Stability of Electrical Properties of Carbon Black-Filled Rubbers

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ABSTRACT: Conducting composites were prepared by melt mixing of ethylene–propylene–diene terpolymer (EPDM) or styrene-butadiene rubber (SBR) and 35 wt % of carbon black (CB). Stability of electrical properties of rubber/CB composites during cyclic thermal treatment was examined and electrical conductivity was measured *in situ*. Significant increase of the conductivity was observed already after the first heating–cooling cycle to 85°C for both composites. The increase of conductivity of EPDM/35% CB and SBR/35% CB composites continued when cyclic heating-cooling was extended to 105°C and 125°C. This effect can be explained by reorganization of conducting paths during the thermal treatment to the more conducting network. EPDM/35% CB and SBR/35% CB composites exhibited very good stability of electrical conductivity during storage at ambient conditions. The electrical conductivity of fresh prepared EPDM/35% CB composite was 1.7×10^{-2} S cm^{-1}, and slightly lower conductivity value 1.1×10^{-2} S cm^{-1} was measured for SBR/35% CB. The values did not significantly change after three years storage. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2918–2924, 2009

Key words: ethylene–propylene–diene terpolymer; styrene-butadiene rubber; carbon black; mechanical and electrical properties; conductive polymer composites

INTRODUCTION

Flexible conductive composites have attracted attention in recent years because of the explosive growth in the utilization of electrical and electronic devices in industrial and commercial applications as self-temperature-control plane heaters,[1] pH sensors,[2] chemical sensors[3] or electrochemical sensors.[4] Conductive polymer composites are increasingly used as EMI shielding materials because their low density, low cost, designs flexibility, corrosion resistance and more versatile electric properties.

Electrically conductive polymeric composites are usually prepared by mixing of an insulating polymer matrix with appropriate type and amount of conductive filler. Fillers can be present in various forms of particles, flakes or fibers. The group of common conductive additives includes conductive carbon black,[5,6] modified carbon black,[7,8] graphite[9] and graphite fibers,[10,11] metal particles, metal powders,[12] conducting polymers,[13–17] and recently carbon nanotubes.[18,19] The most important property of conductive composites for application is stability of electrical properties. Changes in electrical conductivity during storing depend on structure of composite, weather, exposure to light and temperature.[20] In our previous papers,[7,8] the stability of electrical conductivity was investigated also for conductive composites consisted on semicrystalline polyethylene matrix and carbon black Vulcan® XC-72R, and carbon black modified with polypyrrole or polyaniline. A significant increase of conductivity was found in composites during cyclic thermal treatment in the broad temperature range below melting temperature of polyethylene matrix. The increase of conductivity during slow cooling was explained by re-organization process in the nonconductive polyethylene matrix.[7] The thermal ageing during heating above the melting point of polymer matrix resulted in a decrease of conductivity of polyethylene-carbon black composites, but an increase of conductivity was observed in composites containing carbon black modified by polypyrrole and polyaniline. The modified fillers create thermally resistant conducting network in polyethylene matrix.[7]

Sau et al.[20] studied the effect of temperature on the resistivity of conducting polymer composites of

EPDM, NBR and their 50/50 blends filled with carbon black (Vulcan XC-72). The influence of temperature on the electrical resistance during heating–cooling cycle was investigated. It was found that heating of conducting composite to 120°C caused a decrease of the electrical resistance, what is known as negative temperature coefficient (NTC) effect. Continual decrease of resistance during following cooling of the system to the room temperature was observed. The dependence of resistivity during the heating–cooling cycle does not follow the same path.[20] This creates an "electrical set" (difference in initial and final resistivity before and after cycles) and the "electrical hysteresis." After second heating–cooling cycle of the system "electrical set" was reduced.[20] He at al.[21] studied thermal ageing in composites prepared from either amorphous EPDM containing 55 mol % of ethylene or semicrystalline EPDM (high ethylene content 81 mol %), filled with CSF carbon black with particles diameter about 70 nm. During rising temperature practically only NTC effect in amorphous EPDM/CB composite was exhibited (resistivity decreases with temperature). In semicrystalline EPDM/CB composite with carbon black content slightly below the percolation threshold, the sample exhibits only a NTC.[21] Composites with amount of carbon black above the percolation threshold exhibited positive temperature behavior (PTC) followed by NTC with increasing of temperature.

Motivation for this study is investigation of the stability of electrical conductivity during cyclic thermal treatment of rubber/carbon black composites formed by two kinds of rubber matrices. The same amount of carbon black 35 wt %, which is above the percolation threshold, was used for preparation of conducting composites. In the first step, we studied stability of electrical properties during cyclic thermal treatment of two different rubbers filled with 35 wt % carbon black. In addition, thermogravimetric analysis was used for comparison of thermo-oxidation stability of rubber matrices and composites before and after thermal ageing. Conducting rubber composites showed also good elongation ability. Coupling of these two properties of rubber/carbon black composites induce a potential for creation of an interesting material that can be used in many applications.

EXPERIMENTAL

Materials

Ethylene–propylene–diene terpolymer (EPDM, Keltan 4703, DSM Elastomers), Mooney viscosity, ML (1 + 4) at 125°C is 65 contains 48% of ethylene and 9% of 5-ethyliden norbonen (ENB), without oil. Styrene-butadiene rubber (SBR, SKS 30, KAUČUK Kralupy a. s., Czech Republic), ML (1 + 4) at 100°C is 47–56

contains 0.6% of ash and 22.5–24.5% of bound styrene. Carbon black (Vulcan XC-72R, Cabot Corp.) with 40 S cm^{-1} of conductivity and density 1.8 g cm^{-1} was used as conducting filler. The composition of additive system (vulcanization components and antioxidant Irganox 1010) is shown in Table I.

Composites preparation

Composites were prepared by melt mixing of EPDM or SBR rubber with carbon black in a 50 mL mixing chamber of Plasti-Corder kneading machine PLE 330 (Brabender, Germany) at 70°C for 20 min at 35 rpm. The same amount of carbon black (35 wt %) was used for both types of samples. During mixing of rubber and carbon black, the other ingredients were added according to Table I. Sulfur as vulcanization reagent was added in the separate step on roll mill at ambient conditions.

EXPERIMENTAL TECHNIQUES

Testing specimens were prepared by compression molding in laboratory press (Fontijne Holland TP 50) at 145°C for 30 min under 30 MPa followed by cooling between two metallic plates to the ambient conditions.

Thermogravimetric analysis (TGA) was performed in the air flow (50 mL min^{-1}) at a heating rate 10°C min^{-1} to 750°C, using Perkin-Elmer TGA 7 Thermogravimetric Analyzer.

Volume electrical conductivity was measured by the four-point van der Pauw method. Experimental setup included the current source Keithley 238, the scanner Keithley 706 with the matrix cards and the Solartron-Schlumberger 7081 precision voltmeter. The sample holder was placed in the thermostat chamber Heraeus-Vötsch VMT 07/35. A measurement of electrical conductivity contains five temperature runs. One temperature run consists of four heating-cooling cycles. One heating-cooling cycle

TABLE I
Rubber Compounds

Ingredients	Loading (phr)
Rubber[a]	100
Vulcan® XC-72 R	53.85
Sulphenax CBS[b]	1.5
Zinc oxide	3
Stearic acid	1
Irganox 1010[c]	1
Sulphur	1.5

[a] EPDM (ethylene-propylene; diene terpolymer) or SBR (styrene-butadiene rubber).
[b] N-cyclohexyl-2-benztiazolsulphenamid—CBS.
[c] Pentaerytritol-tetra-β-(3,5-di-t-buthyl-4-hydroxy-phenyl)-propionate.

means the heating up from 16°C to the peak temperature (85, 105, 125, 145, or 165°C) followed by cooling down back to 16°C. The temperature step was 5°C and takes 15 min. Both, the temperature and time scale of the experiment were controlled by the computer. Relative parameter of conductivity changes (%) were calculated according to equation:

$$Relative\ parameter\ (\%) = \frac{B - A}{A} \times 100 \qquad (1)$$

where A is conductivity in the first heating of the first run at 60°C and B is conductivity in the last cooling of thermal treatment at 60°C [see Fig. 3b].

Interactions between uncured polymer matrix and conducting filler were estimated by the extraction of composites in cold toluene. The amount of bound polymer (wt. %) was calculated as a mass ratio of dry and original samples after 28 days of extraction.

Equilibrium swelling determined the concentration of elastic active chains of network in vulcanized samples. Samples were used as 0.5 g plates wrapped into glassy textile and they were swelled in cold toluene for 15, 30, 60 min then 4, 8, and 24 h. At the end of swelling, samples were weighed out consecutively dried in heating chamber. The degree of swelling in EPDM and SBR matrices and in rubber composites was calculated as rate of weigh of swelled and dried sample. Concentration of network was calculated by Flory equation from experimental values of degree of swelling.

$$v_e = -\frac{1}{V_1} \frac{\ln(1 - \varphi_2) + \varphi_2 + \chi\varphi_2^2}{\varphi_0^{2/3}\varphi_2^{1/3} - \frac{\varphi_2}{2}} \qquad (2)$$

where v_e [mol m^{-3}] is concentration of active elastic chains of network, φ_2—volume fraction of gel in gel–solvent compound at equilibrium swelling, φ_0—volume fraction of polymer at swelling, V_1 [m^3 mol^{-1}] is molar volume of solvent and $\chi = 0,4$, is parameter of interactions between rubber and toluene.

Testing instrument INSTRON 4301 (UK) was used for measuring of mechanical properties of samples. Testing specimens were tested with the deformation speed, 10 mm min^{-1} and the grip distance was 40 mm by surrounding temperature. There were measured elongation at break and Young's modulus.

RESULTS AND DISCUSSION

Two composites from EPDM or SBR rubbers, both filled with 35 wt % (53.85 phr) carbon black were investigated. From the large variety of carbon blacks, we selected Vulcan XC-72R from Cabot Corp., because of its very good electrical conductivity. This type of carbon black is recommended for using as filler for producing antistatic materials.[22] Composites investigated in this study have electrical conductivity

typical for semiconductors because filler content is above percolation threshold and there is a change of electron transfer mechanism from tunneling effect to direct contact between filler aggregates. Conductivity of EPDM/CB composite is 1.7×10^{-2} S cm^{-1} while slightly lower conductivity, 1.1×10^{-2} S cm^{-1} was measured for SBR/CB composite.

Generally, polymers are sensitive to the temperature especially in a presence of oxygen. Thermo-oxidation stability of rubber matrices and rubber/carbon black composites was tested by thermogravimetric analysis (TGA) in air. From derivation of obtained curves, temperatures of maximum decomposition (T_{max}) were determined for all studied materials. Derivative of thermogravimetric (DTG) curves of untreated EPDM matrix, EPDM/CB composite, SBR matrix and SBR/CB composite are shown in Figure 1. The curves in Figure 1(a) reveal that thermo-oxidative degradation of EPDM rubber in air is one-step
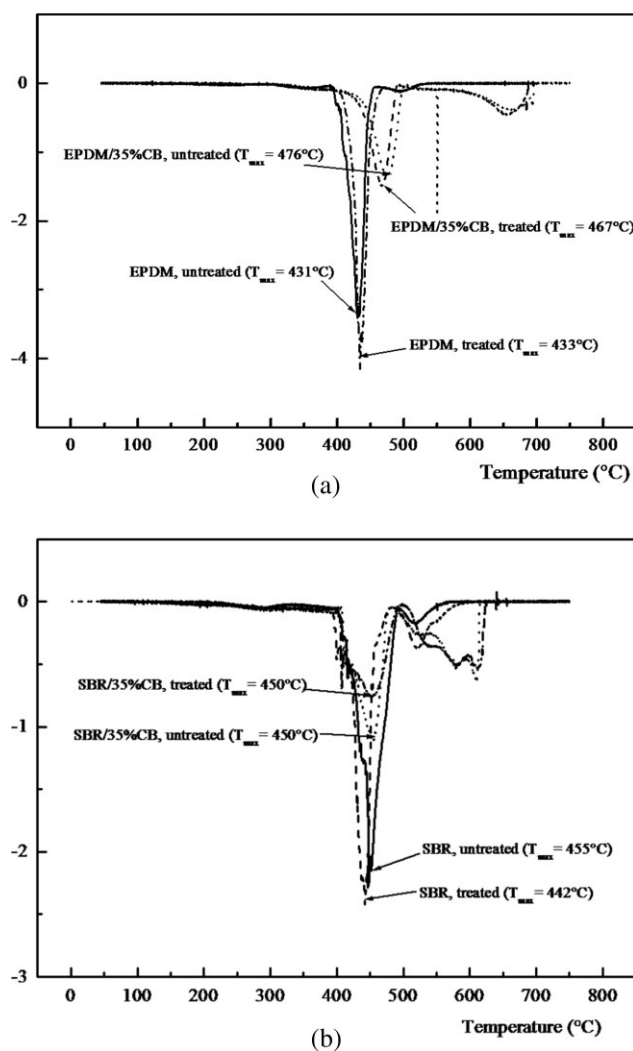

(a)

(b)

Figure 1 Derivative of thermogravimetric curves of EPDM rubber, EPDM/35% CB composite (a), SBR rubber and SBR/35% CB composite (b), untreated and thermally treated at 130°C during 9 days in thermostatic chamber.
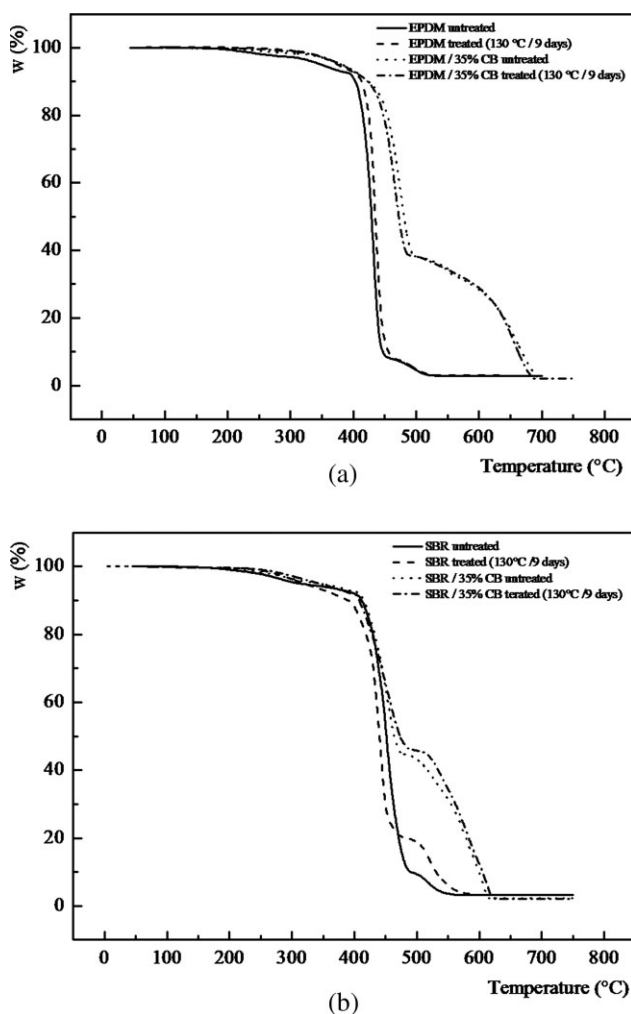
Figure 2 Thermogravimetric curves of EPDM, EPDM/35% CB (a), SBR, and SBR/35% CB (b), untreated and thermally treated at 130°C during 9 days.

decomposition process. The temperatures of maximum decomposition is located at 431°C corresponds to the thermal degradation of untreated EPDM matrix [Fig. 1(a)]. Addition of carbon black to EPDM matrix shifted first step temperature of maximum decomposition by around 40°C higher. The second step,

located around 650°C [Fig. 1(a)], corresponds to the oxidation of carbon black into CO_2 and its evaporation from the composite.[23] This was confirmed by loss of samples weight below the values corresponding to the filler content as seen from TGA curves (Fig. 2). Different results were obtained by thermogravimetric analysis of untreated SBR matrix and SBR-based carbon black composite [Fig. 1(b)]. In Figure 1b, it can be seen that addition of the filler into SBR matrix did not influence the change of the maximum decomposition temperature being 455°C for untreated SBR matrix. The overall weight loss is smaller than 100% for every sample, because they contain vulcanization components, as zinc oxide, sulfur, etc. (Table I) which are stable compounds remaining as residue after heating up to 750°C.

Table II summarized the values of mechanical properties, Young's modulus and elongation at break, for both rubber matrices and for rubber/carbon black composites before and after thermal treatment. The thermal treatment of composites in thermostatic chamber was used as an imitation of thermal treatment of the sample during testing stability of electrical conductivity of filled rubbers. Thermal treatment was performed in the thermostatic chamber at constant temperature 130°C for 9 days which corresponds to the time similar to the experiment of testing stability of electrical conductivity during cyclic thermal treatment (see text below and Figs. 3 and 4). After 9 days treatment steady temperature decrease was applied being 5°C in 15 min. 130°C was chosen for thermal treatment because during cyclic heating-cooling testing the stability of electrical conductivity at this temperature conductivity still increased. From Table II it can be seen that elongation at break for all samples rapidly decreased and Young's modulus increased what was resulted by additional crosslinking of the rubber matrices after thermal treatment. This was confirmed by degree of crosslinking (Table II). Degree of crosslinking is expressed by the concentration of elastic active chains in network in vulcanized samples, ν_e and it was calculated according the

TABLE II
Mechanical Properties and Degree of Crosslinking for Rubber Matrices and Composites Containing 35 wt % CB Before and After Thermal 9 Days Treatment at 130°C

Sample	Fresh sample				Thermally treated sample			
	Elongation at break (%)	Young's modulus (MPa)	$\varphi_2{}^a$	$\nu_e{}^b$ (mol m^{-3})	Elongation at break (%)	Young's modulus (MPa)	$\varphi_2{}^a$	$\nu_e{}^a$ (mol m^{-3})
EPDM	326	17	0.11	40	81	31	0.33	480
SBR	673	9	0.14	60	97	64	0.50	1600
EPDM/35%CB	433	18	0.28	460	166	30	0.53	3100
SBR/35%CB	441	14	0.28	460	87	42	0.70	8600

[a] φ_2 is volume fraction of gel in gel–solvent compound at equilibrium swelling.
[b] (ν_e) is concentration of elastic active chains of network in vulcanized samples which was calculated from experimental results of degree of crosslinking according to eq. (2).
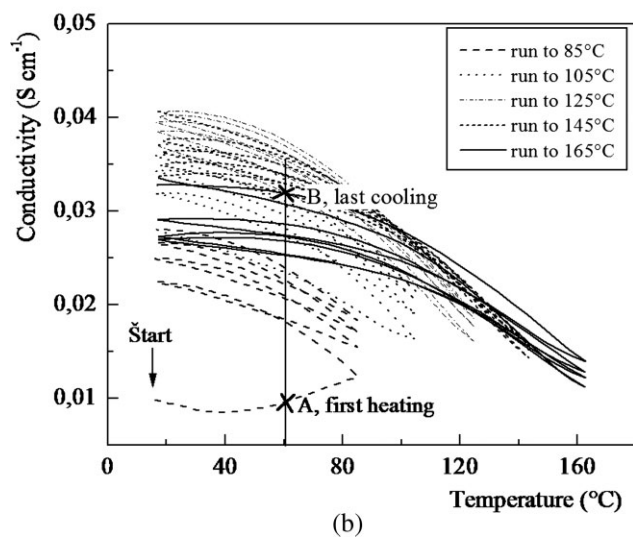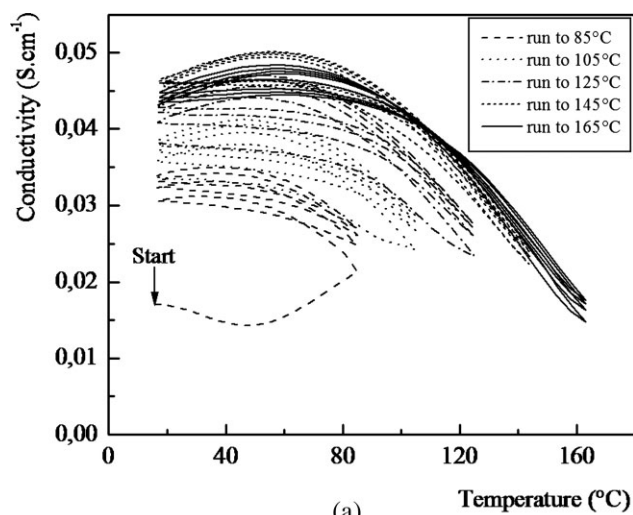
Figure 3 Temperature dependence of the conductivity during cycling heating cooling procedure of original EPDM/35% CB (a), and SBR/35% CB (b) composites.

eq. (2). The increase of ν_e values was found for both types of studied composites after thermal treatment.

Stability of electrical properties is important for using of such materials in practical application. Stability of electrical properties of both EPDM/CB and SBR/CB composites was tested during cyclic thermal treatment (Fig. 3). Measurement of electrical conductivity consists of five temperature runs. One temperature run means four heating–cooling cycles. In the first cycle of the first run to 85°C, slight decrease of conductivity (positive temperature coefficient—PTC) was observed in temperature interval from 16 to $\sim$ 45°C, followed by an increase of conductivity (negative temperature coefficient-NTC) in both types of composites. NTC effect means the increase of conductivity (or decrease of resistivity) with rising temperature due to reorganization of aggregates and/or agglomerates of carbon blacks during thermal treat-

ment of rubber matrix and is typical for amorphous polymers.[20] PTC is just opposite effect. Further heating–cooling cycles resulted in an increase of conductivity of tested composites. Similar trend was observed for composite consisted of another type of EPDM filled with Vulcan XC-72,[20,21] but the authors studied behavior of composites only in two cycles to 120°C. Following increase of temperature to 85°C in our composites induced the increase of conductivity in both EPDM/CB and SBR/CB composites. After first run to 85°C original conductivity (measured at 16°C) of EPDM/CB composite increased from 1.7×10^{-2} S cm^{-1} to 3.4×10^{-2} S cm^{-1} [Fig. 3(a)] and conductivity of SBR/CB composite increased from 1.1×10^{-2} S cm^{-1} to 3.0×10^{-2} S cm^{-1} [Fig. 3(b)]. During next two runs up to either 105°C or 125°C less pronounced increase of conductivity for both types of composites was observed. Table III shows the comparison of relative parameter of conductivity changes,
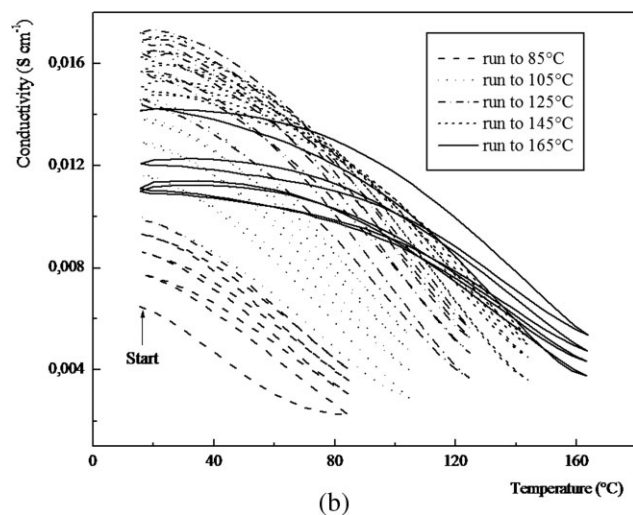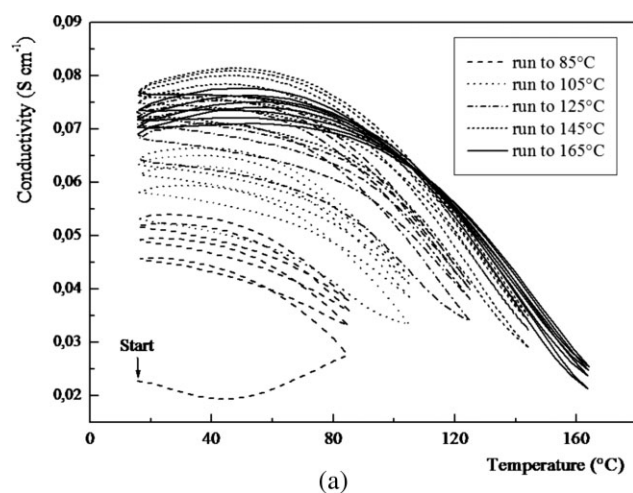

Figure 4 Temperature dependence of the conductivity during cycling heating cooling procedure of EPDM/35% CB (a), and SBR/35% CB composites (b) 3 years stored at ambient conditions.

TABLE III
Relative Parameter of Conductivity Changes (%)
Calculated According to the eq. (1), Before and After
Thermal Treatment at 130∘C During 9 Days for EPDM
Filled With 35 wt % Carbon Black and SBR Filled With
35 wt % Carbon Black Composites

	Relative parameter of conductivity changes (%)			
	EPDM/35% CB		SBR/35% CB	
	Fresh sample	Stored sample	Fresh sample	Stored sample
After 1st run to 85°C	115	131	140	109
After 2nd run to 105°C	161	202	231	264
After 3rd run to 125°C	202	253	267	371
After 4th run to 145°C	223	277	219	342
After 5th run to 165°C	205	249	207	338

before and after thermal treatment of studied composites, calculated according to eq. (1) at 60°C. After first run to 85°C, higher values of relative parameter was observed for SBR/CB compared to EPDM/CB composites for fresh prepared materials (Table III). Important increase of relative parameter in the next three runs to 105, 125, and 145°C for EPDM/CB composite was found. Similar increase of relative parameter was calculated for SBR/CB composite in the second and third temperature runs. After third temperature run, an increase of relative parameter of conductivity changes was calculated to be 267% representing the highest observed value in all experiment for fresh SBR/CB composite. Following growth of temperature to 145°C resulted in the decrease of relative parameter to 219% after fourth temperature run. After the last temperature run to 165°C, decrease of relative parameter of conductivity changes to around 205% was calculated for both types of composites (Table III). However, as a result of completed cyclic process, conductivity of EPDM/CB composite after testing process increased from 1.7×10^{-2} S cm^{-1} to 4.7×10^{-2} S cm^{-1}. The same effect was observed for SBR/CB composite in the end of the cyclic thermal treatment, when conductivity increase from 1.1×10^{-2} S cm^{-1} to 3.3×10^{-2} S cm^{-1} was measured (Table IV).

At the beginning of testing the stability of electrical conductivity, in the first cycle from 16 to 85°C, the decrease of conductivity in the first heating cycle approximately up to 40°C was observed because of expanse of rubber matrix[24] and enlarging of distances between carbon blacks aggregates. This effect was also investigated on the silicone rubber filled with 20 phr of Vulcan VXC-72 carbon black.[25] Authors declared the high degree of crosslinking eliminates the NTC effect and increase the size of the PTC anomaly.[25] Following increase of temperature to 85°C leads to a thermal initiation of rearrangement of conducting paths and improving mobility of carbon black aggre-

gates thereby conductivity increased. During cooling process of conducting compounds to 16°C gradual increase of conductivity was found caused by reorganization of conducting paths to more perfect conducting network. This explanation corresponds to outcome from Sau et al.[20] study, where the authors published similar results obtained from the first two heating–cooling cycles of conductive rubber.

In Figure 1, DTG curves are shown of untreated and thermally treated samples of EPDM, SBR rubber and EPDM/CB, SBR/CB composites. From those curves it can be concluded that thermal treatment to 165°C did not contribute to the decomposition process of both rubber matrices and their carbon black composites. Our results correspond with testing thermo-oxidative stability of SBR/CB composites in oxygen.[23] In that paper it was found that thermal stability is higher in nitrogen than in oxygen atmosphere and higher filler loading results in a decrease of activation energy of degradation in oxygen.[23]

EPDM/CB and SBR/CB composites showed very good stability of electrical conductivity in the original, fresh samples as well as the ones after 3 years storage at ambient conditions (Fig. 4). Small differences in values of conductivity of composites after storage were observed. Conductivity of original EPDM/CB composite was around 2×10^{-2} S cm^{-1} and no changes after 3 years storage was found. The same trend was observed for SBR/CB composite (Table IV). Relative parameter of conductivity changes were calculated in the case of stored samples similar to fresh samples (Table III). Comparison of the progress of cyclic thermal treatment of both fresh and stored composites revealed the difference in the first cycle of the first run to 85°C in the case of SBR/CB. Smaller increase of relative parameter of conductivity changes was observed for stored SBR/CB composite according to values calculated after first temperature run to 85°C (Table III). Further values of relative parameter of conductivity changes obtained from the other four temperature runs are summarized in Table III and indicate similar behavior of stored composites. Conductivity of 3 years stored EPDM/CB composite at

TABLE IV
Conductivity of Fresh and 3 Years Stored EPDM/35%
CB and SBR/35% CB Composites Before
and After Cyclic Thermal Treatment

	Conductivity (S cm^{-1})	
	Before cyclic thermal treatment	After cyclic thermal treatment
EPDM/35% CB, fresh	1.7×10^{-2}	4.7×10^{-2}
EPDM/35% CB, stored	2.2×10^{-2}	7.4×10^{-2}
SBR/35% CB, fresh	1.1×10^{-2}	3.3×10^{-2}
SBR/35% CB, stored	0.7×10^{-2}	1.4×10^{-2}

the end of cyclic thermal treatment increased. In the case of stored SBR/CB composite cyclic thermal treatment resulted in an increase of conductivity from 0.7 to 1.4×10^{-2} S cm^{-1}. Even more pronounced increase was observed for EPDM/CB composite (Table IV). This phenomenon can be explained by the reorganization of conducting paths to the more conducting network during thermal treatment and by the lower thermal stability of SBR/CB composite. Tendency of progress of cyclic thermal treatment of stored samples is nearly the same as for original, fresh composites for both types of compounds.

Stability of carbon black filled rubbers is closely related to interactions between rubber matrix and carbon black. Interactions were estimated according to so called bound rubber formation determined by the extraction of EPDM/CB and SBR/CB composites in toluene at RT. The amount of insoluble part of EPDM/CB composite was 40%. Although all filler is supposed to be trapped in the insoluble portion, the amount of bound polymer in EPDM/CB was 5%. During extraction of SBR/CB, all polymer part was extracted to toluene. These results indicate that interactions between rubber matrix and carbon black filler were stronger in EPDM/CB composite than in the SBR/CB composite. Stronger bounding of EPDM matrix on the carbon black surface corresponds with postulation of a cationic interaction between the double bounds of an elastomers and carboxy groups of the carbon black[26] leading to simultaneous increase of electrical conductivity during cyclic thermal treatment of EPDM/CB composite.

CONCLUSIONS

Prepared rubber composites of ethylene–propylene–diene terpolymer (EPDM) or styrene-butadiene rubber (SBR) containing 35 wt % (53.85 phr) carbon black showed very good stability of electrical properties during cyclic thermal treatment. Cyclic thermal treatment of conducting rubber composites resulted in an increase of conductivity during heating-cooling cycles for both types of tested rubber/carbon black composites. The most pronounced increase for both composites was found after finishing the first cycle to 85°C defined by the relative parameter of conductivity changes. After 3 years storage of rubber composites at ambient conditions, no significant changes of electrical conductivity of both types of composites were observed. Stronger interactions between EPDM matrix and carbon black filler induced better thermal stability of electrical properties of this composite during cyclic thermal treatment confirmed by thermogravimetric analysis.

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