Original Article

Silica surfaces chemistry and thermooxidation of vulcanized styrene butadiene rubber compounds

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Abstract : Styrene butadiene rubber (SBR) is foremost synthetic rubber used mainly in combination with reinforcing fillers for automotive tire treads. Carbon black and silica are the most important reinforcing fillers and surface chemistry of both these fillers is different. One SBR compound filled with carbon black (CB) only and one compound filed with CB and silica were prepared and vulcanized. The thermal oxidative stability of obtained SBR-CB and SBR-CB-Si samples was tested by different methods. The thermogravimetric curve from thermal gravimetric analysis (TGA) shows main difference between both samples in ceramic yield at high temperatures. The differential thermogravimetric curve shows two distinct peaks of diverse shape for samples with and without silica. One peak for compound SBR-CB and two peaks for compound SBR-CB-Si were obtained by differential scanning calorimetry (DCS). The most significant difference between samples SBR-CB and SBR-CB-Si shows ratio (loss factor) / (absolute value of complex tensile modulus) in dependence on temperature, measured by dynamic mechanical analysis (DMA). Chemical differences between SBR-CB and SBR-CB-Si samples, caused by presence of silica and detectable by FTIR spectroscopy, endure prolonged heating of materials and explain different thermal degradation course of both samples. Surface chemistry of fillers so influences not only interactions filler-filler and filler-polymer (connected with mechanical properties of materials) but also complex of chemical reactions connected with stability of polymers. **© Global Scientific Inc.**

INTRODUCTION

The use of fillers, together with accelerated sulfur vulcanization, has remained the fundamental technique for achieving the incredible range of mechanical properties required for a great variety of modern rubber products[1]. The use of reinforcing fillers–especially, carbon black and silica–induces a simultaneous increase of modulus and deformation at break. This increase explains the ability of reinforced elastomers to provide unique material properties and applications and justify their success in different technological fields[2].

Reinforcement of natural rubber (NR) with car-

bon black (CB) and silica fillers at various rations and total filler content 50 phr was studied and it was shown that present silica influences not only original 100% modulus and elongation at break, but also their changes after aging in air circulating oven at 100°C for 22 h[3].

The thermal oxidative stability of NR examined at 150°C showed controlling role of the surface reactivity and structure of the CB within each system[4]. The thermal degradation of a stabilized, unfilled nitrile rubber (Buna-N) material was investigated at 100 °C, 125 °C and 140 °C. Comparison between the unfilled nitrile rubber and a carbon-black-filled material indicate that the carbon black can fundamentally affect the oxidation mechanism of nitrile rubber[5].

Carbon black surface properties are influenced to a large extent by the foreign elements fixed on the surface, in particular by oxygen, present mainly as carboxyl or carbonyl groups, lactones and phenols. Surface of CB is prone to further oxidation. Oxidation with molecular oxygen is fairly rapid above 300°C, but obviously surface oxides must be formed more slowly at lower temperatures[6].

Fine silicas are largely inactive and exhibit high thermostability. One significant constituent of precipitated silicas is water, which occurs in various quantities either chemically bonded or adsorbed.

Surfaces of fine precipitated silicas used as reinforcing rubber fillers therefore contains water and different number of silanol groups with various arrangement, surroundings and reactivity[7].

The thermal degradation of an unfilled chloroprene rubber was investigated at temperatures up to 140 °C. Heterogeneous oxidation effects were observed using modulus profiling. It was concluded that the degradation profile development is fundamentally described by a diffusion-limited autoxidation mechanism but, at the sample surface, an approximately exponential rise in the modulus with time was observed[8].

Elastomer thermal degradation therefore seems to be a diffusion-limited autoxidation process where most of degradation reactions take place in surface layers and fillers play important role. In this paper vulcanized styrene butadiene rubber (SBR) com-

pounds with carbon black only and with mixture of carbon black and silica are studied. Purpose of this work is to compare thermal degradation course for both samples and explain why the thermooxidation of these vulcanized rubber compounds is different.

EXPERIMENTAL

Materials

Compounds SBR-CB and SBR-CB-Si were prepared according to TABLE 1. In compound SBR-CB was as filler carbon black type N-220 only; in compound SBR-CB-Si was as filler 1:1 ratio of carbon black N-220 to silica type Perkasil KS 408. Both compounds SBR-CB and SBR-CB-Si were vulcanized in press into 2 mm thick sheets.

Thermal gravimetric analysis (TGA)

Vulcanized compounds SBR-CB and SBR-CB-Si were measured by TA TGA Q50 (TA Instruments) in air from 25 to 600°C as a function of increasing temperature with constant heating rate 10°C/min. The results were plotted as a sample residual weight (in %) vs. temperature (the thermogravimetric curve) and as a first derivation of sample residual weight (in %/°C) vs. temperature (the differential thermogravimetric curve).

Differential scanning calorimetry (DSC)

Vulcanized samples SBR-CB and SBR-CB-Si were measured by DSC 1 (Mettler Toledo) in air from 0 to 400°C with constant heating rate 10°C/min. and curves of heat flux (in W/g) versus temperature were obtained.

Dynamic mechanical analysis (DMA)

Vulcanized samples SBR-CB and SBR-CB-Si

TABLE 1 : Standard test formula of styrene butadiene rubber (SBR) by ISO 2322-1985

Material	phr
SBR	100,00
Sulphur	1,75
Stearic acid	1,00
Filler	50,00
Zinc Oxide	3,00
TBBS	1,00

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were measured by dynamic mechanical analyzer DMA DX04T (RMI) in extension mode (in accordance with ISO 4664, but without mechanical conditioning of strips before the DMA test), in air atmosphere, at frequency 1 Hz and sinusoidal strain amplitude 0.33 %, from room temperature to 250 °C with heating velocity 2°C/min. From this measuring the dependence of complex tensile modulus E* on temperature was obtained.

Fourier transform infrared spectrometry (FTIR)

Strips cut from the vulcanized 2 mm thick rubber sheets of compounds SBR-CB and SBR-CB-Si were suspended in commercial oven with circulating air and thermally degraded for 3 hours at 150°C. Surfaces of both original and thermally degraded samples SBR-CB and SBR-CB-Si were then measured by AVATAR 320 - FTIR (Nicolet) in attenuated total reflection (ATR) mode and dependencies of absorbance on wavenumbers were obtained.

RESULTS AND DISCUSSION

The course of thermooxidation for samples of vulcanized rubber compounds SBR-CB and SBR-CB-Si was compared and evaluated on the basis of data from the methods described earlier.

Thermal gravimetric analysis (TGA)

TGA in air to 600°C is able to characterize differences in thermooxidation stability of both samples up to complete decomposition and combustion of present organic compounds. Results from TGA for samples of vulcanized compounds SBR-CB and SBR-CB-Si are shown in Figure 1 and Figure 2.

In Figure 1 we can see how substitution of one half of carbon black by silica influences the TGA trace. The mass loss from 130°C to about 400°C is for SBR-CB-Si somewhat higher than that for SBR-CB. The main reason of this difference is loss of water from silica surfaces for SBR-CB-Si. Different shape of TGA trace at temperatures higher than 400°C is mainly result of different course of thermooxidative degradation in the presence of carbon black and silica surfaces.

At temperatures higher than 570°C only a ceramic yield of both samples was left. In ceramic yield of the SBR-CB sample is present mainly zinc oxide (part of vulcanizing system) and in ceramic yield of the SBR-CB-Si sample is present zinc oxide and silica. More exact picture of thermal degradation reactions in both samples is in Figure 2, as the difference of mass loss is seen more prominently in the first derivative of the mass loss curve.

On the first derivative TGA curve in Figure 2 it can be seen any change in rate of residual weight loss. At increasing temperatures the complex processes of oxidation, decomposition and combustion of present organic compounds are under way. In case of SBR-CB-Si sample the curve is affected also by water released from silica surfaces at increasing temperature.
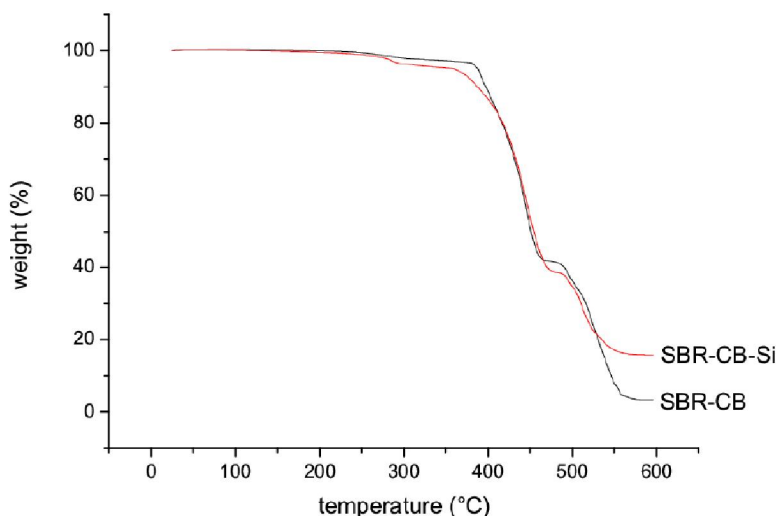
At temperature 282°C is in Figure 2 for both

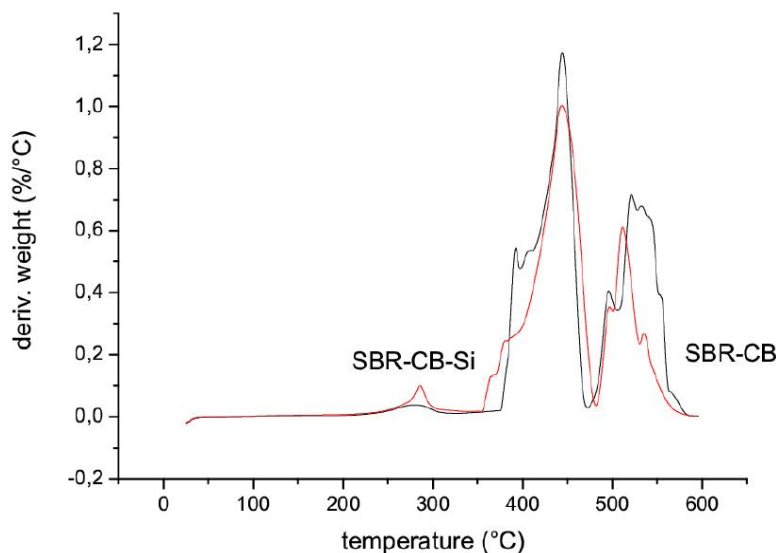**Figure 1 : Residual weight (in %) vs. temperature for vulcanized compounds SBR-CB and SBR-CB-Si**

Figure 2 : The first derivation of sample residual weight (in %/°C) vs. temperature for vulcanized compounds SBR-CB and SBR-CB-Si
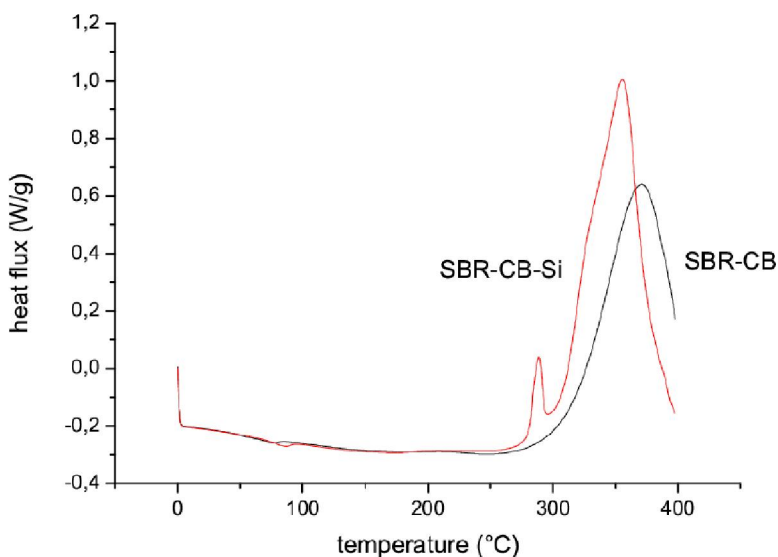

Figure 3 : Heat flux vs. temperature for samples SBR-CB and SBR-CB-Si

samples apparent the first mass loss peak. At temperatures over 300°C are on the curves present two more peaks for next two stages of degradation. The second mass loss peak in Figure 2 is for SBR-CB sample located between 370°C and 470°C, for SBR-CB-Si sample between 350°C and 480°C. The third peak is broader in case of SBR-CB than for SBR-CB-Si and both the second and the third peaks in Figure 2 are higher for SBR-CB than for SBR-CB-Si. This behavior means that the presence of silica in carbon black compound significantly affects degradation of vulcanized SBR rubber samples.

Differential scanning calorimetry (DSC)

DSC is very suitable method for characterization of polymer oxidative stability. The changes in our samples can be seen from DSC measured in air at temperatures from 0° to 400°C. In Figure 3 is the dependence of heat flux on temperature with one peak for SBR-CB (at 370°C) and two peaks (at 287 and 353°C) for SBR-CB-Si. The temperatures of main DSC peaks in Figure 3 so nearly coincide with beginning of TGA second peaks in Figure 2. The lower peak for SBR-CB-Si sample at 287°C roughly corresponds to peak at 282°C on TGA curve in Figure 2.
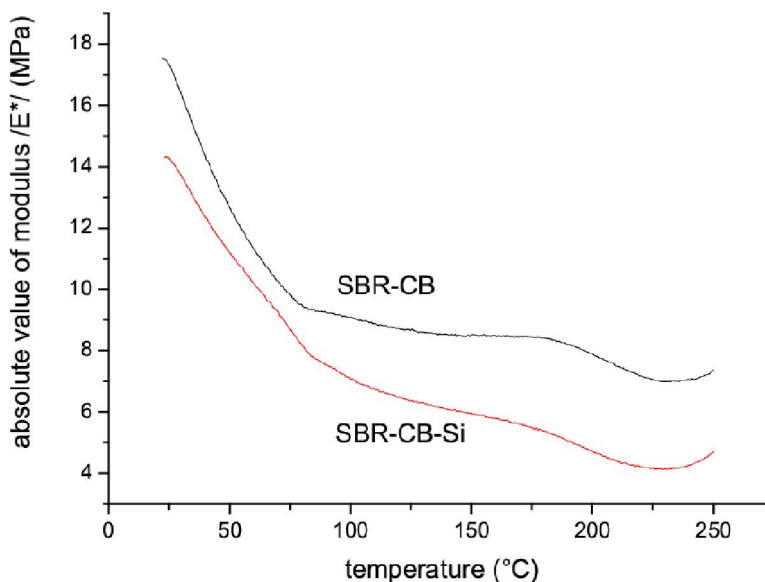
Dynamic mechanical analysis (DMA)

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Figure 4 : Absolute values of complex tensile modulus IE*I vs. temperature for samples SBR-CB and SBR-CB-Si
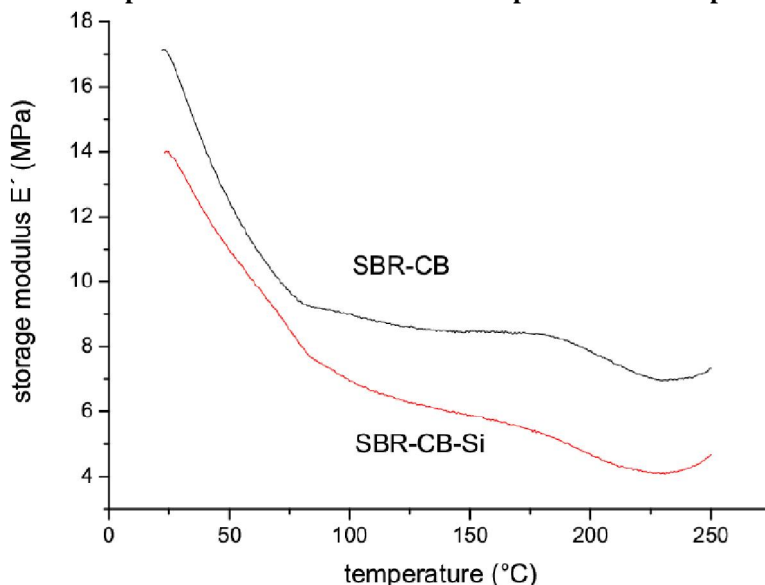
Figure 5 : Tensile storage modulus E´ vs. temperature for samples SBR-CB and SBR-CB-Si

Oxidation of diene rubbers (such as SBR) takes place also at temperatures lower than 280°C, where on TGA and DSC traces we see no peaks. These processes we studied by dynamic mechanical analysis (DMA). The temperature dependences of complex tensile modulus E*, from room temperature to 250°C, we characterized by absolute value of complex tensile modulus IE*I, storage modulus E´, loss modulus E", and by loss factor tan (δ).

The temperature dependences of absolute values of complex tensile modulus IE*I are in Figure 4. The values of IE*I for SBR-CB-Si are lower than for SBR-CB. Lower values of IE*I for SBR-CB-Si

are result of inferior interaction between silica surfaces and SBR matrix (interaction of SBR with CB is better).

Absolute values of complex tensile modulus IE*I of SBR-CB and SBR-CB-Si samples decrease with increasing temperature as result of thermally activated break-up of filler-filler networks, decreasing polymer-filler interactions and gradual thermooxidation of samples.

Tensile storage modulus E´ in Figure 5 characterizes change of elastic part of E* modulus with increasing temperature. Elasticity of samples SBR-CB and SBR-CB-Si is relatively high. Values of stor-
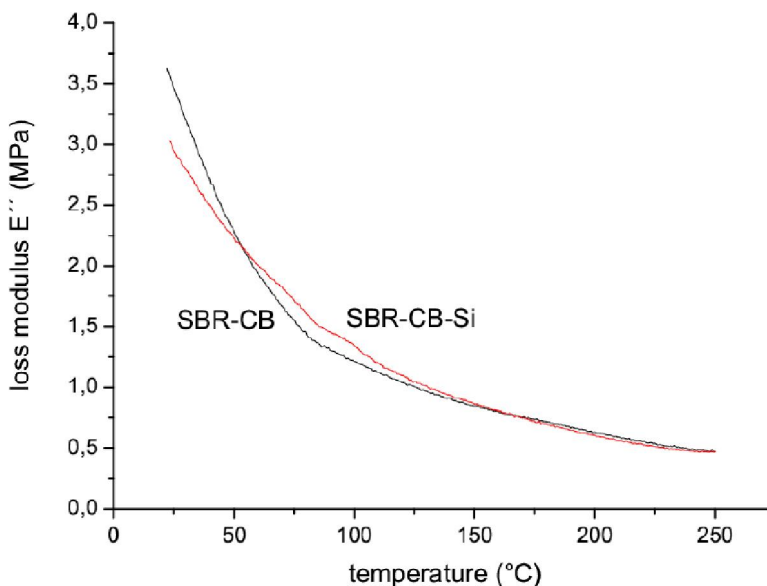
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Figure 6 : Tensile loss modulus E" vs. temperature for samples SBR-CB and SBR-CB-Si

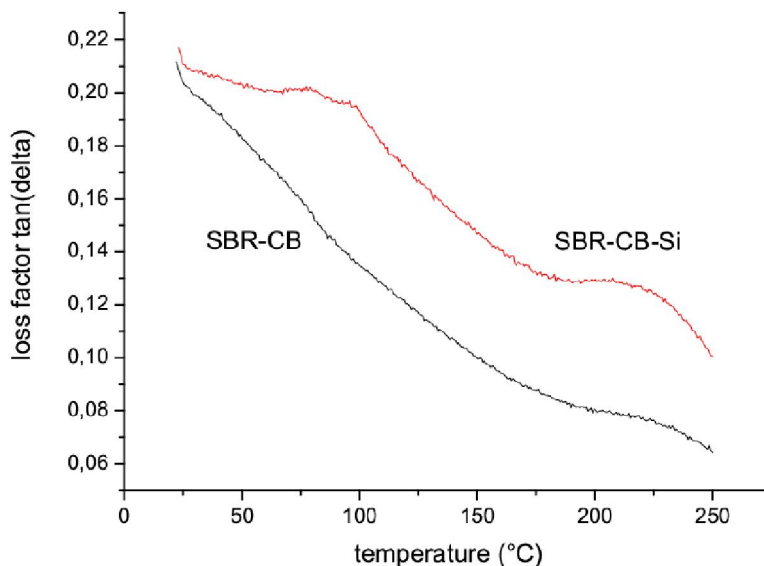Figure 7 : Loss factor tan (δ) vs. temperature for samples SBR-CB and SBR-CB-Si

age modulus E´ and absolute values of complex tensile modulus IE*I are therefore not very different and dependences in Figure 4 and Figure 5 are similar.

The dependences of tensile loss modulus E" in Figure 6 characterize change of viscous part of modulus E* with increasing temperature. Loss modulus E" of samples SBR-CB and SBR-CB-Si also decreases with increasing temperature, but values of E" are quite low and difference between both samples is small.

Higher differences between samples SBR-CB and SBR-CB-Si we see in Figure 7, where is de-

pendence of loss factor tan (δ) on temperature. The loss factor tan (δ) characterizes energy transformed by dynamic deformation of viscoelastic materials to heat. Higher values of loss factor tan (δ) for sample SBR-CB-Si result from low interaction between nonpolar polymer matrix and polar silica surface. Low interaction between polymer chains and silica facilitate slippage of polymer chains on silica surfaces and higher friction cause higher heat generation.

The loss factor tan (δ) in Figure 7 is more sensitive to differences between samples SBR-CB and SBR-CB-Si than the tensile loss modulus E" in Fig-
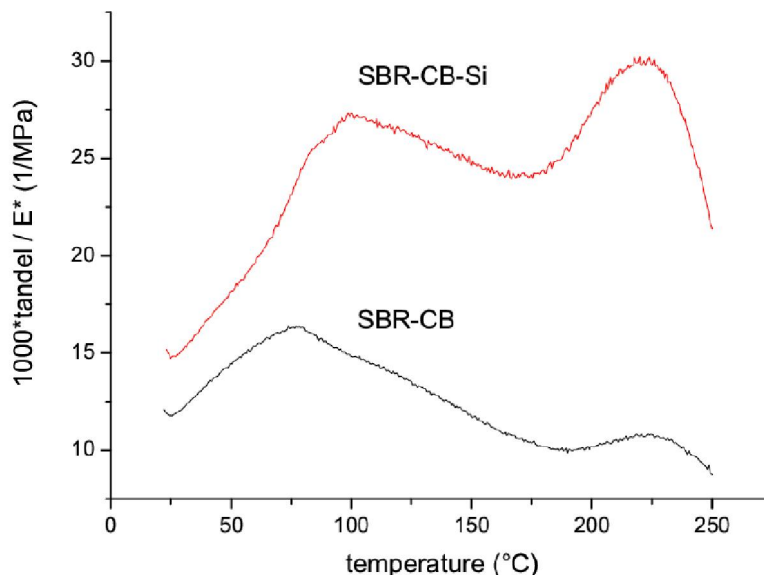
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Figure 8 : Ratio tan (δ) to IE*I vs. temperature for samples SBR-CB and SBR-CB-Si
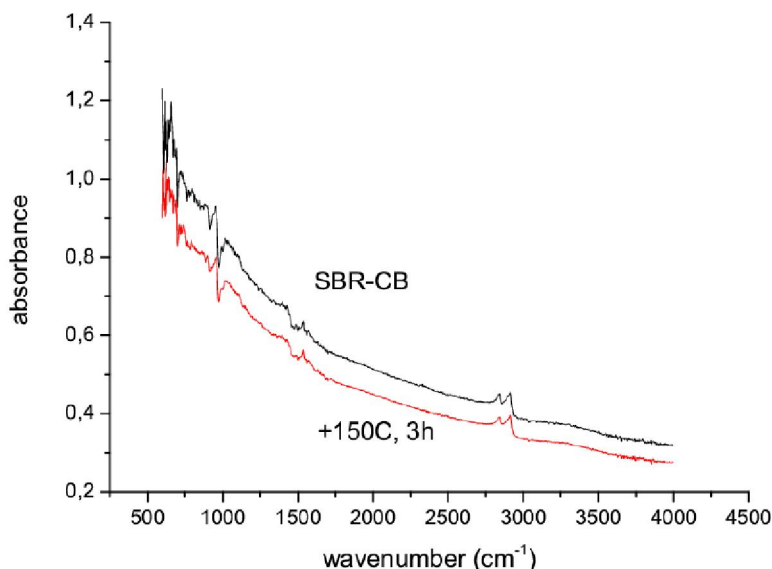

Figure 9 : ATR-FTIR spectrum of original SBR-CB sample and sample SBR-CB after 3 hours at 150°C

ure 6. Even more significant differences between both samples we obtained for temperature dependence of ratio tan (δ) to IE*I in Figure 8. (It was already shown that values of ratio tan (δ) to IE*I are very sensitive to stability of vulcanized rubber at higher temperatures[9].)

Because ratio tan (δ)(IE*I) = E''/ (E´. IE*I) and absolute values of complex tensile modulus IE*I and storage modulus E´ are not very different, we could obtain temperature dependences similar to Figure 8 also for ratios E''/ (E´)² and E''/ (IE*I)², where E''/(IE*I)² = D'', i.e. imaginary part of complex tensile compliance (called often tensile loss compliance).

Fourier transform infrared spectrometry (FTIR)

The ATR-FTIR in Figure 9 and Figure 10 enable to determine influence of silica in SBR-CB-Si on change of spectrum after thermal oxidation. As we can see, 3 hours heating at 150°C shifted absorbances for both SBR-CB and SBR-CB-Si in Figure 9 and Figure 10 to lower values. In the spectrum of SBR-CB in Fig.9 are apparent no other changes.

Three peaks corresponding to three different silanol groups are commonly detected by IR spectroscopy on the surface of raw silica fillers[7]: peak of isolated groups (3745 cm⁻¹), peak of vicinal groups (3640 cm⁻¹), and peak of groups bonded by water
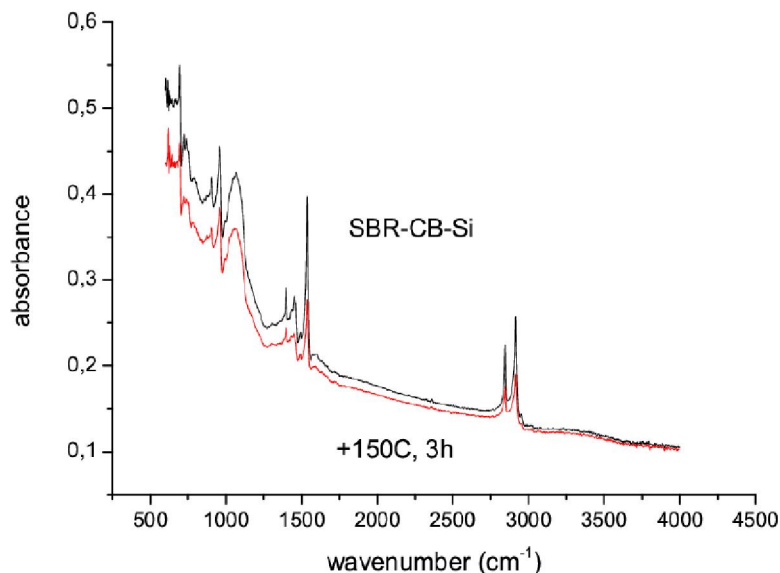
Figure 10 : ATR-FTIR spectrum of original SBR-CB-Si sample and sample SBR-CB-Si after 3 hours at 150°C

bridge (3420 cm^{-1}). But the spectra of SBR-CB-Si in Figure 10 have no peaks at wavenumbers higher than 3000 cm^{-1}.

Instead are in Figure 10 peaks at 1540, 2850 and 2910 cm^{-1}. These peaks rather decreased after 3 hours heating at 150°C but do not disappear completely. Chemical differences between SBR-CB and SBR-CB-Si, detectable by ATR-FTIR spectroscopy and visible in Figure 9 and Figure 10, thus persist also after prolonged heating and explain different thermal degradation course of both samples.

CONCLUSIONS

Styrene butadiene rubber (SBR) is foremost synthetic rubber used mainly in combination with reinforcing fillers for automotive tire treads. Carbon black and silica are the most important reinforcing fillers and surface chemistry of both these fillers is different.

One SBR compound filled with carbon black (CB) only and one compound filed with CB and silica in commonly used 1:1 ratio were prepared and vulcanized. The thermal oxidative stability of samples was tested by different methods.

The thermogravimetric curve from thermal gravimetric analysis (TGA) shows mainly difference in ceramic yield at high temperatures, caused by presence of silica in one sample. The differential thermogravimetric curve shows two distinct peaks of diverse shape for samples with and without silica.

By differential scanning calorimetry (DCS) we obtained one peak for compound filled with carbon black only and two peaks for compound where silica is added. The temperatures of DCS main peaks for both samples nearly coincide with beginning of TGA second peaks.

The most significant difference between both SBR-CB and SBR-CB-Si samples we obtained for dependence of ratio (loss factor) / (absolute value of complex tensile modulus) on temperature, measured by dynamic mechanical analysis (DMA).

Chemical differences between SBR-CB and SBR-CB-Si, caused by presence of silica and detectable by FTIR spectroscopy, remain also after prolonged heating of material and explain different thermal degradation course of both samples. Surface chemistry of fillers so influences not only interactions filler-filler and filler-polymer (connected with mechanical properties) but also degradation stability of rubbers.

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