Thermal stability and flammability of styrene–butadiene rubber (SBR) composites

Effect of attapulgite, silica, carbon nanofiber, and the synergism of their action on the properties SBR composites

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Abstract The article presents the effect of attapulgite (ATT) and its synergic action with carbon or silica on the thermal properties and flammability of cross-linked styrene–butadiene rubber. It has been shown that ATT is active filler improving the thermal and mechanical properties of composites containing this aluminosilicate. The decreased flammability of vulcanizates containing ATT compared to that of unfilled vulcanizates results from good insulating properties of the ATT used. The considerable reduction in the flammability of composites containing ATT and carbon nanofiber or silica is connected, first of all, with the formation of a homogeneous boundary layer.

Keywords Styrene-butadiene rubber · Attapulgite · Carbon nanofibers · Thermal stability · Flammability

Introduction

Recent years have witnessed a great interest in polymeric materials with special properties, resistant to the action of considerably lowered or elevated temperature, flame-retardant or non-flammable, being characterized by suitable mechanical strength at the same time.

In the making of polymeric materials with increased thermal stability and resistance to the action of fire, one uses various types of mineral fillers, such as calcium carbonate,

silica, halloysite, or montmorillonite [1–3]. From recent literature reports it follows that fibrous aluminosilicate (attapulgite, ATT) can also be active mineral filler [4].

ATT of chemical formula: $\text{Mg}_5[\text{Al}]\text{Si}_8\text{O}_{20}(\text{OH})_2-(\text{OH}_2)_4 \times 4\text{H}_2\text{O}$ is characterized by a high sorption capacity ranging from 15 to 30 mval/100 g, showing features of a molecular sieve as zeolites [5, 6]. ATT is widely used as absorbent, catalyst carrier, disinfectant, adhesive agent, food or drug additive as well as filler of polymers [4]. It has a three-level structure. Single fibrous crystals are the smallest structural unit with a length of 500–2,000 nm and a diameter of 10–30 nm. Each single crystal consists of many laminar units such as tetrahedrons comprising two silicon atoms and two oxygen atoms [7–9]. Between neighboring layers are five aluminum atoms tetrahedrally combined with five oxygen atoms. Individual structural units are combined with oxygen atoms to form a crystalline structure in the form of fiber. Particular fibrous nanocrystals are arranged in bundles that undergo agglomeration visible in a micro-scale as large solid particles [10].

This article presents the results of examining the effect of ATT and its modification procedure on the thermal stability and flammability of styrene–butadiene rubber (SBR) cross-linked by means of an organic peroxide or sulfur. A particular attention was paid to the structure of the rubber combustion residue. The effect of the synergic action of ATT and carbon nanofiber or silica on the properties of cross-linked SBR was also assessed.

Experimental

Materials

The object of our study was SBR, KER 1500 form Synthos, containing 23.5 % of combined styrene. The rubber was

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cross-linked by means of dicumyl peroxide (DCP) in the presence of zinc oxide (ZnO) or by means of sulfur in the presence of ZnO and *N*-cyclohexyl-2-benzoylsulfenamide (Tioheksam CBS). The resultant peroxide vulcanizate was denoted with SN, while the sulfur vulcanizate with SS.

The following fillers were used: ATT (Bentonit SWDC) from BDC Poland (Fig. 1a), silica (Aerosil 380) with a specific surface of $380 \text{ m}^2 \text{ g}^{-1}$ from Evonik Degussa (Fig. 1c) and carbon nanofiber (Pr-25-XT-PS) from Pyrograf (Fig. 1d). These were added to cross-linked rubbers in a quantity of 8 phr, while their blends were added to the polymeric matrix in proportion 1:1.

To improve the miscibility of ATT with the rubber, i.e., to decrease its hydrophilicity, the filler was modified with the use of 3-aminopropyltriethoxysilane (Unisil Poland) (Fig. 1b). The modification of ATT consisted of mixing it with an aqueous solution of the silane (1:1) at a temperature of 55°C for 2 h, followed by drying to a constant weight.

Methods

The SEM images of fillers were taken by means of a SEM Quanta 250 FEG microscope (Fig. 1).

Elastomeric blends were prepared at room temperature with the use of a laboratory rolling mill ($D = 150 \text{ mm}$, $L = 300 \text{ mm}$). The rotational speed of the front roll was 20 rpm, friction 1.1.

The blends were vulcanized in steel molds placed between electrically heated press shelves. The optimal vulcanization time ($\tau_{0.9}$) at a temperature of 160°C was determined by means of a WG-2 vulcameter according to PN-ISO 3417:1994.

The thermal properties of the vulcanizate obtained were tested under air within the temperature range of $25\text{--}800^\circ\text{C}$ by means of a MOM derivatograph (Budapest), using Al_2O_3 as a reference substance. Weighed portions were 90 mg each, heating rate $7.9^\circ\text{C min}^{-1}$, and the sensitivities of thermal curves were as follow: TG = 100, DTA = 1/5, DTG = 1/30.

The flammability of vulcanizates was determined by the oxygen index (OI) method, according to ISO 4589 using an apparatus from Fire Testing Technology Ltd and $50 \times 10 \times 4 \text{ mm}$ specimens. The value of the OI is defined as the minimal oxygen concentration $[\text{O}_2]$ in the oxygen/nitrogen mixture $[\text{O}_2/\text{N}_2]$ that either maintains flame combustion of the material for 3 min or consumes a length of 5 cm of the sample, with the sample placed in a vertical position (the top of the test sample is inflamed with a burner).

Fig. 1 SEM images. **a** ATT, **b** ATT modified with the use of silane, **c** silica Aerosil 380, and **d** carbon nanofiber PR-25-XT-PS

With a constant nitrogen flow rate through a measurement column ($\varnothing = 75$ mm), amounting to (40 ± 2) mm $\times$ s⁻¹, the oxygen concentration was selected so that the sample was completely burned within time $t = 180$ s [2, 3, 11]. The sample top was ignited for 5 s by means of a gas burner supplied with LPG.

We also tested flammability in air using identical samples as in the case of OI method. A sample in a vertical position was ignited with a gaseous burner for 5 s and its combustion time (t_s) was measured.

The vulcanizates under investigation were examined by the FAA micro-calorimeter from Fire Testing Technology Limited, with constant flow ratio oxygen to nitrogen amounting 1:4. The temperature of pyrolyser was 750 °C, while that of combustor 900 °C. During measurement the following parameters were recorded: ignition temperature, maximal heat emission rate, temperature of maximal heat emission rate, total heat emitted, heat capacity, and percentage oxygen consumption.

Flammability of vulcanizates under conditions of real fire was tested with the use of a cone calorimeter from Fire Testing Technology Limited. Elastomer samples with dimensions $(100 \times 100 \pm 1)$ mm and a thickness of (20 ± 0.5) mm were tested in a horizontal position, with a density of heat radiation flux amounting to 35 kW m⁻².

During tests, the following parameters were recorded: initial sample weight, time to ignition, sample weight during testing, total heat released, effective combustion heat, average weight loss rate, sample final weight, time to extinction, and test duration.

The structure of the rubber combustion residue analyzed by means of a cone calorimeter was assessed on the basis of photographs and SEM images taken under a microscope equipped with the recording software Motic Images Plus, and electronic microscope Quanta 250 FEQ.

The use of SEM equipped with the detector of X-ray dispersion energy (EDS EDAX Genesis XM 4i (USA)) made it possible to obtain in a single stage of analysis information about the chemical composition and concentration of particular elements in the combustion residues.

The tensile strength of the vulcanizates tested was determined by means of a Zwick apparatus, model 1435, linked to a computer with appropriate software, according to standard PN-ISO 37:1998. The test samples used consisted of dumbbells, whose measurement section had a width of 4 mm and a thickness of about 1 mm.

Results and discussion

From the literature review and the test results obtained it follows that ATT undergoes a clear four-stage decomposition within the temperature range $\Delta T = 25$ –800 °C

(Fig. 2). The first stage of mass loss amounting to 12.23 %, recorded at a temperature below 130 °C is connected with the release of water physically occluded between the fibrous crystals and some water physically combined with the crystal surface (so-called zeolitic water). The second stage of mass loss at $\Delta T_2 = 130$ –230 °C, amounting to 2.2 % consists of releasing the remaining portion of zeolitic water. The third stage of mass loss at $\Delta T_3 = 230$ –730 °C, amounting to 11.2 % is due to the removal of water chemically combined with aluminosilicate (hydroxyl groups of water combined with the surface of ATT). At a temperature above 730 °C the remaining portion of water chemically combined with ATT is released and the organic substances adsorbed on the ATT surface are burned [12, 13].

The modification of ATT with silane to reduce its hydrophilicity partly uncovers its fibrous structure, making no significant difference in the course of TG and DTG curves (Figs. 2, 3).

The first step of the thermal decomposition of ATT modified with silane occurs at $\Delta T_1 = 80$ –150 °C and is accompanied by a weight loss of 4.5 %, which corresponds to the release of water physically combined with ATT. The second step occurring at $\Delta T_2 = 150$ –260 °C, accompanied by a further mass loss of 2.3 % is connected with the loss of the remaining zeolytic water combined with ATT.

Fig. 2 Thermal analysis of ATT

Fig. 3 Thermal analysis of ATT modified with the use of silane

At $\Delta T_3 = 260\text{--}580\text{ }^{\circ}\text{C}$ both the water chemically combined with ATT and a small quantity of the modifier uncombined with the ATT surface are released (Fig. 3).

From the comparative analysis of the test results listed in Table 1 it clearly follows that the thermal stability of the peroxide vulcanizates of SBR, expressed by parameter T_5 , is higher than that of sulfur vulcanizates as the energy of the crosswise C–C bonds of the elastomer cross-linked with dicumyl peroxide is considerably higher than that of the sulfide bridges formed during cross-linking with sulfur.

The fillers used ambiguously influence the thermal stability of the composites investigated, determined with parameters T_5 and T_{50} . In the case of peroxide vulcanizates, unmodified ATT itself and that mixed with carbon nanofiber (ATT–CNF) or with silica (ATT–Si) considerably increases the value of parameter T_5 . A significant improvement in the thermal stability of sulfur vulcanizates determined with parameter T_5 occurs under the influence of the ATT modified with silane.

Regardless of the spatial network structure the fillers used bring about a significant reduction in the thermal decomposition rate (dm/dt) of the vulcanizates investigated (Table 1). These also decrease the sample mass loss rate (MLR) during their combustion (Figs. 5, 6). The considerable reduction in the thermal decomposition rate of the vulcanizates investigated in relation to unfilled samples (SN, SS) is due to the decreased segmental mobility of

Table 1 Thermal analysis of vulcanizates

Sample ^a	$T_5/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$dm/dt/\text{mm}$	$T_{\text{RMAX}}/^{\circ}\text{C}$	$P_w/\%$	$T_s/^{\circ}\text{C}$	$P_{800}/\%$
SN	350	419	80	415	19	475	5
SN–ATT	365	405	56	410	22.2	480	11.1
SN–ATTM	305	405	52	400	22.2	480	11.1
SN–ATT–CNF	360	410	45	405	30	480	14.4
SN–Si	360	405	52	390	22.2	480	11.1
SN–ATT–Si	365	410	53	405	28.8	480	17.7
SS	300	400	70	365	20	490	8.8
SS–ATT	305	405	43	390	36.6	475	13.3
SS–ATTM	330	410	42	390	28.8	480	13.3
SS–ATT–CNF	260	405	35	390	28.8	480	10
SS–Si	270	400	55	400	23.3	480	10
SS–ATT–Si	310	405	37	390	30	480	17.7

SN peroxide vulcanizate of SBR, SS sulfur vulcanizate of SBR, SN–ATT peroxide vulcanizate containing ATT, SN–ATTM peroxide vulcanizate containing ATT modified with the use of silane, SN–ATT–CNF peroxide vulcanizate containing ATT and carbon nanofiber, SN–Si peroxide vulcanizate containing silica, SN–ATT–Si peroxide vulcanizate containing ATT and silica, SS–ATT sulfur vulcanizate containing ATT, SS–ATTM sulfur vulcanizate containing ATT modified with the use of silane, SS–ATT–CNF sulfur vulcanizate containing ATT and carbon nanofiber, SS–Si sulfur vulcanizate containing silica, SS–ATT–Si sulfur vulcanizate containing ATT and silica, T_5 and T_{50} temperature of sample 5 and 50 % mass loss, respectively, $dm \times dt^{-1}$ maximum rate of thermal decomposition of vulcanizates, T_{RMAX} temperature of maximum rate of thermal decomposition of vulcanizates, P_w residue after the thermal decomposition of vulcanizates, T_s temperature of residue burning after the thermal decomposition of vulcanizates, P_{800} residue after heating up to $T = 800\text{ }^{\circ}\text{C}$

^a Each of the filler were added to cross-linked rubber in a quantity of 8 phr. Blends of the fillers were added to the polymeric matrix in proportion 1:1

Fig. 4 EDS analysis residue after burning. **a** Sulfur vulcanizate SS (C = 27.51 %, O₂ = 2.58, S = 7.16, Zn = 62.75 %), **b** sulfur vulcanizate containing SS-ATT (C = 18.09 %, O₂ = 21.93 %, Mg = 2.52 %, Al = 2.25 %, Si = 9.84 %, S = 1.84 %, Ca = 0.61 %, Fe = 5.1 %, Zn = 37.82%), **c** sulfur vulcanizate containing silica SS-Si (C = 44.52 %, O₂ = 27.55 %, Si = 12.81 %, S = 0.93 %, Zn = 14.19 %)

elastomer chains around the filler particles. The decreased segmental mobility reduces the amplitude of thermal vibrations and consequently inhibits degradation and destruction processes.

The higher values of parameter dm/dt (Table 1) and MLR (Fig. 6) of the composites containing ATT compared

Fig. 5 MLR curves of peroxide vulcanizates of SBR rubber

Fig. 6 MLR curves of sulfur vulcanizates of SBR rubber

to those of the vulcanizates containing silica are probably connected with the presence of metal oxides, resulted from the thermal decomposition of ATT. The metal oxides present on the surface of the composite boundary layer increase the activity of hydrocarbon radicals resulted from the polymer thermal decomposition in consequent thermal processes [10].

The elementary analysis of the combustion residue of ATT-containing composite showed the contents of Mg, Al, Ca, and Fe amounting to 2.52, 2.25, 0.61, and 5.1 %, respectively (Fig. 4b).

Considerably lower values of the parameters dm/dt and MLR (Table 1; Figs. 5, 6) of vulcanizates filled with carbon nanofibers and ATT compared to those of the remaining composites result from the fact that carbon nanofiber as carbon black can be a scavenger of radicals. Thus, its presence inhibits free-radical reactions increasing

Fig. 7 SEM images of residue after burning SS-ATT-CNF vulcanizate. **A** ATT needles and **B** carbon nanofibers

at the same time the probability of the primary macro-radical recombination through increasing their dwell time in the cage [14–16].

One of the basic parameters of the thermal stability of polymers and polymeric materials is the residue from thermal decomposition (Pw). It exerts a significant effect on the flammability of polymeric composites. An increase in the value of this parameter makes the amount of flammable and non-flammable destruction products passing to flame be lower. The presence of both silane-modified ATT and unmodified ATT or silica influences the value of Pw to the same extent. The EDS analyses of the residues from the combustion of unfilled composites and those containing ATT or silica showed that ATT, unlike silica, did not initiate carbonization processes (Fig. 4a–c).

The considerable increase in the content of carbon in the combustion residue of the vulcanizate containing silica, in relation to the unfilled one, facilitates the formation of a thermally stable boundary layer hindering the flow of mass and energy between flame and solid phase. It was found that in the case of the peroxide vulcanizates of SBR, the highest values of Pw were shown by the composites containing both carbon nanofiber and ATT (SN-ATT-CNF). From the investigations carried out so far it follows that an increase in the content of carbon nanofiber in polymer is accompanied by a decrease in the value of parameter Pw in relation to unfilled samples. There are also decreases in the temperature of maximum combustion rate of the residue from the thermo-oxidative decomposition of vulcanizates filled with nanofibers [17]. Both carbon nanofibers and carbon black are completely burned above $\Delta T = 400\text{--}450\text{ }^{\circ}\text{C}$. The SEM images of the combustion residue from the vulcanizates containing ATT and carbon nanofiber clearly show however the presence of both carbon nanofiber and crystalline ATT filaments (Fig. 7).

According to the literature data, the boundary layer temperature ranges from 420 to 520 $^{\circ}\text{C}$ depending on elastomer, while the flame temperature can reach 950–1000 $^{\circ}\text{C}$ [14, 18]. Thus, one can assume that ATT is characterized by good isolating properties hindering the combustion of carbon nanofiber contained in the sample.

The increase in the thermal stability of the elastomer investigated under the influence of the fillers incorporated is accompanied by the reduction in its flammability (OI, t_s , T_z , and HRR_{max} ; Table 2; Figs. 8, 9), as confirmed by both the decreased thermo-oxidative decomposition rate of SBR (dm/dt) and increased residue from this process. The analysis of results listed in Table 2 leads to a conclusion that vulcanizates containing modified ATT or silica are characterized by comparable values of OI. The lower flammability of composites containing ATT compared to unfilled vulcanizate results, first of all, from the isolating properties of ATT that protects the polymer against consequent reactions of degradation and thermal destruction, especially in the initial stage of combustion. In the subsequent stage of combustion (flame combustion), the flame-retardant effect of ATT is decreased as the so-called aluminosilicate islets are formed in the boundary layer (Fig. 10a) that do not constitute any barrier for mass and energy transfer to flame, as well as oxygen diffusion inside the sample (Tables 2; Figs. 10a, 11, 12).

On the other hand, barrier properties play a significant role in reducing composite flammability by decreasing the transport rate of volatile and flammable destruction products to the flame zone (Fig. 10b). In the presence of silica, cavitation and carbonization processes in the solid phase of the sample under combustion proceed to a larger extent (Fig. 4). Its great heat capacity is also of importance (Table 2). Silica has the

Table 2 Flammability test of vulcanizates

Sample	OI	t_g/s	$T_z/^\circ C$	$HRR_{max}/W\ g^{-1}$	Total HR/ $kJ\ g^{-1}$	HR capacity/ $J/g\ K$	Oxygen consumption/ %
SN	0.210	194	350	450	34.5	501	40.11
SN-ATT	0.229	347	375	390	34.4	426	81.17
SN-ATTM	0.233	218	362	376	34.3	388	63.91
SN-ATT-CNF	0.245	363	374	348	30.2	395	56.92
SN-Si	0.234	332	366	397	33.4	517	38.72
SN-ATT-Si	0.240	319	377	315	30.3	417	30.32
SS	0.220	273	355	399	34.3	397	44.91
SS-ATT	0.235	316	370	371	32.2	367	46.90
SS-ATTM	0.238	298	360	375	33.4	369	45.09
SS-ATT-CNF	0.255	360	373	310	30.9	303	40.20
SS-Si	0.240	332	367	341	32.3	334	34.57
SS-ATT-Si	0.250	302	376	290	29.9	320	29.37

OI: oxygen index, t_g : combustion time in air, T_z : ignition temperature, HRR_{max} : maximal heat release rate, total HR: total heat release, HR: heat release

Fig. 8 HRR curves of peroxide vulcanizates of SBR rubber **Fig. 9** HRR curves of sulfur vulcanizates of SBR rubber

capability to trap free radicals resulting from the thermal degradation and destruction of polymer. However, according to Kashiwagi, the decreased flammability of polymer/silica composites is connected to a considerably larger extent with physical processes proceeding in the condensed phase than chemical reactions in the gaseous phase [19]. Of paramount importance is the equilibrium between the filler density and specific surface and the viscosity of the molten polymer. It depends on the equilibrium whether silica will accumulate near the surface of the sample under combustion going into the composition of boundary layer or if it will be immersed in the polymer melt [19–22]. One should pay attention to the increase in oxygen content in the residues from burned composites filled with ATT or silica compared to that of unfilled vulcanizates (Fig. 4a–c). It points to intensive chemisorption processes, i.e., strongly exothermic oxidative reactions

between the solid phase of the sample under combustion and gaseous phase.

The considerable reduction in the flammability of vulcanizates containing both silica and ATT, compared to that of the composite filled only with silica, determined by OI and T_z (Table 2; Fig. 8, 9) is connected with the increase in the homogeneity of the residue from the combustion of SN-ATT-Si and SS-ATT-Si vulcanizates (Fig. 10b, c).

Thus, one should assume that the synergic action of ATT and silica considerably influences the formation of a homogeneous insulating boundary layer during the combustion of composite containing these fillers. SBR vulcanizates filled with silica and ATT, regardless of the elastomer spatial network, are also characterized by the lowest values of the fire hazard parameters from among the elastomeric materials investigated (HRR_{max} , Total HR;

Fig. 10 Images of residues from combustion vulcanizates. **a** SS-ATT, **b** SS-Si, **c** SS-ATT-Si, and **d** SS-ATT-CNF

Fig. 11 Oxygen consumption during combustion peroxide vulcanizates of SBR rubber

Fig. 12 Oxygen consumption during combustion sulfur vulcanizates of SBR rubber

Table 2). During their combustion, one can observe the lowest consumption of oxygen (Table 2; Figs. 11, 12).

From the comparative analysis of parameters listed in Table 2 it follows that the flammability of vulcanizates containing carbon nanofiber and ATT is the lowest from among the material investigated, as confirmed by the values of OI , t_s , T_z . Carbon nanofiber is characterized by a large specific surface amounting to $65\text{--}75\text{ m}^2\text{ g}^{-1}$. Thus, it fulfills the function of sorbent of gaseous products of the elastomer thermal decomposition passing to the combustion zone as well as the

function of free radical scavenger mentioned above. It is not an unimportant fact that during thermal decomposition resulting from the combustion of a sample containing carbon nanofiber and ATT, there is a uniform boundary layer formed with no visible cracks, as confirmed by the homogeneous structure of the combustion residue (Fig. 10d), which effectively reduces the mass and energy transport during the combustion of polymeric material.

In this connection, the presence of carbon nanofiber reduces the thermal decomposition rate of the composite

Table 3 Mechanical properties of composites

Sample	Stress/MPa			T_s /MPa	E_b /%
	100/%	200/%	300/%		
SN	0.7	0.94	1.23	1.80	580
SN-ATT	0.85	1.21	1.57	2.12	428
SN-ATTM	0.93	1.19	1.67	2.15	430
SN-ATT-CNF	1.37	1.92	2.30	4.26	691
SN-Si	1.15	1.79	2.58	5.16	483
SN-ATT-Si	1.11	1.53	1.94	4.41	622
SS	1.02	1.54	2.02	2.37	363
SS-ATT	1.48	2.12	2.65	2.93	345
SS-ATTM	1.60	2.28	3.10	3.01	340
SS-ATT-CNF	3.03	4.66	5.79	5.95	297
SS-Si	1.24	1.80	2.49	3.29	385
SS-ATT-Si	1.61	2.39	3.17	5.20	445

T_s tension strength, E_b Elongation at break

filled with carbon nanofiber and ATT (Figs. 5, 6) as well as limits the fire hazard defined by the maximum heat release rate (HRR_{max}) and the oxygen consumption during its combustion (Table 2; Figs. 8, 9, 11, 12). From the results of our previous investigation it follows that the boundary layers of vulcanizates filled with carbon nanofiber have a honeycomb structure [17]. The addition of ATT to carbon nanofiber, as in the case of silica, increases the homogeneity of boundary layers.

From the point of view of the functional properties of polymeric materials a great role is played by their mechanical properties (Table 3). Regardless of the filler used, under the influence of its action the mechanical parameters of vulcanizates are improved. A high tensile strength, T_s , is shown by SBR vulcanizates filled with ATT and carbon nanofiber or ATT and silica. As expected, the vulcanizates containing only silica also show a considerable tensile strength.

Conclusions

Our findings have shown that ATT is active filler improving the thermal and mechanical properties of cross-linked SBR as well as reducing the flammability and fire hazard of the vulcanizates of this elastomer.

The fillers used increase the thermal stability of the cross-linked SBR defined by the rate of its thermo-oxidative decomposition and the residue from that process, which exerts a significant effect on reducing the flammability of the elastomeric material obtained.

A considerable increase in the resistance of cross-linked SBR and its reduced fire hazard result to a large extent from the structure of the boundary layer formed during the

combustion of polymeric materials. ATT and its mixtures with carbon nanofiber or silica also improve the mechanical parameters of the vulcanizate investigated.

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