

Effect of hybrid filler (HNTs-phthalocyanine) on the thermal properties and flammability of diene rubber

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ABSTRACT: Rubber is an essential polymer widely used in the auto-industry. We report a method for the synthesis of zinc phthalocyanine (ZP), chloroaluminum phthalocyanine (CP), and their hybrid fillers obtained by the synthesis of the two phthalocyanines in the presence of halloysite nanotubes (HNTs). The hybrid fillers were characterized by means of microscopic, thermal, and particle size measurement analysis. The effect of these fillers on the properties of diene rubbers were assessed in comparison with a physical mixture of halloysite and ZP or CP pigment. The dispersion degree of hybrid fillers inside an elastomeric matrix (rubber) was assessed with the atomic force microscopy. The influence of the hybrid fillers on the thermal and mechanical properties and flammability of butadiene-acrylonitrile (NBR) and butadiene-styrene (SBR) rubbers was assessed by analyzing the measurement results obtained by means of thermogravimetric analysis, differential scanning calorimetry, Zwick Tensile testing, FAA micro-calorimeter, and oxygen index determination. We found that regardless of the spatial network structure of NBR and SBR rubbers, the incorporation of hybrid fillers into the matrix of the elastomers showed an improvement in their thermal and mechanical properties as well as a significant reduction in flammability. The improvement is attributed to the smaller size and much better dispersion of HZ and HC in relation to the particles of phthalocyanine. The colored composites of NBR rubber, containing hybrid filler (HZ or HC), showed an increase in the heat capacity compared to the uncolored samples, which can increase safety by facilitating the processes of self-extinguishing.

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INTRODUCTION

An improvement in the functional parameters of polymeric materials, with a simultaneous considerable reduction in their flammability, can be obtained by the use of fillers with nanoscopic dimensions.^{1,2} The incorporation of nanofillers into a polymer causes the formation of decisively stronger mutual polymer–filler and filler–filler interactions compared to those of polymeric composites containing conventional fillers. Above a critical filling, increasing mutual filler–filler interactions result in the formation of an internal 3D spatial filler network, responsible for the increase in the viscosity of liquid destruction products being formed during the polymer thermal decomposition, which after solidification form a protective layer on the burning polymer surface. This layer radically reduces the mass and energy transport between polymer and flame.

Nanocomposites are characterized by a low filling degree (0.1–2% by volume), consistent interactions between filler particles in the elastomer matrix (their mutual orientation), high density

of the filler particle packing in relation to the polymer volume unit (10^6 – 10^8 nanoparticles/mL), large surface of interfacial interactions (10^3 – 10^4 m²/mL), and small distances between nanoelements varying within the range of 10–50 nm at a filling amounting to 1–8% by volume.^{3,4} A prerequisite for obtaining unique properties of polymeric nanocomposites is the uniform dispersion of nanofillers providing the formation of a large surface for interfacial interactions in the polymer matrix. This is technologically difficult task to perform as nanoelements, mainly under the influence of Van der Waals forces, show a strong tendency to aggregation and agglomeration.⁵ A significant increase in homogeneous dispersion on mineral nanofillers in the polymeric matrix can be obtained in the presence of organic phthalocyanine pigments. Phthalocyanine occurs in the form of a characteristic aromatic macro-cycle composed of four indole rings combined with azomethine bridges, forming a system of conjugate double bonds containing 18 delocalized π electrons. Indole rings form a closed aromatic plane, constituting a core of the compound.^{6–10}

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From the recent literature reports it follows that phthalocyanine pigments not only beneficially affect the dispersion of nanofillers in the polymer matrix, but also themselves considerably reduce the flammability of polymers containing them.^{11,12}

The present study shows a method for the preparation of hybrid filler obtained with the use of halloysite nanotubes (HNTs) during the synthesis of appropriate phthalocyanine [zinc phthalocyanine (ZP) or chloroaluminum phthalocyanine (CP)] as well as the effect of that filler on its dispersion degree in the polymer matrix and the thermal properties and flammability of cross-linked diene rubbers, such as butadiene-acrylonitrile (NBR) and butadiene-styrene (SBR) rubbers.

MATERIALS AND METHODS

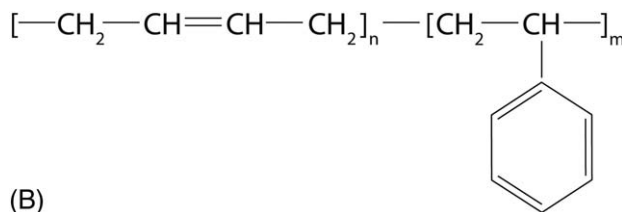
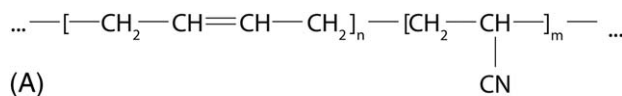
Materials

Pigments Preparation. The synthesis of both ZP and CP was carried out by the dry method. These processes consisted in sintering 1,2-dicyanobenzene (phthalonitrile) with zinc dust or anhydrous aluminum chloride.^{6,7,12}

Preparation of zinc phthalocyanine (ZP). Phthalonitrile and zinc dust, weighed in a proportion of 8 : 1 (by weight) (16 g of phthalonitrile and 2 g of zinc dust), were placed in a porcelain crucible and then fused at a temperature of 160°C. The liquid product obtained was heated for 2 h at $\Delta T = 245\text{--}260^\circ\text{C}$ until the desired organic pigment was made. The pigment was then roasted for 1 h at $\Delta T = 260\text{--}280^\circ\text{C}$. The yield of the chemical reaction of making ZP was 77%. To remove unreacted phthalonitrile from the ZP obtained, the pigment was purified with 5% HCl solution (150 mL), 5% NaOH solution (150 mL), and 96% ethyl alcohol (150 mL). The final yield of the synthesis of ZP after purification was 59%.

Preparation of chloroaluminum phthalocyanine (CP). Phthalonitrile and anhydrous aluminum chloride, weighed in proportion of 3 : 1 (by weight), was placed in a porcelain crucible in the presence of sodium sulfate (ratio phthalonitrile : sodium sulfate 1 : 2) and then heated at a temperature of 250°C for 60 min. Once the synthesis was completed, the pigment was rinsed with hot water to remove sodium sulfate. The yield of this synthesis was 78%. To remove unreacted phthalonitrile, the pigment was purified using 5% HCl solution (150 mL), 5% NaOH solution (150 mL), and 95% ethyl acetate (150 mL). The final yield of the process after the product purification was 58%.

Preparation of hybrid "halloysite-zinc phthalocyanine" filler (HZ). Phthalonitrile, zinc dust, and halloysite were placed in a porcelain crucible. The ratio of phthalonitrile to zinc dust was 8 : 1 (by weight), while that of phthalonitrile to halloysite was 2 : 1 (by weight). The mixture was slowly heated up to a temperature of 250°C, and then it was maintained for 60 min. At $\Delta T = 140\text{--}180^\circ\text{C}$, the mixture assumed a form of dark brown liquid that at $\Delta T = 180\text{--}220^\circ\text{C}$ changed its color to green. Over $T = 220^\circ\text{C}$, the mixture thickened, solidifying at $\Delta T = 240\text{--}250^\circ\text{C}$, and simultaneously assuming the form of fine-grained powder. To remove unreacted phthalonitrile from the zinc phthalocyanine-halloysite hybrid obtained, this filler was purified with 5% HCl solution (150 mL) and 5% NaOH solution (150 mL). The final yield of the synthesis of HZ filler after purification was 44%.



Scheme 1. Structure of rubbers: (A) NBR and (B) SBR.

Preparation of hybrid "halloysite-chloro-aluminumphthalocyanine "filler" (HC). Phthalonitrile, anhydrous aluminum chloride, and halloysite were placed in a porcelain crucible. The ratio of phthalonitrile to aluminum chloride was 3 : 1 (by weight), while that of phthalonitrile to halloysite was 2 : 1 (by weight). The mixture was heated up to a temperature of 300°C, and then maintained at this temperature for 60 min. At $\Delta T = 180\text{--}250^\circ\text{C}$, the mixture assumed the form of brown liquid. During the synthesis, the mixture obtained in this stage showed a high volatility and low density. Then, over 250°C, it solidified on halloysite "grains" in the form a homogeneous blue product assuming red opalescence.

To remove untreated phthalonitrile from the HC hybrid, this filler was purified with 5% HCl solution (150 mL) and 5% NaOH solution (150 mL). The final yield of the HC synthesis after purification was 76%.

Rubbers. The objects of studies were the following rubbers (Scheme 1):

- Butadiene-acrylonitrile rubber (NBR), NBR2255V, containing 22% of combined acrylonitrile from Lanxess [Mooney Viscosity ML (1 + 4) 100°C 57 ± 5 ; Volatile matter ≤ 0.7],
- Butadiene-styrene (SBR), KER 1500, containing 23.5% of combined styrene from Synthos [Mooney Viscosity ML (1 + 4) 100°C 45 ± 5 ; Volatile matter ≤ 0.7].

The rubbers were cross-linked by means of dicumyl peroxide (DCP) (1 phr. phr-parts by weight per hundred parts by weight of rubber) in the presence of zinc oxide (ZnO) (5 phr) or by means of sulfur (1 phr) in the presence of ZnO (5 phr) and N-cyclohexyl-2-benzylsulfenamide (Tioheksam CBS) (1.5 phr). The resultant peroxide vulcanizates of NBR rubber were denoted with NN, while the sulfur with NS. The peroxide vulcanizates of SBR rubber were denoted with SN, while the sulfur with SS.

Fillers. As a filler, elastomeric blends use:

- Halloysite. This filler was incorporated into the elastomeric matrix in a quantity of 8 parts by wt.^{1,20,24,25}

The filler of halloysite vulcanizates of NBR rubber were denoted as:

- NN8H, peroxide vulcanizate of NBR rubber, containing 8 phr of halloysite,

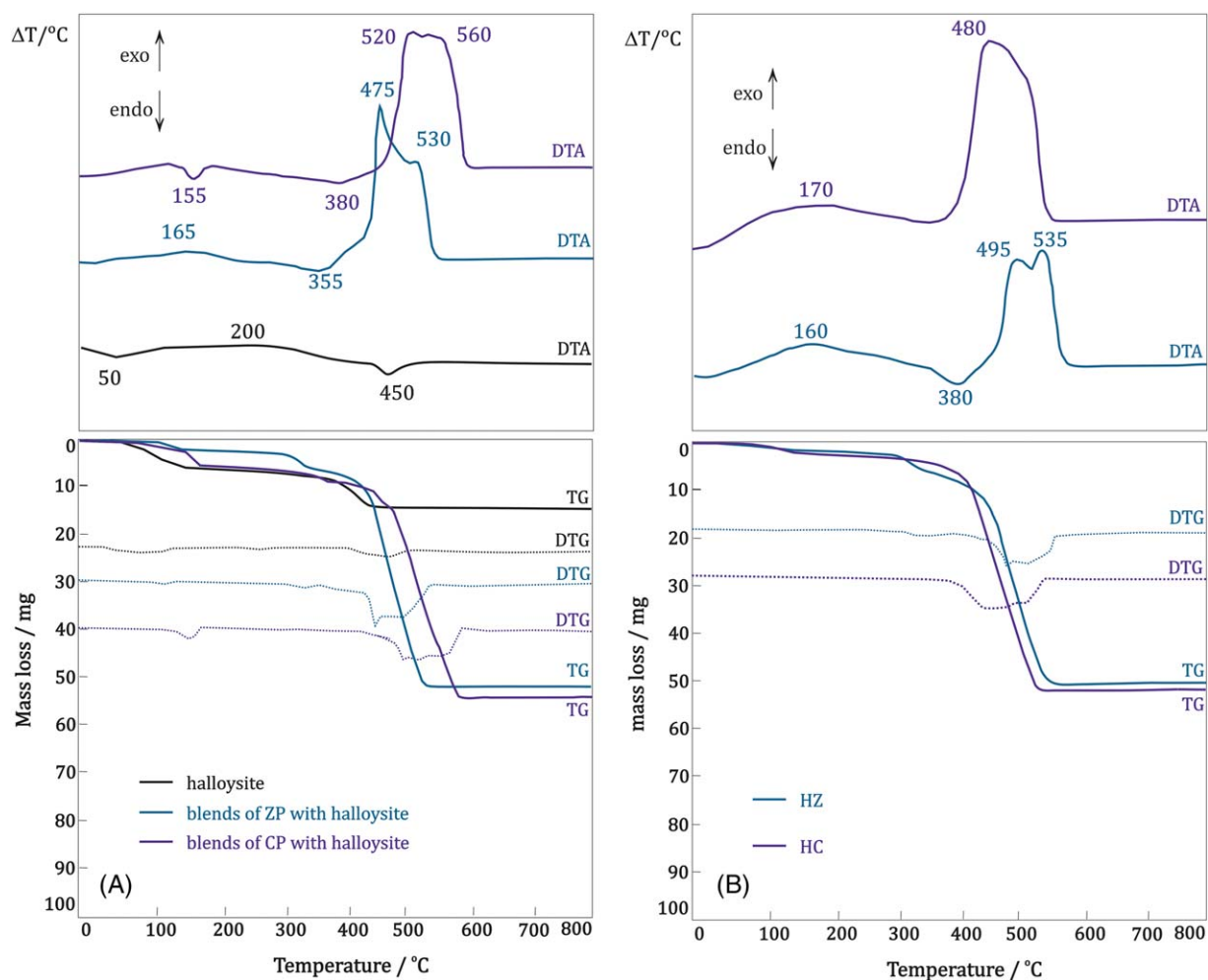


Figure 1. DTA, TG, and DTG curves. (A) halloysite and its mixtures with pigments (ZP) or (CP), and (B) hybrid fillers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Thermal Properties of Halloysite and Its Mixtures with (ZP) or (CP) and Hybrid Fillers

Sample	T_5 (°C)	T_{50} (°C)	ΔT (°C)	dm/dt (%/min)	Um (%)	P ₅₀₀ (%)	P ₈₀₀ (%)
Halloysite	105	-	35-130	2	5.6	85.6	84.4
			130-440	1	10.0		
			440-580	4	15.6		
Mixture ZP + halloysite	315	520	35-220	2	2.8	61.1	42.2
			220-390	1.5	8.3		
			390-580	17	57.8		
HZ hybrid filler	320	535	35-275	0.5	3.3	64.4	43.3
			275-405	2	10.0		
			405-580	13	56.7		
Mixture CP + halloysite	145	560	35-210	4	6.1	77.8	38.9
			210-440	0,5	12,2		
			440-615	14	61.1		
HC hybrid	365	520	35-340	1	3.9	57.8	42.2
			340-570	11	57.8		

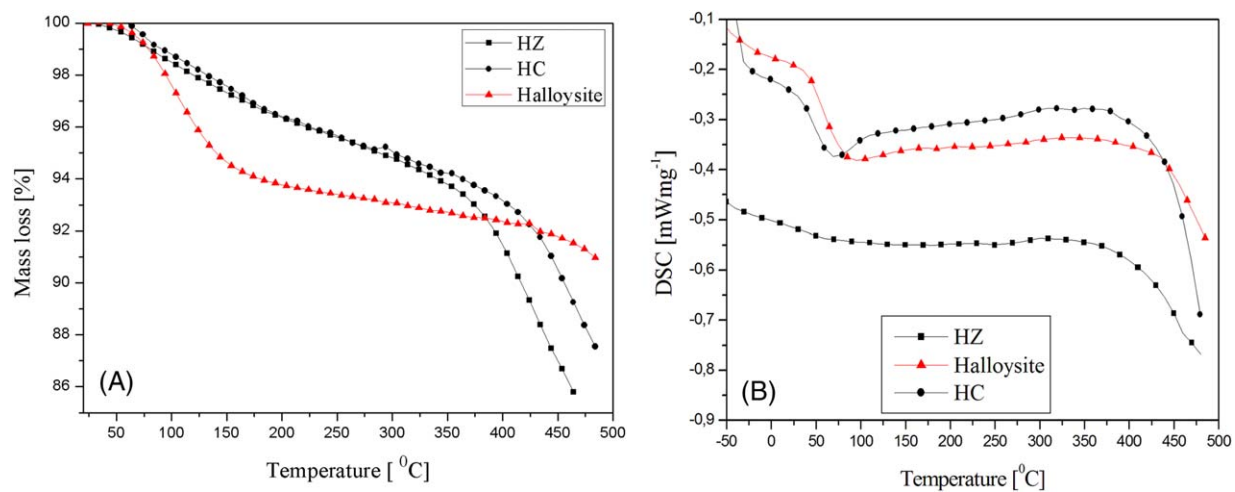


Figure 2. Thermal properties of halloysite and the hybrid filler: (A) TG curves and (B) DSC curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

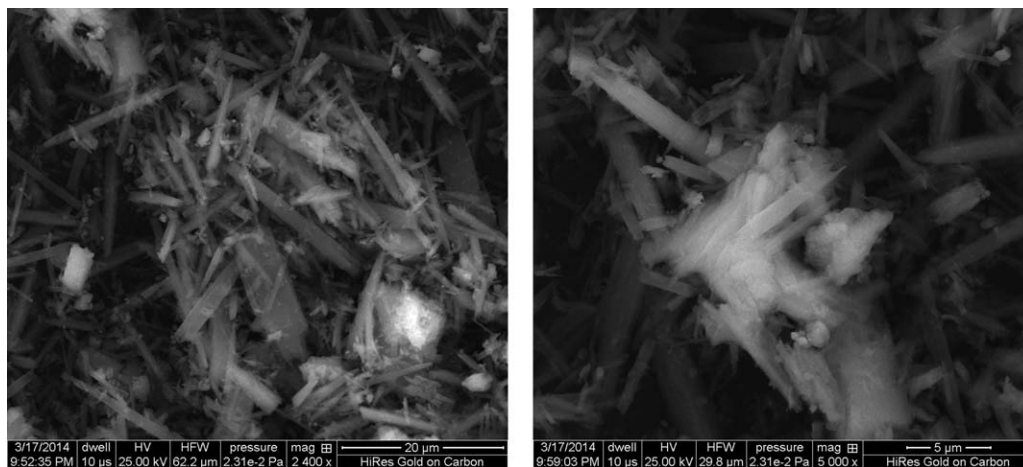


Figure 3. SEM pictures of mixture halloysite with zinc phthalocyanine.

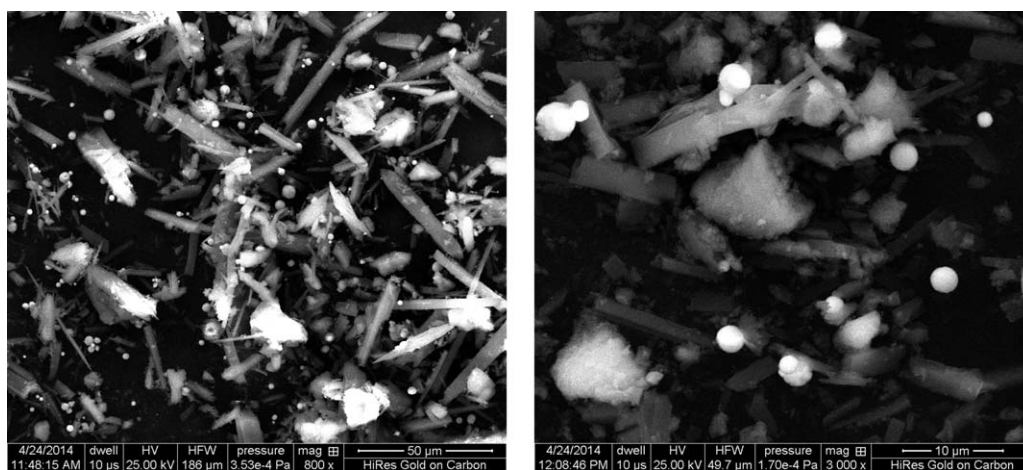


Figure 4. SEM pictures of hybrid filler HZ not purified.

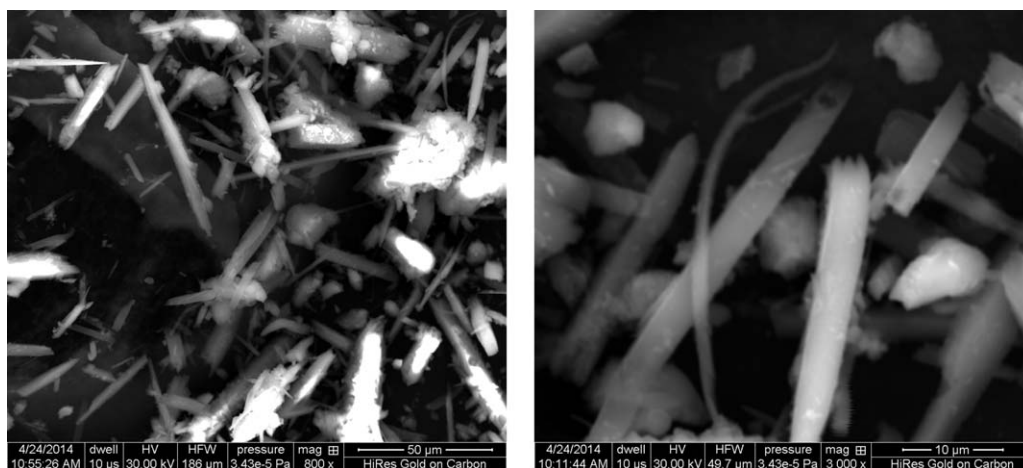


Figure 5. SEM pictures of hybrid filler HZ after its purification with HCl solution.

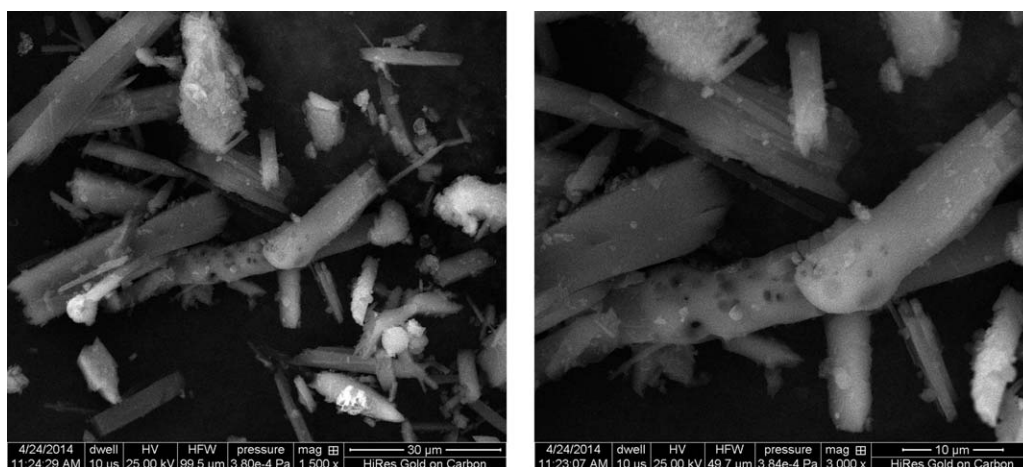


Figure 6. SEM pictures of hybrid filler HZ after its purification with NaOH solution.

- NS8H, sulfur vulcanizate of NBR rubber, containing 8 phr of halloysite.

The filler of halloysite vulcanizates of SBR rubber were denoted as:

- SN8H peroxide vulcanizate of SBR rubber, containing 8 phr of halloysite,
- SS8H sulfur vulcanizate of SBR rubber, containing 8 phr of halloysite.

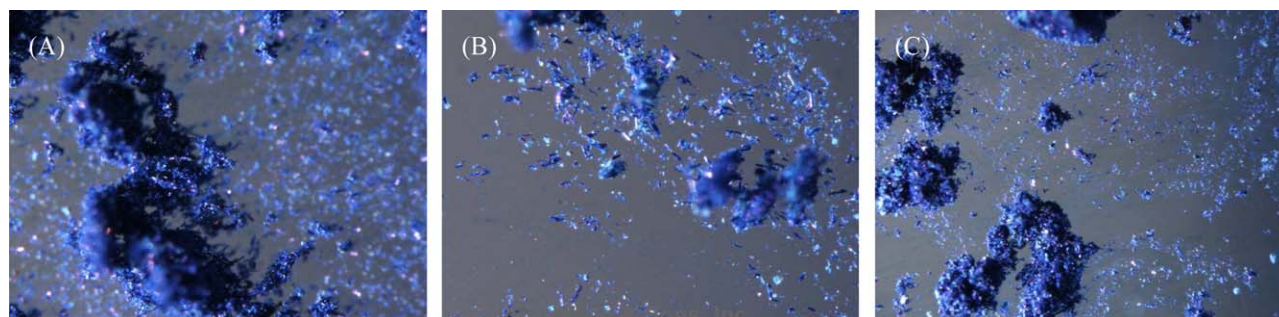


Figure 7. Pictures of hybrid filler HZ taken by stereoscopic microscope in comparable enlargement: (A) filler HZ not purified; (B) HZ after its purification with HCl solution; and (C) HZ after its purification with NaOH solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

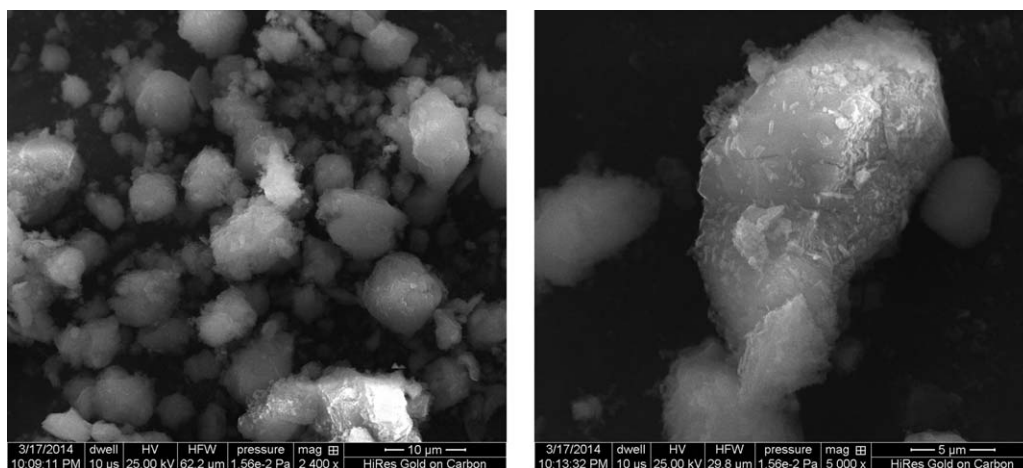


Figure 8. SEM pictures of mixture halloysite with chloro-aluminum phthalocyanine.

- Physical mixture of phthalocyanine pigments (ZP) or (CP) with halloysite. The mixture contains 5 phr of phthalocyanine (ZP) or (CP) and 8 phr of halloysite.

The vulcanizates of NBR rubber containing phthalocyanine pigments were denoted as:

- NN8H5ZP(CP)—peroxide vulcanizate of NBR rubber contains 8 phr of halloysite and 5 phr of phthalocyanine pigment (ZP) or (CP),
- NS8H5ZP(CP)—sulfur vulcanizate of NBR rubber contains 8 phr of halloysite and 5 phr of phthalocyanine pigment (ZP) or (CP).

The vulcanizates of SBR rubber containing phthalocyanine pigments were denoted as:

SN8H5ZP(CP)- peroxide vulcanizate of SBR rubber contains 8 phr of halloysite and 5 phr of phthalocyanine pigments (ZP) or (CP),
 SS8H5ZP(CP)- sulfur vulcanizate of SBR rubber contains 8 phr of halloysite and 5 phr of phthalocyanine pigments (ZP) or (CP).

Hybrid fillers (HZ) or (HC). The fillers were incorporated to the elastomeric blend in the quantity of 5, 8, and 12 phr.

The filler of (HZ) or (HC) vulcanizates of NBR rubber were denoted as:

- NN5HZ (HC); NN8HZ (HC); NN12HZ (HC) peroxide vulcanizates of NBR rubber containing respectively of 5, 8, and 12 phr of hybrid filler (HZ) or (HC),
- NS5HZ (HC); NS8HZ (HC); NS12HZ (HC) sulfur vulcanizates of NBR rubber containing, respectively, 5, 8, and 12 phr of hybrid filler (HZ) or (HC).

The filler of (HZ) or (HC) vulcanizates of SBR rubber were denoted as:

- SN5HZ (HC); SN8HZ (HC); SN12HZ (HC) peroxide vulcanizates of SBR rubber containing, respectively, of 5, 8, and 12 phr of hybrid filler (HZ) or (HC),
- SS5HZ (HC); SS8HZ (HC); SS12HZ (HC) sulfur vulcanizates of SBR rubber containing, respectively, 5, 8, 12 phr of hybrid filler (HZ) or (HC).

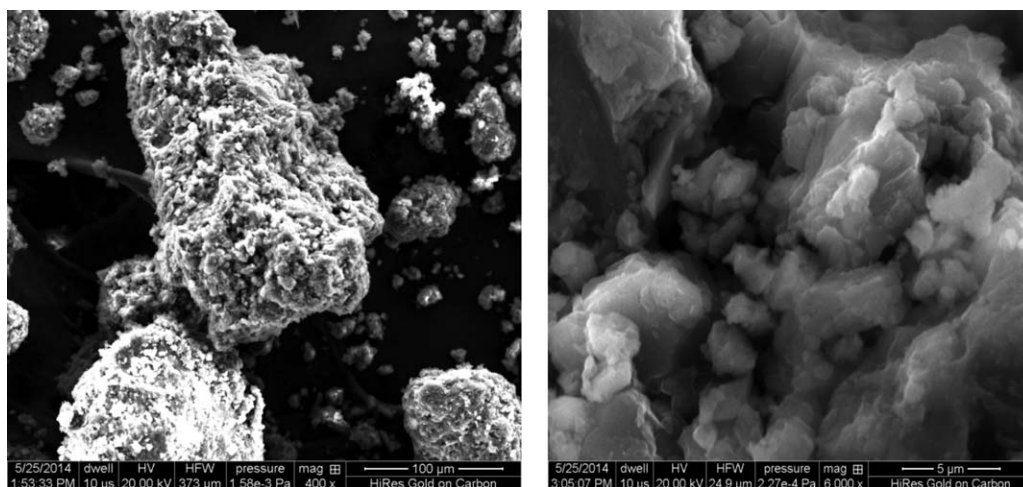


Figure 9. SEM pictures of hybrid filler HC not purified.

Table II. Particle Size of Halloysite, Its Mixtures with Pigments ZP or CP and Hybrid Fillers (HZ and HC)

Sample	Particle size (μm)
Halloysite	147
Mixture ZP + halloysite	459
HZ hybrid	215
Mixture CP + halloysite	374
HC hybrid	270

Methods

Microscopic Analysis. SEM. The SEM photographs were taken by means of a SEM Quanta 250 FEG microscope equipped with the detector of X-ray dispersion energy [EDS EDAX Genesis XM 4i (USA)].

Stereoscopic microscopy. Stereoscopic microscopy observations were made by means of a Nikon SMZ1500 camera, using NIS-Elements Basic Research program. Pictures were taken at an enlargement of 100.

AFM. Atomic Force Microscopy (AFM) measurements were performed by means of Metrology Series 2000, Molecular Imaging (USA) apparatus. Imaging was carried out with the use of a scanning siliceous head with conical shape (dilation angle $<20^\circ$) and height about 15–20 μm operating in oscillatory mode with a resonance frequency of about 170 kHz. Samples for measurements were vulcanized in a steel mold. A glass plate was placed in the mold to obtain a low coarseness of vulcanizate surface. Before placing in the mold, the glass plate surface was rinsed

acetone and dried in with air jet to decrease it and remove impurities.

The image analysis was carried out by means of the WS×M program worked out and made available by Horcas *et al.*¹³

Determination of Particle Size. The particle size of halloysite and hybrid fillers was measured by means of a Zetasizer Nano Series S90 apparatus from Malvern Instruments within the range of 1–3000 nm. Measurements were made in distilled water, preparing dispersions of filler and hybrid filler with a concentration of 0.01 g/L. To obtain proper suspension of the substances tested, the solutions were subjected to the action of ultrasounds for 5 h using an Ultrasonic Cleaner W-217 Honda.

Preparation and Vulcanization of Elastomeric Blends. Elastomeric blends were prepared at room temperature with the use of a laboratory rolling mill ($D = 150$ mm, $L = 300$ 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 vulcanizates which contain pigment or hybrid filler have a nice blue color.

Thermal Analysis. Thermal analysis of pigments and composites and nanocomposites was carried out in air by means of the Derivatograph MOM, Hungary, using approximately 90 mg samples at a heating rate of 7.9°C/min within the temperature range from 20°C to 800°C. Sensitivity of curves: DTA = 1/5, DTG = 1/30, and TG = 100. DTA and DTG sensitivity (n^{-1}) means that the distance between two points on sensitized paper,

Table III. Thermal Properties Composites of NBR Rubber

Sample	T_5 (°C)	T_{50} (°C)	T_R (°C)	dm/dt (%/min)	Pw (%)	T_s (°C)	P_{800} (%)
NN8H	355	420	380	51	30	535	11.1
NN8H5ZP	355	415	385	48	30	535	9.4
NN5HZ	350	415	365	47	26	535	6.1
NN8HZ	365	420	370	47	29	535	9.4
NN12HZ	360	420	365	45	29	525	8.3
NN8H5CP	375	425	375	35	37	535	12.8
NN5HC	370	425	375	45	29	550	7.2
NN8HC	375	415	370	42	30	535	4.4
NN12HC	375	425	375	41	36	535	11.1
NS8H	330	410	365	44	28	525	10.0
NS8H5ZP	370	425	380	48	33	535	10.0
NS5HZ	300	410	365	43	22	535	8.2
NS8HZ	330	415	360	41	28	535	9.4
NS12HZ	305	415	360	43	29	525	8.9
NS8H5CP	330	425	365	36	32	535	10.6
NS5HC	330	415	365	41	31	535	8.3
NS8HC	365	420	365	41	33	545	10.0
NS12HC	355	425	370	37	35	545	10.6

Table IV. Thermal Properties Composites of SBR Rubber

Sample	T_5 (°C)	T_{50} (°C)	T_R (°C)	dm/dt (%/min)	Pw (%)	T_s (°C)	P_{800} (%)
SN8H	235	400	365	43	23.9	520	8.9
SN8H5ZP	260	405	365	45	26.7	525	10.0
SN5HZ	340	410	365	48	19.4	525	8.3
SN8HZ	320	410	365	46	18.9	530	5.6
SN12HZ	325	410	365	47	23.9	505	7.2
SN8H5CP	235	405	365	41	29.4	535	10.0
SN5HC	305	405	355	48	20.6	515	6.7
SN8HC	315	405	355	47	21.1	515	4.4
SN12HC	325	410	365	46	26.7	535	7.8
SS8H	270	400	355	41	22.8	525	10.0
SS8H5ZP	275	400	355	41	26.1	525	10.6
SS5HZ	300	400	350	44	21.1	525	7.2
SS8HZ	305	405	355	47	23.9	525	8.9
SS12HZ	285	405	355	41	28.3	525	10.0
SS8H5CP	270	405	355	40	28.3	525	12.2
SS5HC	280	405	355	46	21.7	535	6.1
SS8HC	315	410	360	39	26.1	535	8.3
SS12HC	295	415	360	40	27.2	540	8.9

corresponding to zero and the maximum deflection of the galvanometer mirror was reduced n times. Sensitivity TG 100 means that the distance between two points on sensitized paper, mapping zero and the maximum deflection of the mirror corresponds to a change of weight amounting to 100 mg.

Vulcanizates were also studied in an inert atmosphere using a Netzsch DSC-204 differential scanning calorimetry with approximately 5 mg samples at a cooling and heating rate of 10°C/min from 20°C to -150°C and -150°C to 500°C, respectively.^{14,15}

Flammability Tests. Oxygen index and combustibility in air methods. The combustibility of the vulcanizates was determined by the oxygen index (OI) method according to the standard

PN-ISO 4589-2:1998. The combustibility was also tested in air, using the same apparatus.¹⁶

Microcalorimetric method. Flammability tests were carried out with the use of a micro calorimeter from Testing Technology Limited.^{16,17}

Pyroliser temperature was 750°C and that of combustor 900°C. During the measurements the following parameters were recorded: ignition temperature (T_z), maximal heat release rate (HRR_{MAX}), total heat release (THR), heat release capacity (HRC), and percent of oxygen consumption (OC) during combustion.

A sample was heated using a linear temperature program, and the volatile decomposition products were carried off from the

Table V. DSC Results Vulcanizates of NBR Rubber

Sample	Cooling		Heating				
	T_g (°C)	ΔT_g (°C)	T_g (°C)	ΔT_g (°C)	T_{tc} (°C)	ΔH_{tc} (J × g ⁻¹)	T_d (°C)
NN8H	-39	-27 to -51	-37	-46 to -28	360	566	463
NN8H5ZP	-40	-28 to -51	-37	-46 to -28	354	576	461
NN8HZ	-42	-31 to -53	-40	-48 to -32	352	598	459
NN8H5CP	-39	-28 to -50	-37	-46 to -27	357	586	457
NN8HC	-38	-26 to -49	-36	-45 to -26	357	590	460
NS8H	-39	-32 to -46	-33	-41 to -25	361	538	461
NS8H5ZP	-39	-32 to -46	-33	-40 to -25	358	518	457
NS8HZ	-36	-30 to -42	-36	-44 to -28	357	518	456
NS8H5CP	-38	-28 to -48	-34	-42 to -26	357	473	458
NS8HC	-35	-32 to -37	-32	-40 to -25	360	533	449

Table VI. DSC Results Vulcanizates of SBR Rubber

Sample	Cooling		Heating				
	T_g (°C)	ΔT_g (°C)	T_g (°C)	ΔT_g (°C)	T_{tc} (°C)	ΔH_{tc} (J \times g ⁻¹)	T_d (°C)
SN8H	-54	-45 to -63	-50	-55 to -45	350	388	440
SN8H5ZP	-58	-45 to -71	-49	-56 to -43	363	427	464
SN8HZ	-54	-44 to -64	-49	-54 to -44	367	478	465
SN8H5CP	-52	-40 to -65	-49	-54 to -45	364	337	442
SN8HC	-53	-46 to -59	-49	-54 to -26	369	460	448
SS8H	-54	-48 to -60	-50	-41 to -44	359	440	460
SS8H5ZP	-48	-42 to -55	-43	-48 to -38	365	444	462
SS8HZ	-47	-37 to -57	-43	-48 to -38	365	406	457
SS8H5CP	-47	-45 to -55	-43	-47 to -38	373	455	460
SS8HC	-48	-42 to -54	-45	-50 to -39	369	444	454

pyrolyzer chamber by means of inert gas and combined with excess oxygen in a tube oven at the flame temperature to force flameless total combustion (oxidation) of the fuel. Combustion products: CO₂, H₂O, and acidic gases were removed from the gas stream, and the HRR was calculated on the basis of measured intensity of their flow and oxygen concentration after the correction of flow dispersion. The maximal heat released rate, standardized in relation to the initial sample mass and heat ratio, was determined with the material flammability parameter determined with the unit of released heat capacity (J/g \times K) that depends exclusively on the sample chemical composition and is proportional to the material combustion rate during fire.

Table VII. Flammability Test Vulcanizates of NBR Rubber

Sample	OI (%)	ts (s)
NN8H	25.8	461
NN8H5ZP	26.6	103 ^a
NN5HZ	26.5	169 ^a
NN8HZ	26.7	116 ^a
NN12HZ	28.6	85 ^a
NN8H5CP	26.6	91 ^a
NN5CP	25.1	458
NN8HC	25.6	149 ^a
NN12HC	25.2	64 ^a
NS8H	25.4	418
NS8H5ZP	25.8	432
NS5HZ	25.6	385
NS8HZ	26.1	435
NS12HZ	26.7	445
NS8H5CP	26.0	236 ^a
NS5HC	27.1	358
NS8HC	25.8	218 ^a
NS12HC	26.5	70 ^a

OI—oxygen index; ts—time of burning in air atmosphere.

^aSelf-extinguishing samples.

Mechanical Properties. Tensile strength properties were determined according to the standard PN-ISO 37:1998 by means of a Zwick tensile tester, model 1435, linked to an appropriately PC software. Samples for testing were in the shape of dumbbell with a measurement section width of 4 mm and thickness 1 ± 0.001 mm.

RESULTS AND DISCUSSION

Characteristics of Hybrid Fillers

Thermal Analysis of Hybrid Fillers Under Air. From a literature review, it follows that halloysite undergoes a clear three-stage thermal decomposition at $\Delta T = 35$ –800°C. The first thermal decomposition stage at $\Delta T_1 = 35$ –130°C, accompanied by the endothermic transition recorded in DTA curve, is due to the desorption of water, physically combined with the surface of aluminosilicate, whose content amounts to 5.6%. The second stage at $\Delta T_2 = 130$ –440°C is connected with the release of water physically occluded in nanotubes and water chemically combined with the surface of halloysite. This stage is accompanied by a 10% loss of sample weight. The final stage of thermal decomposition at $\Delta T_3 = 440$ –580°C is connected with the decomposition of the carbon fraction occurring in the form of carbonates and organic carbon on the surface of HNTs. This stage is accompanied by a 15.6% loss of sample weight.^{18–21}

The test results obtained by the method of thermal analysis show that the physical mixture of ZP or CP pigment and HNTs, as halloysite, undergoes three-stage thermal decomposition. Under the influence of ZP or CP pigment, there is a change in the temperature range, within which the successive stages of the thermal decomposition of halloysite occur. The physical mixture of ZP or CP pigment and halloysite also considerably reduces the mass loss connected with the desorption of water physically combined with the surface of aluminosilicate, which is connected with its lower weight content in the mixture sample tested [Figure 1(A)].

The addition of phthalocyanine, especially zinc phthalocyanine to halloysite, increases the value of parameter T_5 (5% sample mass loss) of the mixture compared to the value of parameter T_5 recorded for pure halloysite. It should be also noticed that

Table VIII. Flammability Test Vulcanizates of SBR Rubber

Sample	OI (%)	ts (s)
SN8H	23.4	265
SN8H5ZP	24.8	299
SN5HZ	21.3	203
SN8HZ	22.8	272
SN12HZ	26.9	310
SN8H5CP	23.1	249
SN5HC	23.1	221
SN8HC	23.4	240
SN12HC	27.8	311
SS8H	24.2	291
SS8H5ZP	24.5	290
SS5HZ	25.6	297
SS8HZ	23.1	296
SS12HZ	25.6	287
SS8H5CP	24.8	295
SS5HC	25.9	291
SS8HC	25.1	306
SS12HC	27.3	318

the mixture of ZP or CP with halloysite is characterized by a higher value of the thermal decomposition rate, dm/dt , in relation to “pure” halloysite, which directly results from the fact that, beside the decomposition of carbon fraction occurring, first of all, on the surface of halloysite, there also occurs a vio-

lent thermal decomposition of ZP or CP pigments contained in the mixtures. According to expectations, the mixtures of the pigments investigated with halloysite are characterized by a lower residue after their heating to 500°C and 800°C, respectively, (parameters P_{500} and P_{800}) in relation to aluminosilicate (Table I). HZ and HC hybrid fillers show a similar, but what is important, not identical thermal decomposition compared to the physical mixtures of halloysite with pigments ZP or CP.

HZ hybrid as halloysite and its physical mixture with zinc phthalocyanine undergoes three-stage thermal decomposition; however, the successive stages of this decomposition occur at a higher temperature than that of the thermal decomposition of halloysite or the mixtures of pigments with aluminosilicate (standard samples). Also the thermal stability parameters: T_5 , T_{50} , P_{500} and P_{800} of the hybrid filler synthesized are higher than those of the physical mixture of hybrid and ZP [Figure 1(B)].

From the test results obtained, it follows that the HC hybrid filler is characterized by a significantly higher thermal stability, determined with parameter T_5 than the physical mixture of halloysite and CP. The thermal decomposition of HC hybrid filler proceeds in two stages, which result from the modification of halloysite that occurred during the synthesis of HC. The desorption of water physically and chemically combined with hybrid filler, whose total content amounts to 3.9%, occurs at $\Delta T_1 = 35\text{--}400^\circ\text{C}$. The second stage of thermal decomposition at $\Delta T_2 = 340\text{--}570^\circ\text{C}$ is connected with the combustion processes of hybrid filler.

Thermal Analysis of Hybrid Fillers Under Inert Gas. From the analysis of TG curves recorded under inert gas, it follows

Table IX. Fire Hazard Parameters Composites of NBR Rubber

Sample	Tz (°C)	HRR _{MAX} (W × g ⁻¹)	THR (kJ × g ⁻¹)	HRC (J × g ⁻¹ × K ⁻¹)	OC (%)
NN8H	346	453	28	354	73
NN8H5ZP	360	409	29	403	75
NN5HZ	365	347	28	439	68
NN8HZ	360	330	28	426	59
NN12HZ	355	382	29	383	53
NN8H5CP	361	331	24	293	50
NN5HC	371	424	30	412	64
NN8HC	357	403	28	394	68
NN12HC	348	351	27	347	65
NS8H	368	398	29	361	55
NS8H5ZP	361	361	27	354	46
NS5HZ	376	363	30	373	70
NS8HZ	368	369	28	359	64
NS12HZ	364	365	27	362	47
NS8H5CP	375	334	28	326	75
NS5HC	377	360	30	351	46
NS8HC	378	351	29	349	47
NS12HC	379	348	27	341	51

Table X. Fire Hazard Composites of SBR Rubber

Sample	T _z (°C)	HRR _{MAX} (W × g ⁻¹)	THR (kJ × g ⁻¹)	HRC (J × g ⁻¹ × K ⁻¹)	OC (%)
SN8H	370	425	28	413	95
SN8H5ZP	370	353	26	348	67
SN5HZ	374	352	35	443	79
SN8HZ	375	339	34	430	92
SN12HZ	376	399	33	389	62
SN8H5CP	377	330	26	326	52
SN5HC	373	412	33	409	55
SN8HC	375	377	32	374	43
SN12HC	378	384	30	379	37
SS8H	361	354	31	360	44
SS8H5ZP	369	352	30	346	37
SS5HZ	385	356	33	349	44
SS8HZ	391	341	30	332	49
SS12HZ	409	364	32	355	48
SS8H5CP	371	338	30	333	48
SS5HC	368	363	33	357	42
SS8HC	370	354	32	352	41
SS12HC	381	333	28	331	41

that the thermal decomposition of HZ and HC hybrid fillers at $\Delta T = 30\text{--}350^\circ\text{C}$ is decisively lower in relation to that of halloysite. Parameter T_5 of halloysite is recorded at a temperature of 40°C , while in the case of hybrid fillers (both HZ and HC), it is recorded at $T = 275^\circ\text{C}$ [Figure 2(A)].

From the analysis of DSC curves, it follows that both halloysite and HC hybrid undergo a clear thermal transformation at $\Delta T = 30\text{--}200^\circ\text{C}$. In the case of halloysite, this transformation undoubtedly is connected with water evaporation as confirmed by a clear mass loss recorded in TG and DTG curves. In the

Table XI. Mechanical Properties Composites of NBR Rubber

Sample	Se (MPa)			TS _b (MPa)	E _b (%)	S
	100 (%)	200 (%)	300 (%)			
NN8H	1.10	1.55	2.02	3.08	461	0.83
NN8H5ZP	1.25	1.76	2.23	3.42	474	1.04
NN5HZ	1.07	1.42	1.76	2.05	346	0.91
NN8HZ	1.24	1.77	-	1.91	240	1.21
NN12HZ	1.46	2.20	2.98	2.87	290	1.26
NN8H5CP	1.19	1.56	1.91	3.61	535	0.78
NN5HC	1.32	2.04	2.61	3.50	434	1.11
NN8HC	1.21	1.70	2.16	4.59	576	1.00
NN12HC	1.51	2.10	2.58	4.60	500	1.12
NS8H	1.61	2.14	-	2.48	262	0.93
NS8H5ZP	1.75	2.43	-	2.49	203	0.88
NS5HZ	1.54	2.16	-	2.38	235	1.02
NS8HZ	1.55	2.03	-	2.23	241	0.91
NS12HZ	1.76	2.50	-	2.71	241	0.92
NS8H5CP	1.62	2.18	2.74	2.76	281	1.08
NS5HC	1.54	2.13	2.56	2.69	295	1.05
NS8HC	1.65	2.31	2.98	3.01	303	1.00
NS12HC	1.75	2.40	3.02	3.14	310	1.13

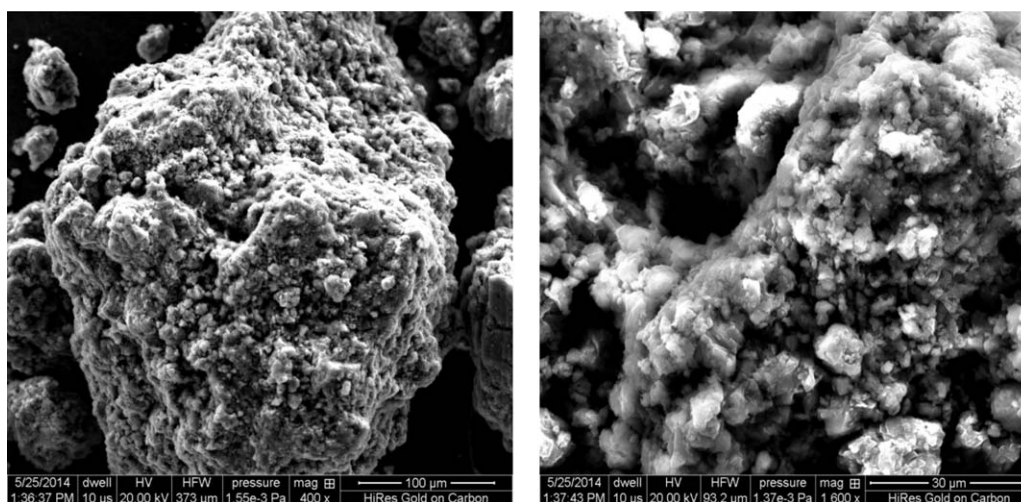
Table XII. Mechanical Properties Composites of SBR Rubber

Sample	Se (MPa)			TS _b (MPa)	E _b (%)	S
	100 (%)	200 (%)	300 (%)			
SN8H	0.72	1.01	1.10	1.23	419	0.49
SN8H5ZP	0.78	1.13	1.21	1.57	399	0.53
SN5HZ	0.81	1.08	1.36	1.87	429	1.00
SN8HZ	0.94	1.36	1.82	2.11	335	0.94
SN12HZ	1.48	2.01	2.45	2.73	358	1.00
SN8H5CP	0.81	1.17	1.27	1.49	415	0.57
SN5HC	1.14	1.57	2.04	2.89	436	0.95
SN8HC	0.99	1.40	1.79	2.43	429	1.01
SN12HC	0.94	1.34	1.68	3.12	629	1.03
SS8H	1.19	1.65	2.07	2.05	294	0.97
SS8H5ZP	1.27	1.78	2.34	2.56	327	0.88
SS5HZ	1.22	1.81	2.42	2.31	272	0.93
SS8HZ	1.25	1.83	2.45	2.45	294	1.00
SS12HZ	1.43	2.22	-	2.71	245	1.01
SS8H5CP	1.35	1.93	2.52	2.61	311	0.87
SS5HC	1.19	1.71	2.32	2.70	323	0.87
SS8HC	1.41	2.10	2.70	2.80	320	0.83
SS12HC	1.40	1.99	2.55	2.82	345	0.82

case of HC hybrid filler, one may believe that this transformation is connected with the release of small amounts of hydrogen chloride [Figure 2(B)].

Microscopic Analysis. The test results obtained by the SEM method clearly show that the hybrid fillers (HZ and HC) distinctly differ from the physical mixture of zinc or chloroaluminum phthalocyanine with aluminosilicate. In the photos showing the physical mixture of ZP and halloysite, one can observe a clear separation of HNTs and zinc phthalocyanine (Figure 3). In the case of HZ hybrid, it is exactly seen that zinc

phthalocyanine homogeneously covers the surface of HNTs (Figures 4–6). Based on the SEM photos, one may also conclude that the pigment is not bound with the internal surface of nanotubes, which is a desirable phenomenon from the point of view of the immobilization of liquid destruction products formed during the thermal decomposition of containing them composites (Figures 5 and 6). It should also be noticed that in the SEM images showing the hybrid filler that was not previously purified with HCl or NaOH solution, one can exactly observe unreacted phthalonitrile in the form of spherical globules with different sizes (Figure 4).

**Figure 10.** SEM pictures of hybrid filler HC after its purification with HCl solution.

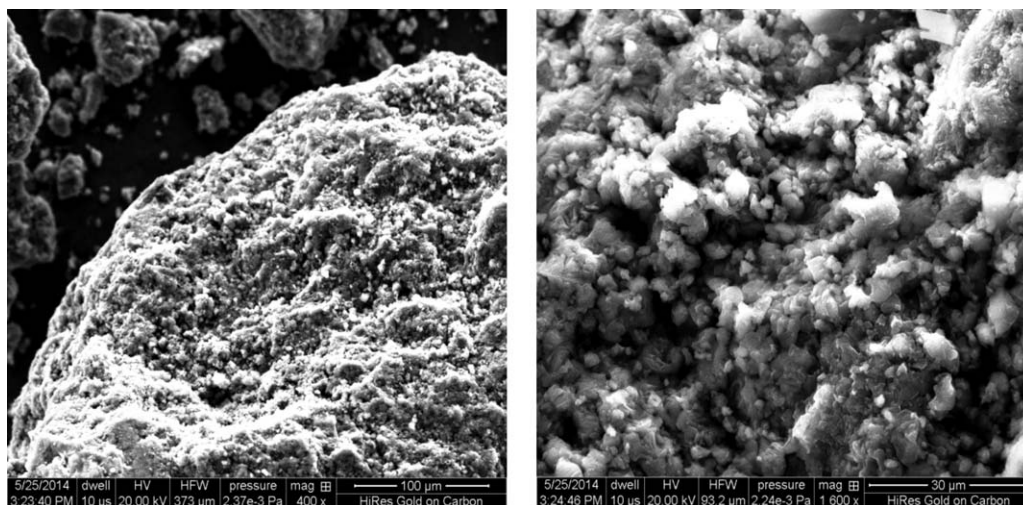


Figure 11. SEM pictures of hybrid filler HC after its purification with NaOH solution.

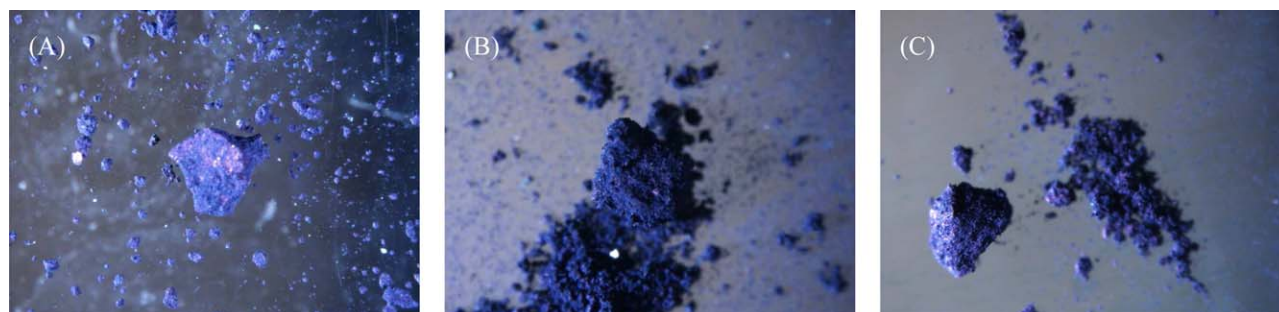


Figure 12. Pictures of hybrid filler HC taken by stereoscopic microscope in comparable enlargement: (A) filler HC not purified; (B) HC after its purification with HCl solution; and (C) HC after its purification with NaOH solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

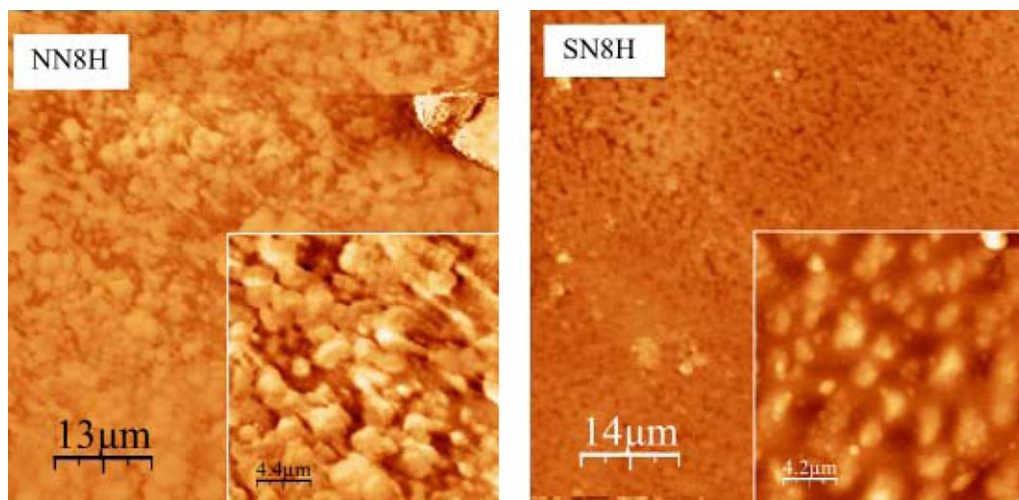


Figure 13. AFM pictures of NBR and SBR vulcanizates containing 8 phr of halloysite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

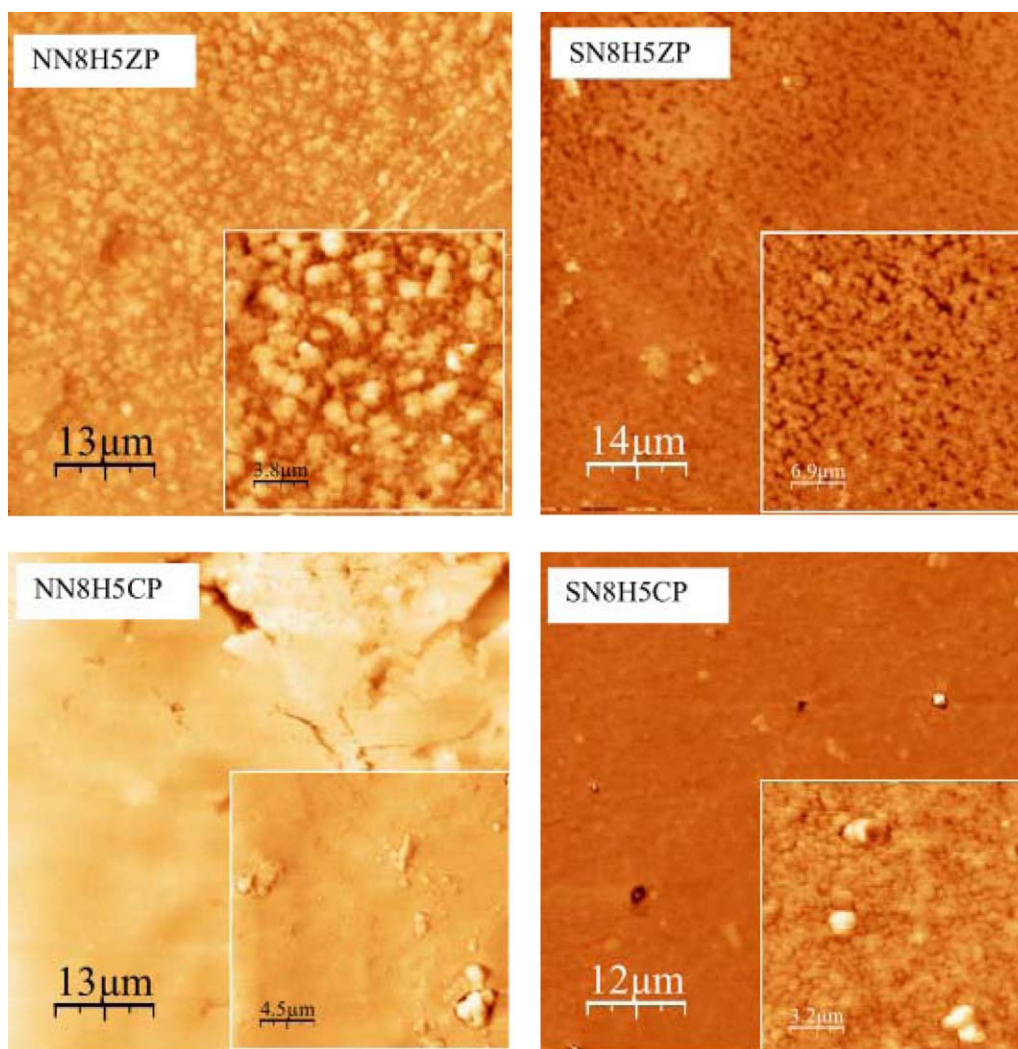


Figure 14. AFM pictures of NBR and SBR vulcanizates which contain mixture of halloysite and phthalocyanine ZP or CP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The photos taken by means of stereoscopic microscope reflect the color, intensity, and shape of the HZ hybrid filler crystals. Based on the analysis of pictures obtained by the stereoscopic technique, one should conclude that the purification of HZ hybrid filler with HCl or NaOH solutions undoubtedly contributed to an increase in its homogeneity (Figure 7).

The analysis of SEM pictures of the physical mixture of halloysite and chloroaluminum phthalocyanine allow one to conclude that chloroaluminum phthalocyanine shows a decisively greater affinity to HNTs surface than ZP phthalocyanine, which is directly connected with the presence of aluminum atom in its molecule and on the surface of aluminosilicate. Thus, the SEM pictures show first of all “pellets” of CP pigment accurately covering HNTs (Figure 8). Meanwhile, during the synthesis of chloroaluminum phthalocyanine in the presence of nanofiller (H), as in the case of the synthesis of HZ, there occurred a stable combination of phthalocyanine pigment with halloysite. Hybrid HC is characterized by a clearly porous surface. After

purification with HCl or NaOH solution, hybrid HC filler still shows a porous structure of particles as confirmed by the pictures taken by SEM and stereoscopic techniques (Figures (9 and 12)). The increase in the HC filler particle size (Table II), from the one hand can negatively affect functional properties, including the flammability of polymeric composites containing it, and on the other hand the porous structure of particles can facilitate its homogeneous dispersion in the polymer matrix.

Measurement of Particle Size. The hybrid character of the fillers synthesized is confirmed by the measurement of their particle size. The measurements of the particle size of hybrid fillers (HZ and HC), halloysite and the physical mixtures of HNTs with appropriate pigment (ZP or CP), were made after their previous dispersing in water, in which they were then subjected to the action of ultrasounds for 5 h (Table II). Under the influence of ultrasounds, the suspension of pigment ZP or CP with halloysite turned blue. In the case of hybrid fillers (HZ and HC), a slight coloring of their aqueous suspensions was

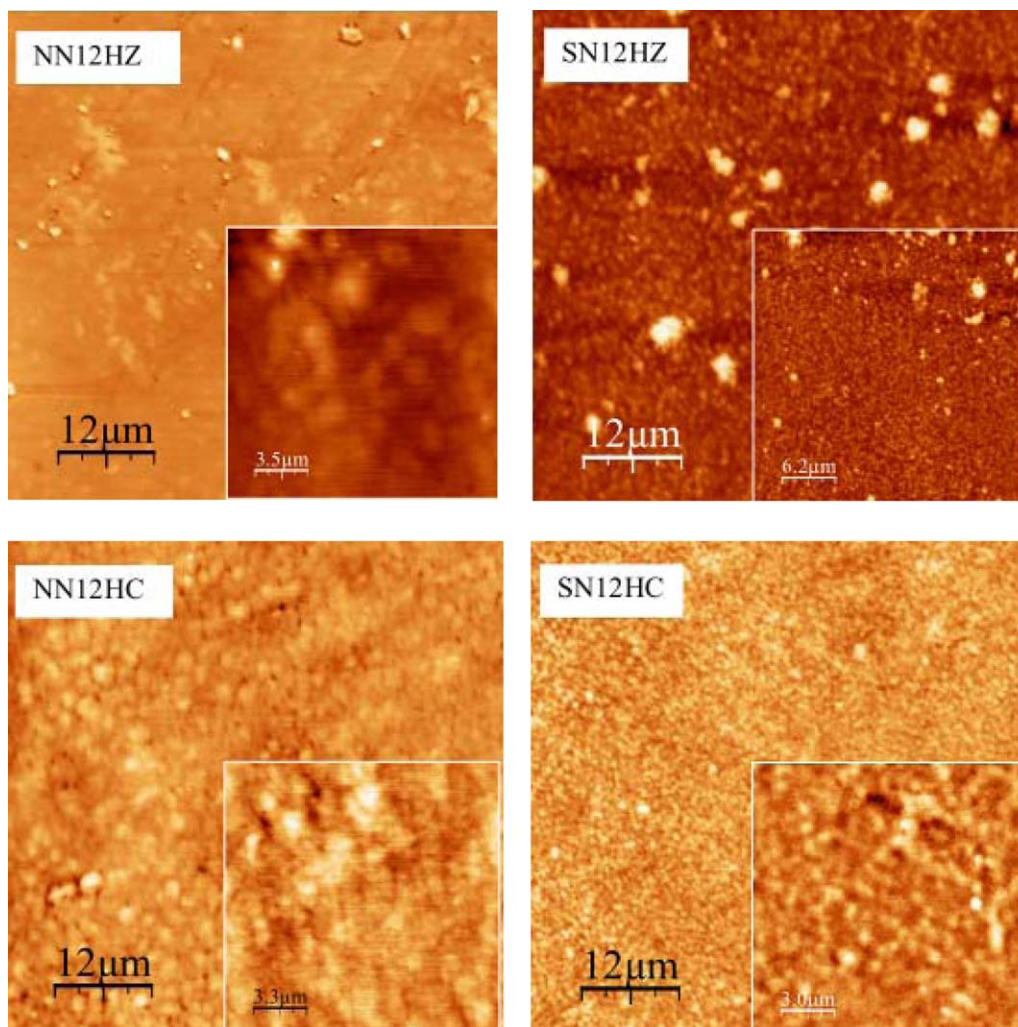


Figure 15. AFM pictures of NBR and SBR vulcanizates containing hybrid filler HZ or HC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

noticeable only when compared with distilled water on the background of white paper.

The results of particle size measurements distinctly show that unmodified halloysite is characterized by the smallest size from among the samples tested. The hybrid fillers HZ and HC synthesized show a considerably smaller particle size than that of the physical mixtures of appropriate phthalocyanine with halloysite. This probably results from a more regular arrangement of pigment particles, first of all, on the surface of HNTs in relation to the loosely placed particles of appropriate phthalocyanines in their physical mixtures with aluminosilicate. The lower particle size of hybrid HZ compared to that of HC is connected with both the lower quantity of pigment deposited on the surface of HNTs and its more uniform distribution directly on the surface of HNTs.

Surface Morphology of NBR and SBR Rubber Vulcanizates

From the pictures taken by the AFM technique, it follows that on the surface of vulcanizates of both NBR and SBR containing halloysite, there are visible aluminosilicate aggregates and

agglomerates of significant dimensions (Figure 13). The addition of the pigment decisively improves the dispersion of HNTs in the polymer matrix. Based on the test results, one may conclude that zinc phthalocyanine facilitates the homogeneous dispersion of particular components of elastomeric blend in the polymer matrix (Figure 14), while chloroaluminum phthalocyanine causes that the vulcanizates containing it are characterized by a surface of balanced softness, on which single particles of the blend composite particles are visible under a higher enlargement (Figure 15).

The rubber composites tested, containing hybrid fillers, are characterized by a better dispersion of components, and the dispersed particles of hybrid fillers are decisively smaller than those in the vulcanizates containing halloysite or the physical mixture of halloysite and the pigment (Figure 15).

Based on the AFM observations made, it should be stated that the hybrid nanofillers HZ or HC in the elastomer matrix do not show any tendency to agglomeration, and so one may stress that it is beneficial to incorporate zinc or CP modified with

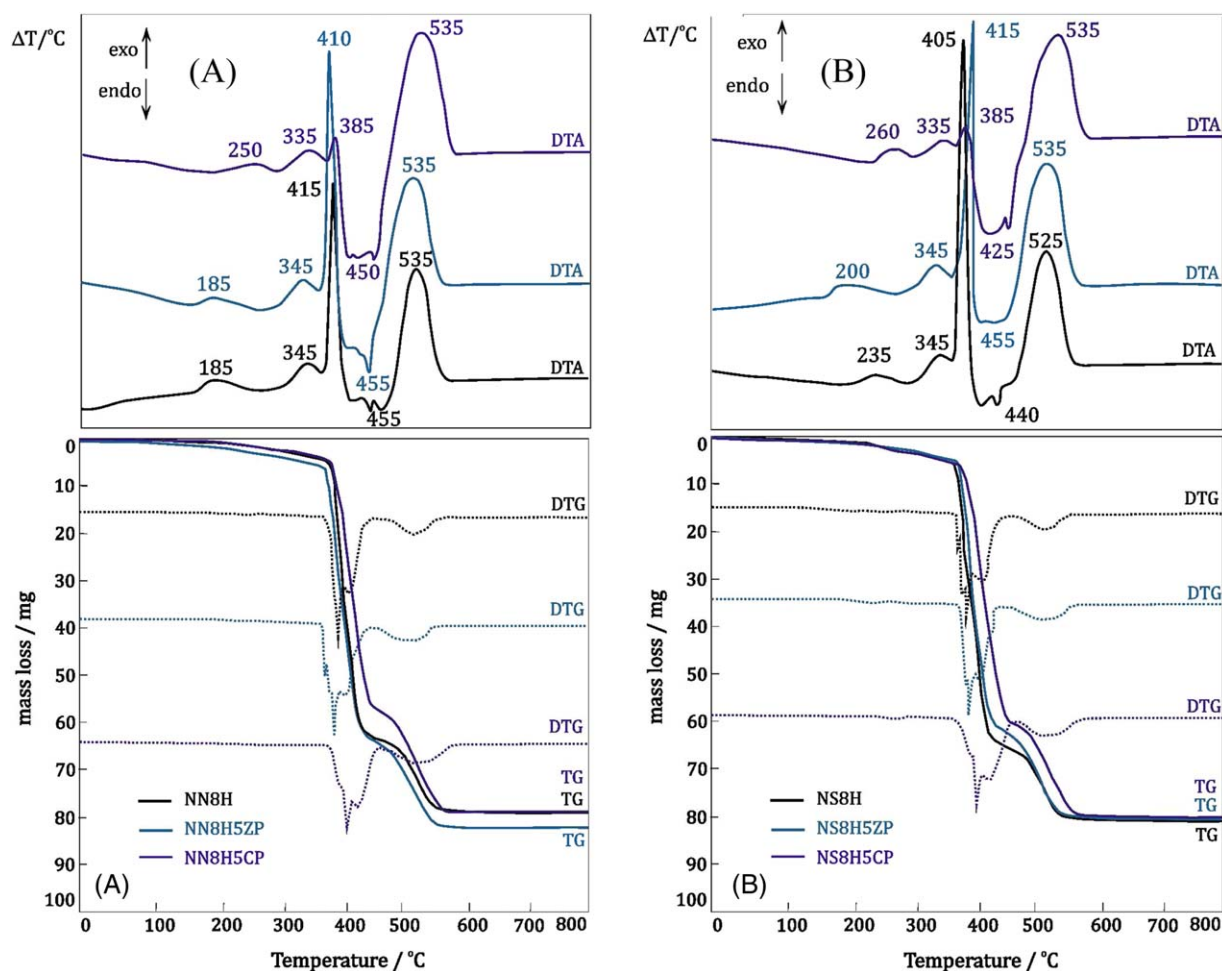


Figure 16. DTA, TG, and DTG curves composites containing halloysite or its mixture with pigment ZP or CP: (A) NBR rubber and (B) SBR rubber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

halloysite to rubber blend instead of using these components separately.

Thermal Analysis

Air Atmosphere. The results of thermal analysis obtained by the method of derivatography show that the phthalocyanine pigment (ZP or CP) obtained as well as hybrid fillers (HZ or HC), especially in the case of SBR rubber, cause a distinct shift of the thermal cross-linking temperature of containing them vulcanizate, toward higher values, in relation to composites filled only with halloysite (Tables III and IV).

From the analysis of the results obtained, it follows that the process of intensive thermal decomposition of the composite investigated, containing halloysite and ZP or CP pigment, begins with a great exothermic signal recorded in DTA curves at $\Delta T = 400\text{--}415^\circ\text{C}$ [Figure 16 (A, B)]. In the case of composites containing HZ or HC hybrid fillers, this signal corresponding to the thermo-oxidative processes is decisively lower [Figure 17(A, B)]. The presence of coloring agents (ZP, CP, HZ, and HC) in the composites does not significantly affect the beginning temperature of their thermal decomposition (Tables III and IV).

It should be, however, underlined that hybrid fillers cause a distinct decrease in the thermal decomposition rate, dm/dt , of containing them composites, especially nitrile rubber compared to vulcanizate only filled with halloysite (NN8H, NS8H) (Table III).

Hybrid fillers do not significantly increase the residue after thermal decomposition, P_w , of NBR and SBR rubber.

Atmosphere of Inert Gas. The presence of coloring agents, both the phthalocyanine pigments (ZP or CP) and hybrid fillers (HZ or HC), does not change the character of thermal transformations of NBR rubber composites recorded in DSC curves [Figure 18(A, B)].

In the DSC curves of SBR rubber composites containing halloysite or its mixture with zinc or chloroaluminum phthalocyanine, there is noticeable an additional transformation at $\Delta T = 80\text{--}170^\circ\text{C}$. This transformation, whose enthalpy amounts to $\Delta H_{\text{NS8H}} = 53$ J/g, $\Delta H_{\text{NS8H5FZ}} = 134$ J/g, $\Delta H_{\text{NS8H5FC}} = 78$ J/g, respectively, is connected with the elastomer cross-linking processes at elevated temperature [Figure 19(A, B)].

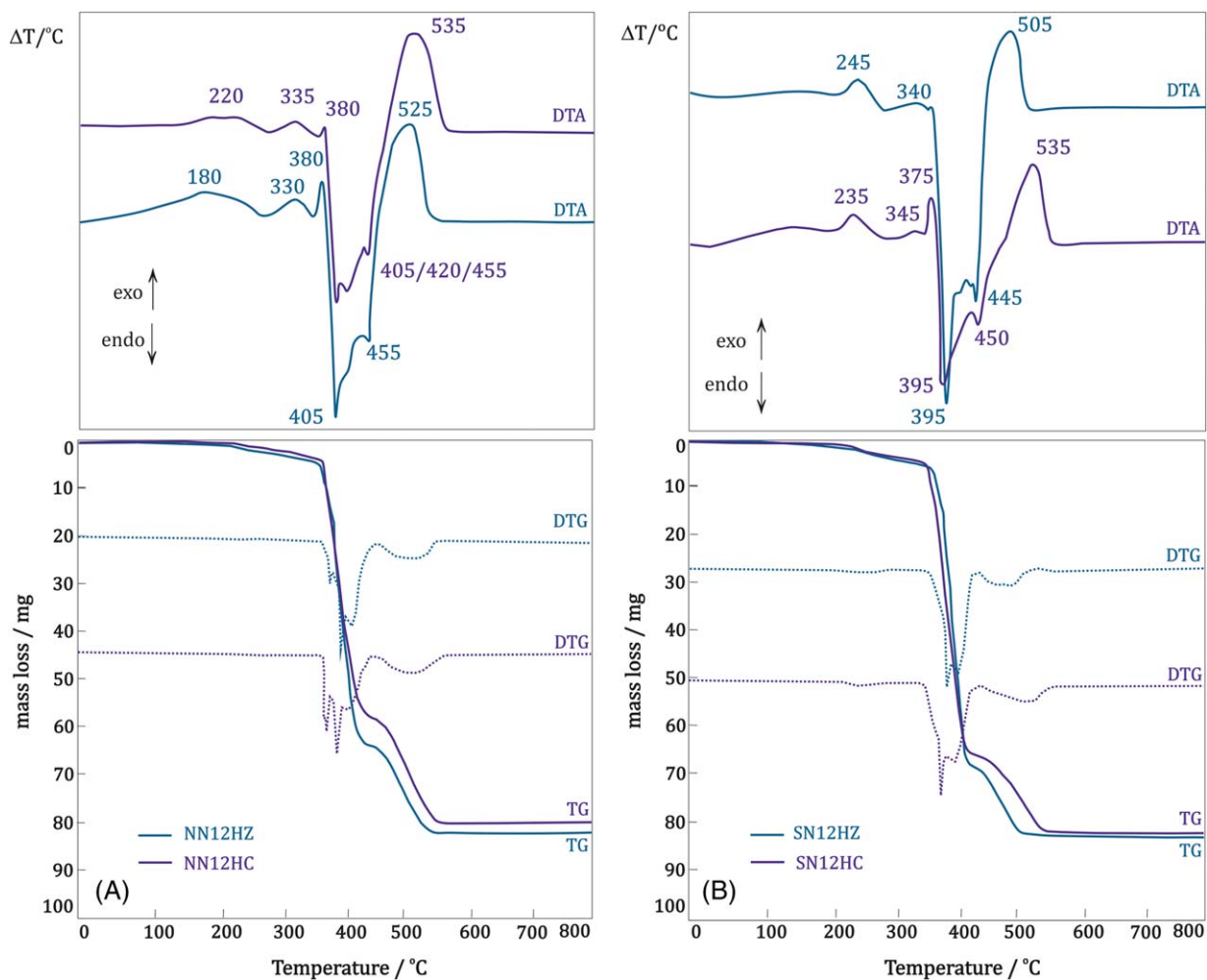


Figure 17. DTA, TG, and DTG curves composites containing hybrid fillers HZ or HC: (A) NBR rubber and (B) SBR rubber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

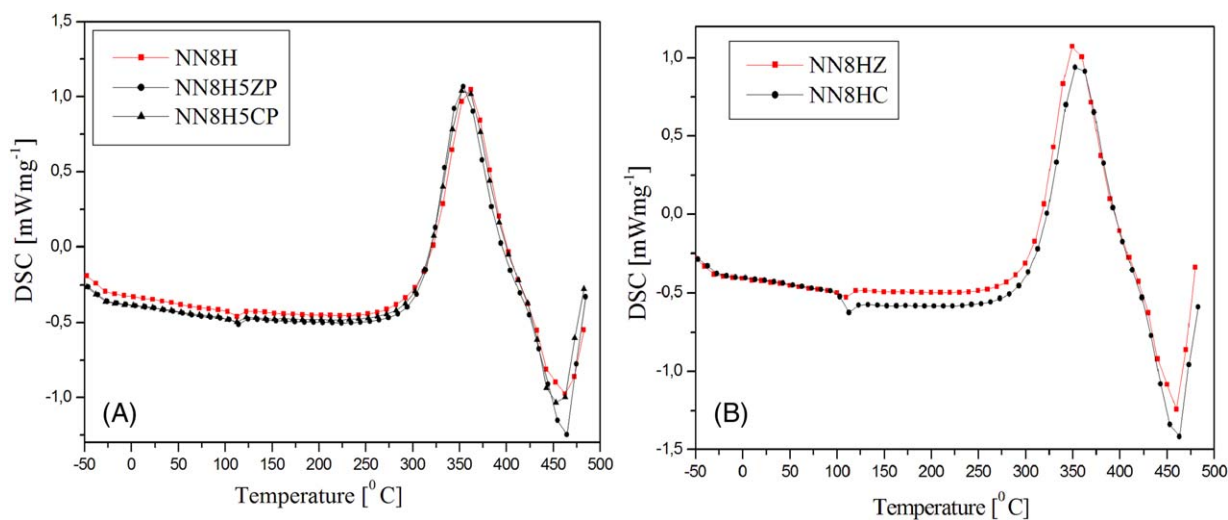


Figure 18. DSC curves vulcanizates of NBR rubber (A) containing halloysite or its mixture with ZP or CP (B) containing hybrid filler HZ or HC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

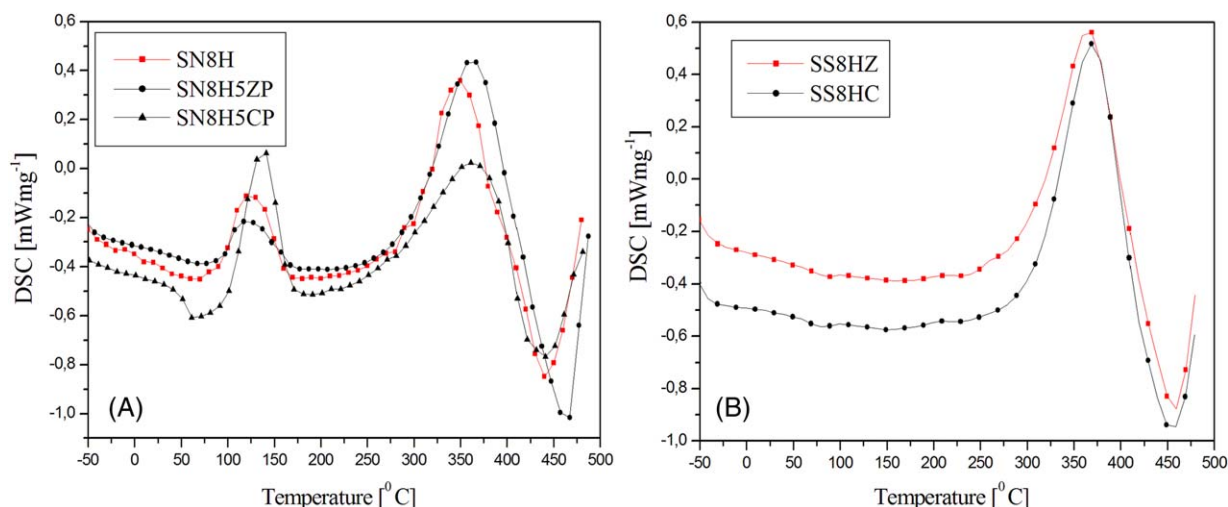


Figure 19. DSC curves vulcanizates of SBR rubber (A) containing halloysite or its mixture with ZP or CP and (B) containing hybrid filler HZ or HC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of phthalocyanine pigments (ZP and CP) and hybrid fillers (HZ and HC) on the glass transition temperature, T_g , of the composites investigated depends on both the rubber macromolecule structure and the spatial network structure of vulcanizates containing these fillers (Tables V and VI).

Phthalocyanine pigments do not affect the value of T_g of cross-linked NBR rubber (Table V), while under the influence of CP there occurs a significant decrease in the glass transition temperature of SBR rubber vulcanizate (Table VI). Hybrid filler (HZ) decrease the glass transition temperature of NBR rubber cross-linked with organic peroxide, while in the case of sulfur vulcanizates of this rubber, hybrid fillers increase its value (Table V). The increase in glass transition temperature under the influence of hybrid fillers is observed, especially in the case of sulfur vulcanizates of SBR rubber (Table VI). The glass transition temperatures of colored sulfur SBR composites are distinctly higher compared with that of reference sample: SS8H. Thus, one may assume that the presence of crosswise sulfide bonds facilitates the mutual interactions of SBR macromolecules with filler and pigment, also in the hybrid form, which reduces their segmental mobility (Table VI).

Flammability of Colored Composites of NBR and SBR Rubbers

During combustion under air of the colored composites of both NBR and SBR rubber, containing physical mixture of ZP or CP pigments with halloysite or hybrid filler (HZ or HC), noticeably less smoke is formed compared to reference samples. Peroxide composites of the rubbers tested burn with releasing small amounts of liquid destruction products, while sulfur composites do not show any tendency to their formation.

The flammability test results lead to a conclusion that the hybrid fillers incorporated into NBR and SBR vulcanizates significantly reduce their flammability determined with the value of OI. The highest value of OI is shown by composites containing 12 parts by weight of hybrid filler HZ (NN12HZ) and 12

parts by weight of hybrid filler HC (SN12HC) (Tables VII and VIII).

The colored elastomeric composites with higher OI show prolonged combustion under air or shortened self-extinguishing time. Substantial majority of colored composites of the rubber tested undergo self-extinguishing under air, leaving 42–93% of the unburned measurement section length.

The reduction in the flammability of elastomeric composites containing the hybrid filler compared to that of unfilled samples results from, among other things, the channeling effect connected with the presence of HNTs in the polymer matrix. Halloysite, as most aluminosilicates, is impermeable for vapors and gases, thus under the conditions of composite combustion, low-molecular products of the thermal decomposition of elastomer can diffuse outside only through accurately specified spaces between dispersed HNTs.^{22–26}

Based on the analysis of SEM pictures, one should conclude that phthalocyanine pigments were combined only with the external surface of HNTs. In that case, a portion of liquid decomposition products can be immobilized inside the cylindrical structures of halloysite. In this connection, there has been significantly decreased transport rate of volatile, including flammable destruction products to the flame zone. The contribution of cavitation and carbonization processes is also increased in the solid phase of the sample under combustion.

It should also be remembered that HNTs at $\Delta T = 35\text{--}440\text{ C}$ undergo dehydration and dehydroxylation processes changing into amorphous halloysite (a material structurally similar to kaolin), while water vapor dilutes the gaseous thermal decomposition products of the burning composite.^{27–29}

From the thermal analysis results, it follows that phthalocyanine pigments combined with the halloysite surface clearly reduce the processes of its dehydration and dehydroxylation $\Delta T = 130\text{--}150\text{ }^\circ\text{C}$. In the case of pure halloysite, dehydration proceeds with a high efficiency already at a temperature of about $130\text{ }^\circ\text{C}$, while

dehydroxylation at $\Delta T = 130\text{--}440^\circ\text{C}$. Hybrid fillers undergo dehydration processes to a small extent at $\Delta T = 35\text{--}350^\circ\text{C}$ as confirmed by a small and very slow mass loss of HZ and HC samples compared to pure HNTs. These reactions proceed with a high yield only after exceeding $T = 400^\circ\text{C}$, i.e., the decomposition temperature of phthalocyanine pigments.

The shift of the dehydration and dehydroxylation of halloysite in hybrid fillers to higher temperatures results in an increase in the ignition temperature of the composites containing these fillers. Apart from that, the formation of a small quantity of HCl from the decomposition of hybrid HC facilitates the inhibition of strongly exothermic radical reactions proceeding in gas phase.

Phthalocyanine pigments (ZP and CP) as well as hybrid fillers (HZ and HC) ambiguously influence the fire hazard of the rubbers investigated, expressed with HRR_{MAX} , THR, or HRC (Tables IX and X).

A lower value of HRR_{MAX} was found especially in the case of NBR rubber cross-linked with sulfur, containing HC nanofiller. However, it should be noticed that the colored NBR composites, containing hybrid filler (HZ or HC) are characterized by an increase in heat capacity compared to untreated (uncolored) samples, which undoubtedly facilitates their self-extinguishing processes.

It is also noteworthy that OC during the combustion of peroxide vulcanizates of BR rubber decreases under the influence of both phthalocyanine pigments and hybrid fillers (Tables IX and X).

Mechanical Properties

The use of phthalocyanine pigments (ZP and CP) to color NBR and SBR rubber blends filled with halloysite results in an improvement in mechanical properties of the colored composites obtained, regardless of the elastomer spatial network structure.

NBR and SBR rubber composites containing hybrid fillers (HZ or HC) show considerable better mechanical properties than those of their equivalents containing phthalocyanine (ZP or CP) and halloysite.

In most cases, the composites containing hybrid fillers (HZ or HC) are characterized by a higher resistance to thermo-oxidative ageing processes compared to that of vulcanizates containing the physical mixture of halloysite and the pigment (ZP or CP) (Tables XI and XII).

SUMMARY

Based on the analysis of the test results obtained, it has been found that regardless of the spatial network structure of NBR and SBR rubbers, the incorporation of hybrid fillers into the matrix of the elastomers investigated results in an improvement in their thermal and mechanical properties as well as a significant reduction in flammability.

The hybrid fillers (HZ and HC) synthesized have a considerably smaller particle size than that of the physical mixtures of appropriate phthalocyanine and halloysite. This is probably due to the more regular arrangement of the pigment particles, first of

all, on the surface of HNTs compared to the loosely distributed particles of appropriate phthalocyanine in their physical mixtures with the aluminosilicate.

The increase in the parameters of thermal stability or resistance to thermo-oxidative aging, and especially reduction in flammability of the vulcanizates containing hybrid filler (HZ or HC) results not only from the smaller size of HZ and HC in relation to the particles of phthalocyanine particles, but first of all from the much better dispersion of HZ and HC in the elastomeric matrix compared to the mixture of halloysite and appropriate phthalocyanine pigment (ZP or CP).

Phthalocyanine pigments (ZP and CP) as well as hybrid fillers (HZ and HC) ambiguously influence the fire hazard of the rubber tested, expressed with the maximal heat release rate, HRR_{MAX} , total heat released, THR, or heat release capacity, HRC. Nevertheless, the colored composites of NBR rubber, containing hybrid filler (HZ or HC), are characterized by an increase in heat capacity compared to uncolored samples, which undoubtedly facilitates the processes of self-extinguishing.

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