143.9	140.3	13399
	314	1265.5	572.5	27779	144.8	125.1	3828
Cyan_3	0.628	129.8	41.7	1268917	33.8	43.5	550798
	5.024	243.4	215.8	406605	74.0	90.3	145999
	94.2	756.4	482.8	59822	170.5	170.8	160889
	314	1026.5	483.0	22690	173.8	149.3	4582
Cyan_4	0.628	566.6	407.1	6976724	75.7	87.9	1160105
	5.024	707.1	566.3	1132380	107.9	112.7	195047
	94.2	1376.9	885.3	109133	186.6	190.2	17763
	314	1657.0	872.5	37454	194.5	159.8	5035
Cyan_5	0.628	1586.0	772.2	17639995	199.7	234.4	3079313
	5.024	1777.1	1434.5	2854766	197.0	197.7	348841
	94.2	3142.7	2039.7	249772	251.9	253.6	23828
	314	3717.3	2014.6	84562	255.4	208.0	6588
Cyan_6	0.628	427.5	307.3	5264607	66.6	75.1	1003978
	5.024	560.5	402.0	862182	97.4	101.1	175427
	94.2	1072.9	674.5	84488	171.9	173.7	16294
	314	1271.1	672.9	29763	182.7	152.3	4758

Dynamic viscosity values both for low and high strain are growing with the increasing quantity of mineral fillers (mica and fluxing agent). The addition of fluxing agent has small impact even for low frequencies (Cyan_1 to Cyan_3, Figure 2 and Table 3). Mica as filler with platelet-shape particles

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changes the viscosity of the composites to the highest extent. It is especially visible for the composite Cyan_5 where the general content of additives is the same as for the composite Cyan_6. For which 25 phr of mica and 25 phr of fluxing agent was exchanged to melamine cyanurate. However, the changes in the mix dynamic viscosity is almost two times (low strain) and three times (high strain) higher.

What is surprising is the large difference between the Cyan_4 and Cyan_5. The composition of both composites differs only by 25 phr of melamine cyanurate and the dynamic viscosity changes from 7 MPa·s to 18 MPa·s (low strain, 0.628 rad/s) and from 1 MPa·s to 3 MPa·s (high strain, 0.628 rad/s). Given the insignificant/slight influence of MCA alone on the mix viscosity (Cyan_1) it is clearly a synergistic effect between the mineral fillers and MCA. Probably this combination of the mineral fillers and melamine cyanurate results in a strong secondary structure formation, in which the mineral particles are connected with low-molecular MCA. It is clear that MCA itself is not able to form a secondary structure in the SBR matrix (Figure 3). However, in presence of additional mineral fillers it behaves like inter-particular low molecular binder resulting in a strong Payne effect. It is especially visible for the composites Cyan_5 and Cyan_6. When the amount of fillers was reduced the viscosity and G′ values dropped significantly. It is noticeable in the literature that application of low-molecular additives into rubber matrices may alter their viscoelastic properties to a significant extend [47].

The viscosity of the mixes is a crucial factor during their processing – especially extrusion, which is commonly used for cables production. If the viscosity of rubber mixes is too high, their processing may be much more difficult of even impossible. Therefore, the knowledge about the ability of mica/glass frit/MCA system to form a strong secondary structure is of great importance.

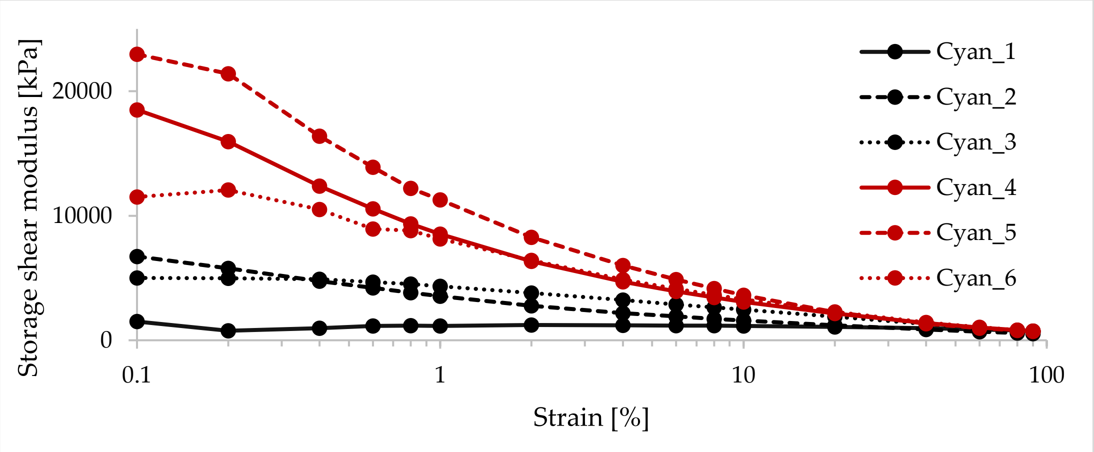

Figure 3. Strain amplitude dependence of storage shear modulus G′ for cured ceramizable composites.

The value of storage shear modulus G′ in function of growing strain shows how the secondary structure formed by fillers is destroyed, thus reducing the viscosity of the system. This effect independent from a polymer matrix properties but is caused by the specific filler-filler interactions, whose range is limited. Melamine cyanurate, both with mica and fluxing agent, create structure with almost the same interactions (Figure 3). The highest values in dynamic viscosity for the Cyan_5 composite can be the result of the strongest interactions which are created between filler particles connected by the low-molecular MCA. This can be explained by the chemical nature of the fillers – all three of them exhibit highly polar characteristics in opposition to the SBR matrix. Therefore, they are more likely to interact with each other resulting in strong filler-filler secondary structure. In each case the addition of all three types of fillers causes stronger interactions than in the case one of the fillers is not used.

3.2. Mechanical properties of composites before ceramization

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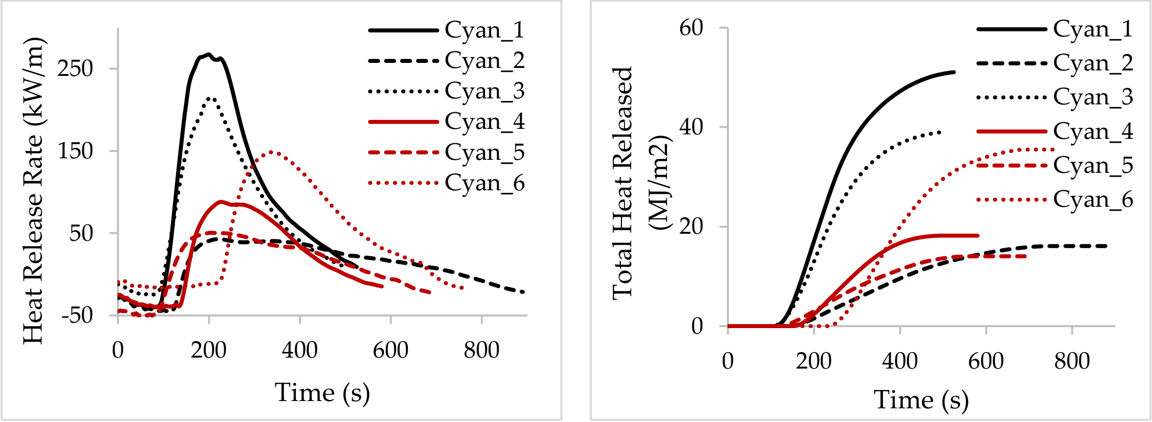
Table 4. Mechanical properties of the vulcanizated composites: tear resistance (TES) stress at 100% (SE100), 200% (SE200) and 300% (SE300) of elongation, tensile strength (TS), elongation at break (Eb) and shore hardness, scale A and D.

Mechanical parameter	**Vulcanized composites description**					
	Cyan_1	**Cyan_2**	**Cyan_3**	**Cyan_4**	**Cyan_5**	**Cyan_6**
TES (N/mm)	5.8 ± 0.5	22.7 ± 1.0	5.3 ± 0.4	12.9 ± 1.3	27.2 ± 3.2	14.2 ± 2.5
SE100 (MPa)	3.0 ± 0.2	4.7 ± 0.1	1.8 ± 0.1	4.4 ± 0.1	5.2 ± 0.2	4.5 ±0.1
SE200 (MPa)	4.8 ± 0.4	5.5 ± 0.2	2.1 ± 0.1	-	-	-
SE300 (MPa)	-	-	3.1 ± 0.1	-	-	-
TS (MPa)	6.3 ± 1.3	6.3 ± 1.5	4.2 ± 0,5	4.8 ± 1.0	6.4 ± 0.5	4.7 ± 0.3
E_b (%)	248 ± 42	211 ± 33	345 ± 11	163 ± 9	188 ± 38	124 ± 34
Hardness (°ShA)	60 ± 1	82 ± 1	71 ± 1	80 ± 1	81 ± 2	81 ± 1
Hardness (°ShD)	11 ± 1	21 ± 1	14 ± 1	21 ± 1	21 ± 1	21 ± 1

The effect of formation of strong interaction between particles of the fillers via MCA acting as a binder is also visible in mechanical properties of the vulcanized composites (Table 4). For the composites which were characterized by the three the highest values of storage shear modulus G′ the elongation at break never reached 200%. However, Cyan_5 which exhibits the highest G′ and tensile strength values shows higher E_b than Cyan_4 and Cyan_6. This is due to the most effective secondary structure formation by an optimal ratio of the incorporated fillers: 200/100/50 for mica/glass frit/MCA respectively. For Cyan_4 the amount of MCA is too low to act effectively as a low-molecular binder for the mica and the glass frit. Whereas, for Cyan_6 the amount of the mineral fillers is too low with respect to MCA, which alone is not able to form a secondary reinforcing structure as showed the Payne effect measurements (Figure 3). Therefore, the largest number of strongly connected filler particles is present in the Cyan_5 composite. Consequently, the value of the Cyan_5 tear resistance reaches 27.2 N/mm, which is the highest value for all the tested composites.

The hardness of the composites is most heavily impacted by the addition of mica. The addition of as little as 100 phr of other fillers to the composite which already has 200 phr of mica do not affect its hardness, whereas the addition of fluxing agent affects the value of hardness but only when mica has not been already added. This is due to the fact that its stiff-platelet particulate structure increases the stiffness of the composites significantly.

3.3. Combustibility



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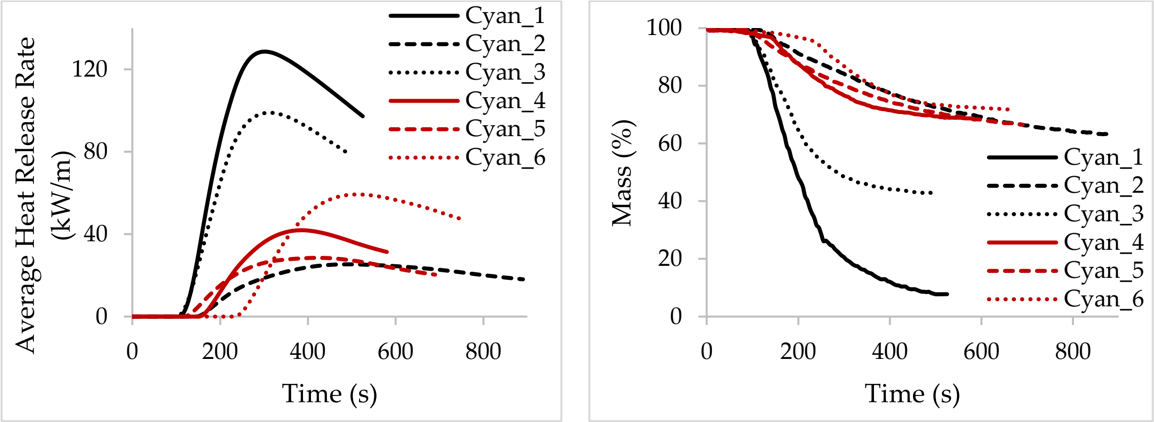


(**c**) (**d**)

Figure 4. Cone calorimetry analysis of the composites: heat release rate (HRR) (a), total heat released (THR) (b), averaged heat release rate (ARHE) (c) and mass loss (d).

Table 5. Flammability parameters: time to ignition (t_i), time to flameout (t_o), heat release rate peak (HRR_p), heat release rate mean value (HRR_m), time to HRR_p (tHRR), HRR_p/tHRR ratio, total heat released (THR), effective heat of combustion peak (EHC_p), effective heat of combustion mean value (EHC_m), mass loss rate peak (MLR_p), mass loss rate mean value (MLR_m), mass loss (m_l) and oxygen index (OI).

Combustibility parameter	**Vulcanized composites description**					
	Cyan_1	**Cyan_2**	**Cyan_3**	**Cyan_4**	**Cyan_5**	**Cyan_6**
t_i (s)	89	119	93	134	86	**222**
t_o (s)	478	**827**	465	519	612	612
HRR_p (kW/m)	267.4	**42.9**	215.7	88.1	50.5	148.5
HRR_m (kW/m)	128.0	**21.1**	104.1	46.1	25.1	88.0
tHRR (s)	200	225	205	225	205	**340**
HRR_p/tHRR (kW/ms)	1.34	**0.19**	1.05	0.39	0.24	0.43
THR (MJ/m^2)	50.2	16.1	38.6	18.2	**14.0**	34.2
EHC_p (MJ/kg)	76.6	59.2	79.0	50.3	**26.4**	72.0
EHC_m (MJ/kg)	20.7	8.5	20.4	12.6	**8.0**	24.1
MLR_p (g/s)	0.169	0.072	0.164	0.097	**0.067**	0.092
MLR_m (g/s)	0.055	**0.022**	0.045	0.032	0.028	0.032
m_l (%)	91.3	35.6	56.6	28.8	31.7	**24.9**
OI (%)	37.0	>37.5	37.5	>37.5	>37.5	>37.5

The synergistic effect of ceramization and melamine cyanurate is visible especially in flammability properties of the tested composites (Figure 4 and Table 5). It's only the addition of mica or fluxing agent to the composition containing MCA that results in decreasing of the THR from 50.2 MJ/m^2 to 16.1 MJ/m^2 or 38.6 MJ/m^2 respectively. Almost for every combustibility parameter the simultaneous effect of ceramization and melamine cyanurate is better than for each of them separately. Especially, the combination of MCA with mica results in significant improvement of the flame retardancy of the composites (Cyan_2). This is due to synergistic effect of carbonaceous char formation from MCA and large aspect ratio mica platelets, which can significantly improve the barrier properties of the char formed. Therefore, decreasing the transport of flammable hydrocarbon compounds formed from the thermal degradation of the SBR rubber into the flame zone. Time to ignition of the composites stays on the same level or increases from 89 s to 222 s (Cyan_6), which is a significant improvement. Mass loss is decreasing with the growing content of fillers which promote ceramization. The value of oxygen index is very high in comparison to flame retarded SBR composites described in the recent literature [48, 49] and reaches 37.0% or 37.5% for the composites without mica and exceeds the value of 37.5% for the composites with mica (37.5% is limit value for the home-made apparatus on which the tests were carried out). The high combustibility parameters values of the composites studied place them among other novel flame retardant systems for rubber application [50].

For evaluating the flammability of the composites the most important indicator is the value of the HRR$_p$/tHRR parameters ratio. This parameter is the value of Heat Release Rate peak divided by the time to reach this peak. Based on this parameter it is easy to compare the general flammability of the composites, which depends not only on the heat generated during burning, but also on the time when this heat was emitted. The lower the value of this parameter the better fire resistance of a composite. Analyzing this parameter, the synergistic effect of ceramization and MCA-based char formation on flame retardancy of the composites are observed. For the composite containing only melamine cyanurate (Cyan_1) the value of this parameter is 1.34, the composite containing 200 phr of mica and 100 phr of fluxing agent – 1.05. In each case, when melamine cyanurate and full ceramization system were used the value for this parameter was lower than 0.5: Cyan_4 – 0.39, Cyan_5 – 0.24, Cyan_6 – 0.43. The presence of fluxing agent reduces the thermal properties (Cyan_2 – 0.19 compare to Cyan_3 – 1.05) but not to a high extend. Nevertheless, this filler is necessary to create a strong ceramic structure during ceramization, which will also work as thermal and mechanical stress barrier. The combustibility parameters values were significantly improved when MCA was applied to the ceramizable compositions in comparison to the e-SBR based composites we studied previously [36] that did not contain MCA.

3.4. Properties of composites after ceramization

The composite containing only melamine cyanurate (Cyan_1), without fillers which promote ceramization, in every case failed to create any ceramic structure, which was expected. The rest of the composites form ceramic structure during heating but only the sample Cyan_3 didn't change its shape much after ceramization to 1100 °C and could be tested for its compression strength.

Table 6. Compression strength of the ceramized composites studied.

Ceramization conditions	**Vulcanized composites description**					
	Cyan_1	**Cyan_2**	**Cyan_3**	**Cyan_4**	**Cyan_5**	**Cyan_6**
1100°C	-	-	62 ± 23	-	-	-
550-1000°C	-	29 ± 3	109 ± 45	358 ± 111	270 ± 80	322 ± 104
950°C	-	113 ± 25	27 ± 12	239 ± 66	228 ± 49	236 ± 33

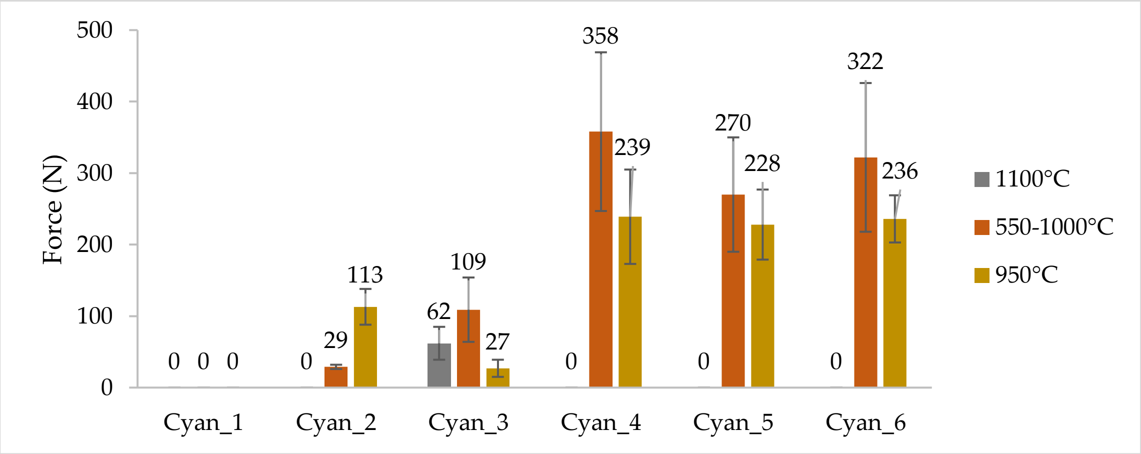
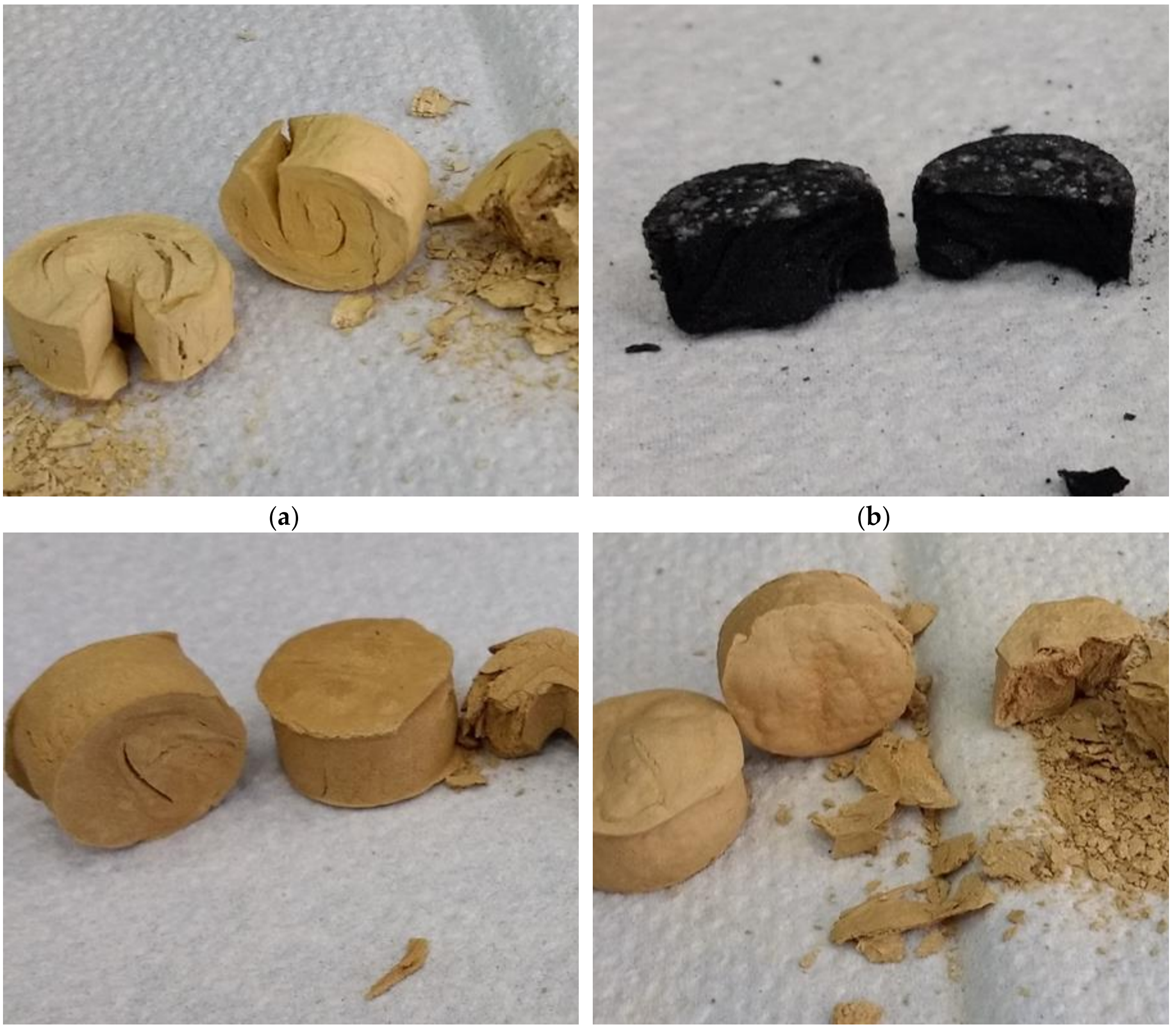


Figure 5. Compression strength of the ceramized composites studied.

The presence of both mica and fluxing agent are necessary to create a strong enough ceramic structure (Figure 5 and Table 6). The addition of mica (Cyan_2) or fluxing agent (Cyan_3) separately to the composite mix also results in the creation of a ceramic structure but with much worse compression strength properties. The application of melamine cyanurate along with mica and the glass frit to the ceramizable compositions does not influence the mechanical properties of the composites after ceramization. In the composites with changing content of MCA (25-100 phr) (Cyan_4 – Cyan_6) the compression strength changes only within the limits of statistical error. Although, it may seem that the error is very high, the samples' morphology after ceramization is far from homogenous (Figure 6). Similarly to random fire conditions, heating up relatively big samples containing many dispersed fillers results in their deformation due to several factors, such as: the initial inhomogeneity of their bulk structure; internal gas formation rate from degrading polymer matrix; carbonization of the polymer and MCA; thermal expansion of the mineral fillers; direction of the gas convection flow formed by the flame direction, etc.



(**a**) (**b**)

(**c**) (**d**)

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(e)

Figure 6. Appearance of the composites after ceramization and the compression test (950): Cyan_2 (a), Cyan_3 (b), Cyan_4 (c), Cyan_5 (d), Cyan_6 (e).

The appearance of the composites after ceramization (Figure 6) for these, which contain mica is almost the same. The Cyan_1 composite evaporated during the heat treatment. The composite in which where the glass frit was not used (Cyan_2) has many visible cracks being marks of a relatively weak inter-particulate bonding. There was no binding material, which could effectively connect particles of mica during heating. The composites Cyan_4 – Cyan_6 look almost the same which is also mirrored in their compression strength. For these samples, a stiff, durable and porous ceramic structure is observed. The sample Cyan_3 differs from the other samples since the fluxing agent during heat treatment could connect only the polymer matrix decomposition products accompanied with MCA carbonization residues. This is the cause of the black color of this sample. However, the fact that Cyan_3 withstand the severe ceramization conditions with only the carbonaceous char formed from MCA, SBR and the glass frit shows a high potential of these ingredients for ceramizable composites manufacturing.

4. Conclusions

The addition of melamine cyanurate flame retardant improves flame retardant properties of ceramizable SBR-based composites. The synergistic effect is particularly visible for fire resistance of the composites measured by cone calorimetry, in which case the parameters improvement can reach six times better properties. Rheological properties of the mixes are also significantly affected by the synergistic effect of mica/glass frit/MCA compositions. The mineral fillers particles connected by MCA particles acting as binders form a very strong secondary structure in the rubber matrix. However, this requires an optimum components ratio and can easily be changed by decreasing the amount of MCA or mineral fillers. Mechanical strength properties of the ceramizable composites vary in significant range, however, the changes are not very significant from the real application point of view. The incorporation of different amounts of melamine cyanurate does not change compression strength of the composites after ceramization simultaneously increasing their fire resistance.

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