INVESTIGATION OF THEMOPHYSICAL PROPERTIES OF STYRENE BUDADIENE RUBBER FILLED BY PINE TREE PARTICLES BY TRANSIENT METHODS.

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Abstract:
The modern composite materials are surprising for their innovative physical properties. The thermophysical properties are ruling the way of use for such materials. This paper discusses the measured properties of specimen series made of styrene-butadiene rubber (SBR) filled with different concentration of jackpine tree particles (Pinus banksiana). Final mix that contains organic wood particles have got increased heat transport ability with increasing pine tree particles concentration.

Keywords:
Styrene-butadiene rubber, pine tree particles, pulste transient method, specific heat, thermal conductivity, thermal diffusivity.

INTRODUCTION

The new materials treated in new non-traditional way shows new properties desired to their use in practice. Recently the innovation progress concentrates on new - more economical materials available for the industrial use. The new materials should have known properties and thus the requirement of the testing methods arises with their use in real life.

Styrene butadiene rubber (SBR) is an elastomeric statistical copolymer - styrene-co-butadiene and it‘s natural form is known as caoutchouc. SBR has good abrasion resistance, ozone, or weather resistant; good electrical properties, good aging and chemical stability in various chemicals. Particular chemical substances are the styrene, also known as vinyl benzene, 1,3-Butadiene that is a simple diene that have conjugated double bonds separated by one single bond with alternating single and multiple (e.g. double) bonds (e.g., C=C-C=C-C) in a molecule. SBR has good abrasion resistance and good aging stability. SBR is stable in mineral oils, fats, aliphatic, aromatic and chlorinated hydrocarbons.

Typical applications are: pneumatic tires and tubes; heels and soles; gaskets. The overall performace of the material should be changed by adding some organic or anorganic particels. It is well known fact that the different content of organic particles in SBR matrix changes the dimensional and stiffness characteristics as well as next physical properties. The interesting question was, in what way we can influence the thermal transport in such material and how big difference in thermophysical properties with the dependence on the content of the wood particles can be found.

Anomalous behaviour of thermophysical properties have previously been observed for composite materials consisting of a matrix blended with powder particles, which have been processed in various ways during manufacturing. It was recorded the dimensional and stiffness changes in various physical characteristics of such a composite materials. When filled with wood

particles, the compound should got better physical and mechanical properties and still posses the chemical, weather and abrasion resistance in various environment.

Crosslinked wood-thermoplastic composite can be utilized in structural applications when low desnity and the long-term of load performance is required. For example in the case of silane wood-thermoplastic the toughness of the silane crosslinked composites was significantly higher than for the non-crosslinked composites [1]. Reinforcing effect was observed in the case of compound made of polymers acrylonitrile-butadiene-styrene and wood sawdust [2]. Similar behaviour we expect for the composite based on styrene-butadiene rubber and jack pine tree particles filler.

The thermophysical properties of materials are sensitive on the change in material structure and their composition and thus are able to answer the question of the material behaviour examined under different conditions. The investigation of the thermophysical properties of a composite material consisting of a matrix filled with particulate powder filler helps to understand the changed properties on a new material.

This paper discusses the effect of different content of jackpine tree particles (Pinus banksiana) in styrene butadiene rubber (SBR) matrix. As a wood filling, the jackpine tree particles were added having the mesh 60.

Thermophysical properties were investigated by the Pulse transient technique[3].

THEORY

Transient pulse method was used for measurements of thermal conductivity, thermal diffusivity and specific heat capacity. The experimental arrangement of this method is based on the assumption that a heat source in the shape of a meander placed inside an infinite and initially isothermal sample. The thermocouple that measure the temperature response is placed apart at certain distance. By passing a pulse electrical current through the nickel heat source, the heat is generated and immediately dissipates into the sample. Simultaneously, the transient temperature response is measured by thermocouple as a function of time. A typical temperature increase versus time is depicted in Figure 1 (right). Typically, the total temperature increase during an experiment is between 0.2 K and 1.5 K – depending on the particular sample and sensor used. A basic experimental setup is illustrated in Figure 1 (left). The ideal model supposes non-limited specimen geometry. The real specimen arrangement is drawn in Figure 1.

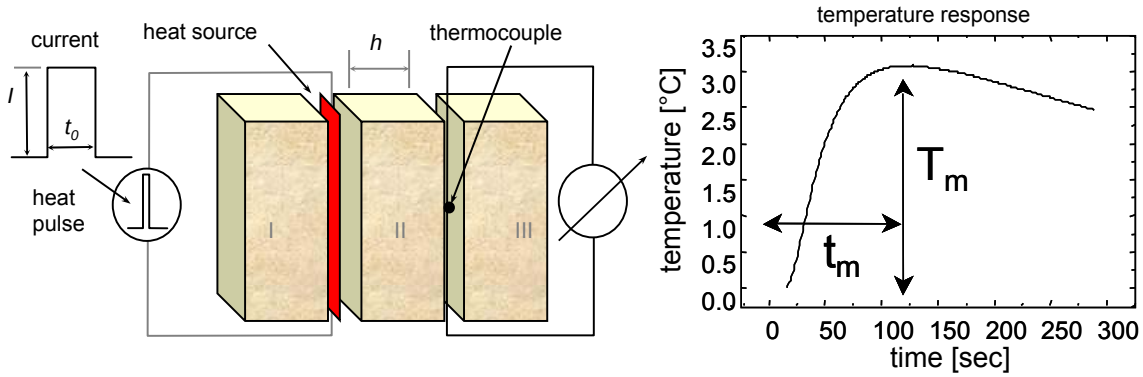

Figure 1. Arrangement of the specimen set that consists of three parts (left). The example of the temperature response for PMMA material is on the right. Tm and tm are the maximum temperature of the temperature response and the time when this maximum is set.

Temperature function. The ideal case of experiment should fulfill several basic conditions. The heat source is infinitely thin and infinitely large having the same thermophysical properties like

investigated material. The specimen is infinitely large also. The heat pulse is generated in the form of Dirac pulse with infinitely large instant heating power. Then, the temperature response to the heat pulse generated by planar heat source is described by temperature function [**Chyba! Záložka není definována.**]. In the case when technically it is not possible to generate heat pulse of required energy that can rise up temperature response large enough for detection, the Dirac's pulse should be replaced by the pulse of lower instant power, but of longer duration (pulse width). This technique is usually used in the cases when big instant power can damage specimen, especially at the materials that could melt or burned easily like polymers, biomaterials etc.

Using model that accounting the heat pulse duration of several seconds, the thermophysical parameters are calculated from the parameters of the temperature response to the heat pulse [**Chyba! Záložka není definována.**].

$$T(h,t) = \frac{2 \cdot Q}{c\rho\sqrt{a}}\left[\sqrt{t} \cdot i\Phi^*\left(\frac{h}{2\sqrt{at}}\right) - \sqrt{t-t_0} \cdot i\Phi^*\left(\frac{h}{2\sqrt{a(t-t_0)}}\right)\right] \tag{1}$$

where

$$i\Phi^* = \frac{e^{-x^2}}{\sqrt{\pi}} - x \cdot erfc(x)$$

The given function should be used for the fitting procedure to evaluate parameters thermal diffusivity $\boldsymbol{a}$ and specific heat at constant pressure $\boldsymbol{c}_p$. For the simplicity of data treatment the next simple formulas for the maximum of the temperature response were derived. The thermal diffusivity is given as

$$a = h^2/2t_m \cdot f_a \ , \tag{2}$$

where

$$f_a = (t_m/t_0 - 1) \cdot \ln\left(\frac{t_m/t_0}{t_m/t_0 - 1}\right)$$

the specific heat,

$$c = \frac{Q}{\sqrt{2\pi e}\rho h T_m} f_c \ , \tag{3}$$

where

$$f_c = 2 \cdot \exp(1/2)\sqrt{\pi\ f_a} \cdot t_m/t_0 \left\{1/\sqrt{\pi}\left[\exp(-f_a/2) - \sqrt{(t_m/t_0 - 1)/t_m}\ \exp(t_m/t_0\ f_a/2(t_m/t_0 - 1))\right] - \right.$$
$$\left. - \sqrt{f_a/2}\left[\Phi^*\left(\sqrt{f_a/2}\right) - ercf\left(\sqrt{t_m/t_0\ f_a/2(t_m/t_0 - 1)}\right)\right]\right\}$$

and the thermal conductivity

$$\lambda = ac\rho \tag{4}$$

where $Q = RI^2 t_o$, $\boldsymbol{R}$ is the electrical resistance of the heat source, $\boldsymbol{\rho}$ is density, $\boldsymbol{T_m}$ is maximum temperature of the temperature response, $\boldsymbol{t_m}$ is time when temperature rich the maximum and other parameters are given in the Figure 1.

These simple formulas [**Chyba! Záložka není definována.**] are used for the standard evaluation of the experiment - one point evaluation. The time of the pulse duration (pulse width) is denoted as t0, erfc is complementary error function.

Fitting evaluation procedure or derived one point evaluation procedure for maximum of the temperature response should be applied to a measured temperature response. The shape of the temperature response is plotted in Figure 1. Relations 2÷4 were used for data evaluation by one point procedure.

EXPERIMENT

At our experiment we used specimen made of SBR-Kralex 1500 produced by Kaučuk Kralupy in Czech republic. The pine wood particles having mesh 60 were prepared at the University Quebec Trois Rivieres, Canada. The jackpine tree particles were dryed at 120 °C for about 1 hour before mixing. The concentrations of 0, 10, 20, 40 and 60 weigt % of pine tree particles were added to styrene butadiene compound to produce desired composite. The prepared mixture before polymerization contains also 5 dsk ZnO, 3.5 dsk Sulfenax CBS (Istrochim, Bratislava), 2 dsk stearin III and finally 3.5 dsk of sulfur is added. The mixing process was performed in the 30ml chamber (Plastograf Brabender) at the temperature 70 °C. The chamber rotation speed was 30 rpm. The mixing was performed in several steps. To a desired amount of caoutchouc was added additives and filling in two minutes. The compound was kept in rest for 6 minutes and than it was cutted on small pieces. After than inserted into a chamber and mixed next 6 minutes. This process warants relativety high hmogeneity of a mixture at short time for mixing that prevent to the inception of the thermic respectively mechanical degradation. After mixing, the blend was compression molded at 150 °C for 35 minutes minutes in a laboratory press (Fontijne, Netherland) at the pressure 20 tons to thermoform the mixture and to cure the material.

A set of composite specimens with different concentrations of pine tree particles were prepared in a form of slabs having dimensions 50x75 mm and thickness 2 and 1 mm. Then it was cutted to a smaller pieces having dimension 30x30 mm. Prepared slabs were sticked together to form a specimen set-up with three parts of 10, 6 and 10 mm thick suitable for the pulse transient method.

RESULTS

The densities of the specimens were determined from the specimen dimensions and their weight. The densities of all specimens in a depencency on weight % of pine tree particles are plotted in figure 2. For comparison, the numerical value of the density of natural pine tree wood is 460 kg m^{-3} and for pure styrene-butadiene rubber 1043 kg m^{-3}. We assume that the density of specimen produced from milled pine tree particles will be higher and dependent on the pressure used at processing. For the measurement we used pulse transient method. Measurements were performed in a chamber RTB 1.02 (IP SAS) havig possibility to stabilize the temperatrure in a secimen from both – upper and lower side of a specimen set-up. The sample was temperature stabilized and the transient experiment was performed each 2 hours. The heat pulse was generated by current between 1 and 1.6 A, and of duration 10s. The thermophysical parameter were calcultaed according one point procedure using realtions 2, 3 and 4.

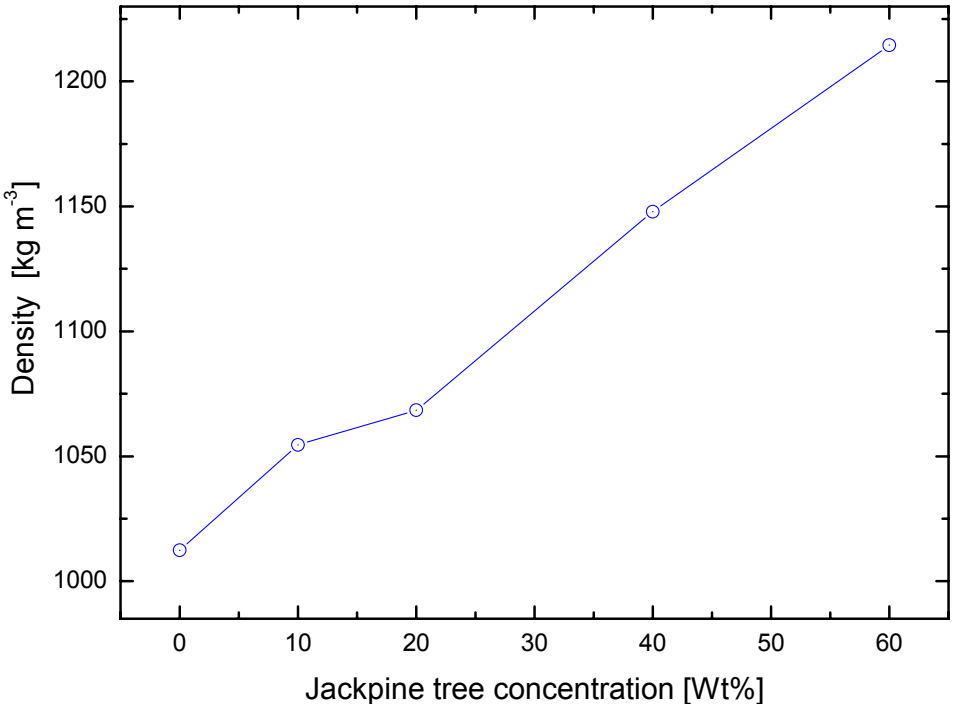

Figure 2. Density of the styrene butadine rubber composite versus concentration of pine tree particles.

Calculated thermophysical parameters of all specimens in a dependency on the concentration of a pine tree particles in a styrene butadiene rubber are plotted in figure 3.

It was found that the thermal transport properties are increasing with increased pine tree particles content, while the value of specific heat is decreasing. The pure bulk properties of rubber and natural pine tree board wood are totally different in comparison with the present composite samples. For pure rubber, the value for thermal diffusivity is 0.124 m^2s^{-1} value for specific heat is 1722.6 $Jkg^{-1}K^{-1}$ and value for thermal conductivity is 0.216 $Wm^{-1}K^{-1}$. In comparison, for natural pine tree wood the values of 0.15 m^2s^{-1} for thermal diffusivity, 1773 $Jkg^{-1}K^{-1}$ for specific heat and 0.12 $Wm^{-1}K^{-1}$ for thermal conductivity were measured by Pulse Transient Technique.

The results show the behaviour when the value of specific heat is decreasing with increasing of pine tree wood particles content. The reason is that pine tree wood in natural state is quite porous comparing to those one milled and having mash 90. Obviously, low density of wood particles results from the high porosity of the wood. The density of bulk wood material without pores should be much higher. Thus, the increase in density with rising filler content is explained by the fact that the pores are gradually filled with the rubber so that real density of bulk wood is ruling parameter regarding the calculation of the density of the composites based on simple mixing rule. This assumption also explains the nonlinearity of the dependence in Figure 2 and 3, since with the increase of the filler content the viscosity of the blend also increases with obvious results on the increase in shear stress and pressure in the mixing chamber. Thus at lower filler content (low viscosity) only larger pores are filled while as soon as the viscosity increases above certain level (high filler content) the matrix material is pressed inside the smaller pores as well. During mixing the particles with the rubber, quite high pressure and shear is applied. It is reasonable to expect that under such conditions the matrix should be squeezed inside the pores resulting in a increase of density of the composite.

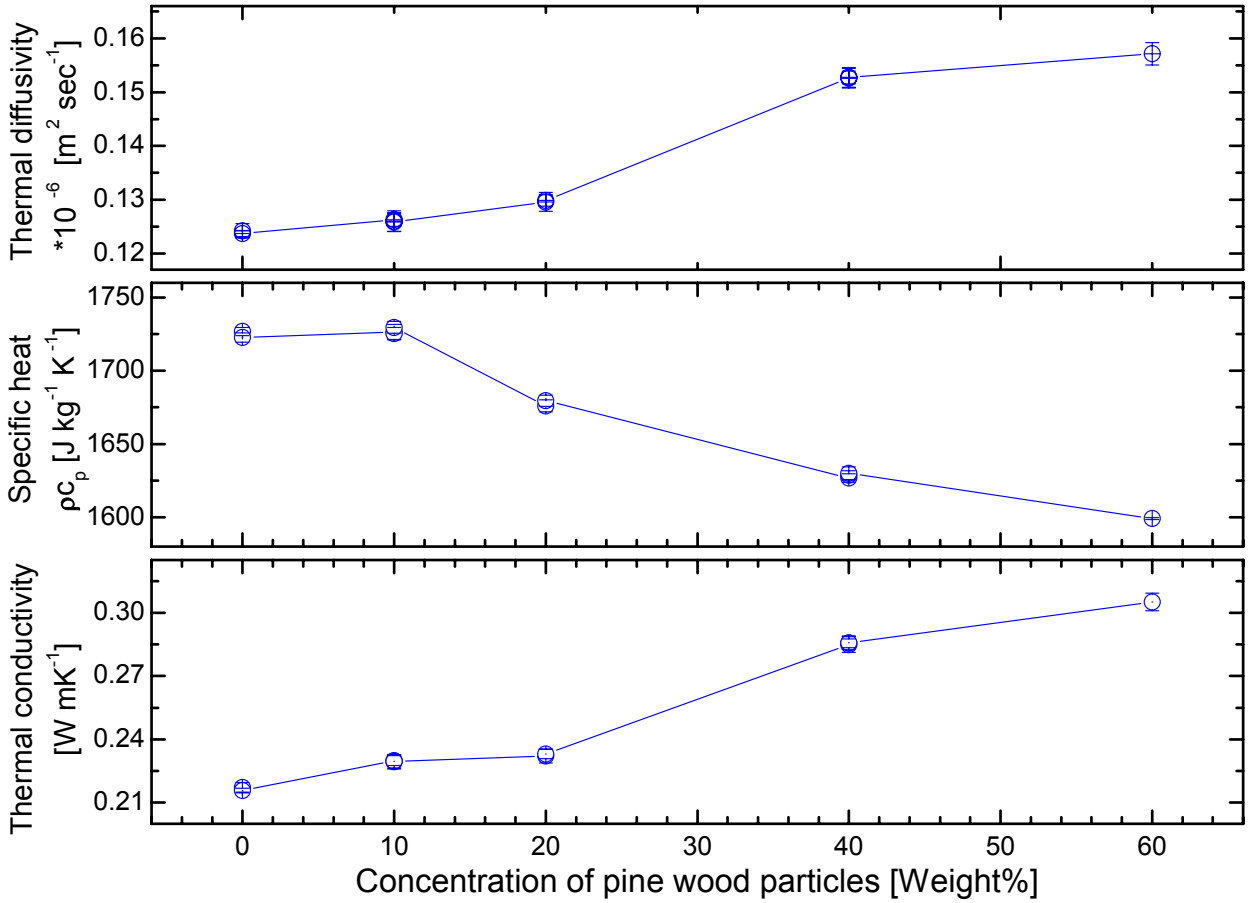

Fig 3. The dependence of the thermal diffusivity, specific heat and thermal conductivity on the concentration of pine tree particles in composite. The value of specific heat for natural pine tree wood board was 1773 $Jkg^{-1}K^{-1}$, thermal conductivity 0.12 $Wm^{-1}K^{-1}$ and thermal diffusivity 0.15 m^2s^{-1}.

The plot of experimental data shows that the thermophysical properties are reasonably dependent on the concentration of pine tree particles. The values of thermal conductivity of the composite samples are higher than that of pure styrene butadiele rubber as well as the board of natural pine tree wood. The values of specific heat for pine tree wood as well as for pure rubber are higher than that one for the composite. This is the consequence of higher compactation, ordering and density of final composite material. Teh free volume (porosity) of a composite is minimal. The value of thermal diffusivity for natural pine tree wood is in a middle of the measured range of calculated values for given composites. Absence of pores in composite is the reason of improved heat transfer.

There were observed two regions of the dependency of the transport thermophysical parameters on density - below and above 1068 kg m^{-3} that correspond to the concentration of 20 wt.% of pine wood particles. This effect should be caused by an increase on percolation effect when pine tree particles become inter-connected in the composite.

CONCLUSIONS

The composites consisting of a rubber matrix filled with various concentrations of pine tree particles were produced. The thermal conductivity and thermal diffusivity of the composites having

different concentration of a pine tree particles as a filler are increasing with their increasing concentration. The values of the specific heat is decreasing in the same time.

The change in dependency with pine tree concentyration was found around 20 wt.%. This should be concluded due to several reasons. The first one is the percolation effect, *i.e.* a change in the mechanisms of conducting heat when the particles in the matrix become interconnected. The next reason is due to processes of mixing and molding under compression before the curing of material mixture. Porosity of the composites as compared to the porosity of the original constituents was reduced. Pores in wooden part of the composite were filled by styrene-butadiene rubber due to increasing of shear stress and pressure in mixing chamber due to increased number of wood particles.

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