Sborník vědeckých prací Vysoké školy báňské - Technické univerzity Ostrava
číslo 3, rok 2009, ročník LII, řada hutnická,
článek č. 1544

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THERMAL PROPERTIES OF RUBBER BLENDS FILLED BY SILICA-CARBON BLACK COMBINED FILLERS

TEPELNÉ VLASTNOSTI GUMÁRESNKÝCH ZMESÍ PLNENÝCH ZMESOU SILIKY A SADZÍ

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Abstract

In the paper we present the measurements of thermal conductivity, diffusivity and specific heat capacity by a flash method for rubber compounds with different ratio of silica - carbon black fillers.

From the presented results it is possible to see that proper filler mixture (silica - carbon black) in a blend offers the rising of all thermal parameters, it lowers the electrical resistance. All trends are favourable to the improvement of useful properties of the blend.

Abstrakt

V článku je prezentované bezkontaktné meranie tepelných parametrov, tepelnej vodivosti, divuzivity a špecifickej tepelnej kapacity pomocou flash metódy s rôznym pomerom plniva siliky – sadzí.

Z nameraných výsledkov je možné vidieť, že zmes (so silikou a sadzami) spôsobuje zvýšenie všetkých tepelných vlastností, ako aj zníženie elektrického odporu. Všetky trendy sú priaznivými ku zlepšeniu úžitkových vlastností zmesi.

Key words: mixture, carbon black, silica, capacity, conductivity

1. Introduction

Thermal properties of rubber blends play an important role in the computer modelling as well as the construction of modern tyres. To understand the dynamical properties of a tyre as a whole, it is necessary to know also the dynamic mechanical properties of various rubber compounds present in the tyre.

The use of reinforcing fillers gives the material unique properties, a combination of high elasticity with high strength. The addition of the filler to the polymer increases both moduli G and E according to a hydrodynamic effect. The filler polymer effects are determined by the structure of the filler. Polymer chains are trapped in the voids of filler agglomerates and agglomerates. They are immobilized and shielded from any deformation. They not contribute to the elastic deformation. Occlude rubber increases the effective filler loading and thus the strain independent contribution to the modulus [1, 2].

Blending of fillers with rubber leads also to a nonlinear phenomenon characterized, for instance, by Payne's effect caused by a filler-filler interaction. This effect is largely reversible once the strain is released and it is independent of the type of a polymer, but it depends on the type of a filler.

The addition of fillers significantly changes the temperature coefficient of the modulus. It can even alter the sign of the coefficient resulting in a decrease of the modulus with increasing temperature, because for unfilled rubber the modulus rises with the rising temperature.

Precipitated silica is traditionally used as a filler material for rubber blends, which maintains good "wet grip", relatively low rolling resistance and also good abrasion resistance. Silica fillers are characterized by a high specific surface energy, which results in a strong filler-filler interaction and a difficult processing behaviour. The structure on a molecular scale of silica filled rubber is fundamentally different from that with the carbon black filler. The polymer is linked to the silica particles by covalent bonds, resulting in a strong filler-polymer network.

When carbon black is blended with a polymer, the physical interaction between the polymer and filler particles is strong. Aggregates of carbon black are made up of small spherical particles aggregated to each other and partly fused together to form three-dimension assembles. The description of these aggregates is still open and authors offer experimental concepts how to do it [1, 3].

In contrast to the previous case, the interaction between silica and the polymer is weak a bond is formed between the both ones only by the use of a coupling agent.

The Payne's effect is stronger for silica as a result of a stronger interaction between filler particles.

Besides the interaction between the polymer and the filler, an interaction of filler particles occurs, predominantly above a critical threshold, the percolation threshold. In this case, the physical properties drastically change as a result of filler-filler network creation. For instance, it is well known over the proportional increase of electrical conductivity for carbon black filled blends [4].

Rubber filler composites and new coupling agents with higher coupling efficiency are on the way of enlarging the possibility for compounders to find the best solution for the desired performance of rubber articles. The success of silica-silane reinforcing materials initialised activities in carbon black. The main goal was to reduce the heat build-up resulting in lower rolling resistance. With new nanostructures blacks, it is possible to increase the specific surface area to enhance tensile and tear strength and maintain the heat build-up at a low level [1]

They influence the heat transport through the rotating tyre so they influence the properties of the tyre and mainly its safety in traffic.

In this work we present the results of the heat capacity cp [$J.kg^{-1}.K^{-1}$], thermal diffusivity α [$m^2.s^{-1}$] and thermal conductivity λ [$W.m^{-1}.K^{-1}$], electrical conductivity σ_{40} [$\Omega^{-1}m^{-1}$] as well as both the temperature dependence of E* modulus and the concentration dependence and tg δ for rubber blends with the combined silica- carbon black filler.

2. Experimental procedure

In the first step, we measured the thermal parameters of blends under investigation by using the apparatus presented in Figure 1 [6].The tested samples were rubber blends, all of a cylindrical shape with the dimensions Ø = 12 mm and thickness approximately 2 mm. The sample was illuminated trough a halogen lamp (electrical power 200 W) switched on by a computer. We used the pyro-sensor type Raytek THERMALERT MID 02 placed at the rear side near the surface of the measured sample in order to sense the temperature. The whole measuring process was controlled and evaluated by a special software which automatically switches the lamp on, measures the time-temperature dependence of pyro-sensor response, determines the temperature difference ΔT from the measured data (see below). Every value was measured ten times in order to obtain the repetition ability of the apparatus. Then the full set of values was transformed to software Matlab. After application of the proper regression procedure of measured time-temperature dependences obtained from the pyro-sensor response by Matlab, we obtained the following values t1/2.

Then

$$\alpha = 1{,}38L^2 / \pi^2 t_{1/2}, \quad (1)$$

where L is the sample thickness, t1/2 is the half time, when the maximum of a thermal response is reached. At the evaluation of the time t1/2 it is necessary to assume that in a real experiment we measure the effective value of thermal diffusivity α and also the effective time tef corresponding to the maximum temperature. We can explain it in the following way. When the heat pulse travels through the sample, the sample is heated and the amplitude of phonons is rising. Their mean free path is decreasing, which results in diffusivity α decreasing and finally in rising of tef . tM derived in the basic form in [7] did not consider this physical fact. It has been shown that the relation between both temperatures can be found in the form [7]

$$t^{ef} = 1.6 t_M . \quad (2)$$

Absorbed heat Q_{metal} ($Q_{metal}=mc_{metal}\Delta t_{metal}$), specific heat capacity c_{rubber} ($c_{rubber}= Q_{metal}/m_{rubber}\Delta t_{rubber}$), thermal diffusivity α and thermal conductivity λ are determined according to the following relation

$$\alpha = \frac{\lambda}{\rho c} \quad (3)$$

We start the experimental analysis of the results from measurement of heat adsorbed in the metallic sample. We calculated it from calorimetric equation Q=mcΔT for Cu sample, with the table value of c_{Cu} = 383 J.kg-1.K-1. Surface of the Cu sample was covered on both sides of the sample by mat black spray. The heat absorbed by Cu sample was approximately equal Q_{Cu} = (0.738±0.037) J.

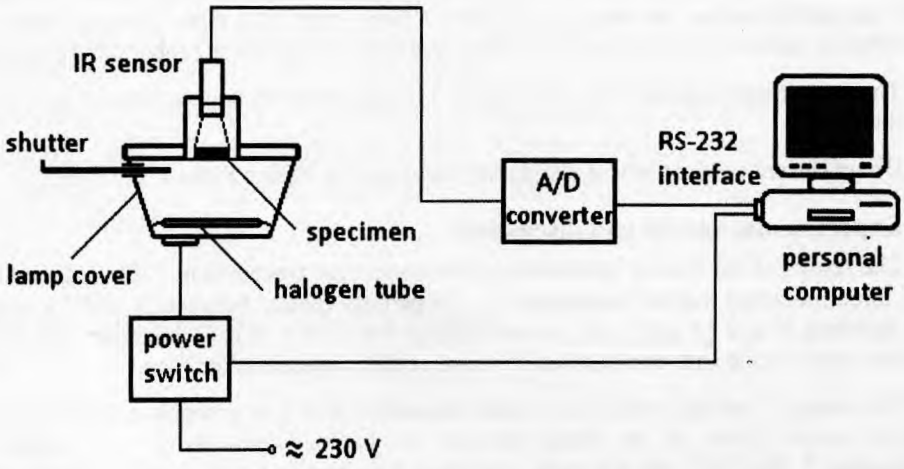

Fig. 1 Schema of the thermal analyser

Heat impulse duration was equal to one second in all experiments. We determined ΔT as a temperature difference of the ambient temperature and maximum surface temperature measured by pyro-sensor on the rare sample surface.

The surface emissivity set was 0.95 and the flash impulse duration was 0.5 s. Density of samples was measured according to Archimedes law.

Samples of rubber blends contained commercial components according to Table 1. The amount of both carbon black and silica is presented in the Table 2.

Table 1 Sample chemical composition

Components of blends
SULPHUR
SULFENAX
SKD 2
BUNA
KRALEX
ULTRASIL (Silica)
VULCAN (Carbon black)
ZnO
DUSANTOX
FLECTOL
STEARIN

Table 2 Content of filers (%from total volume of the blend)

	Blend A	Blend B	Blend C
Content of carbon black (%) v zmesi (%)	6.0	20.5	35.0
Content of silica (%)	30.0	13.5	-

Presented mixtures were prepared in a laboratory mixer GK2 with the volume of blending box 2.5 dm^3 and deflationed at the temperature 150°C. There were used three kinds of rubber mixtures with a different content of the carbon black filler. We have marked these rubber mixtures as A, B, C.

The temperature dependences of complex Young's modulus were measured by DMA Perkin Elmer analyser.

Direct current conductivity of blends was measured by Bridge Fluke PM 6306

3. Experimental results and discussion

The results of the thermal parameters measurement are presented in Table 1. It is clearly seen that all three measured thermal parameters c_p (14 percent change between A and C), α (9 percent change between A and C) and λ (30 percent change between A and C) increase with the growing amount of carbon black and simultaneous decrease of silica content in the blend.

The rising of thermal conductivity from the sample A to C is probably caused by the growing amount of carbon black in the blend because the thermal conductivity λ of carbon black is approximately 5 $W.m^{-1}.K^{-1}$ and the same parameter for silica is 1.4 $W.m^{-1}.K^{-1}$. On the other hand, values of c_p are 837 $J.kg^{-1}.K^{-1}$ for carbon black and 743 $J.kg^{-1}K^{-1}$ for silica. The rising of c_p is most probably caused also by increasing the carbon black amount in the blend which could enhance also silica content which is decreasing from the sample A to C.

Direct current conductivity σ_{40} measured at 40°C rises also with the increasing amount of the carbon black filler from the sample A to C.

Table 3 Results of thermal parameter measurements for different ratio of silica-carbon black and corresponding values of DC conductivity σ_{40} measured at 40°C

Sample	c_p [J.kg^{-1}.K^{-1}]	α [m^2.s^{-1}].e7	λ [W.m^{-1}.K^{-1}]	σ_{40} [Ω^{-1}m^{-1}]
A	1308.216	2.048	0.3045	1.1è11
B	1334.034	2.157	0.3467	4.1e11
C	1486.645	2.233	0.3913	8.4e11

4. Conclusions

All presented results in the work support the idea that mixing of combination of silica-carbon black fillers is a good way to obtain rubber blends where there is, in a good sense, influenced the heat transport as well as the electrical conductivity (both are rising with carbon black amount in the blend).

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