

THERMOPHYSICAL PROPERTIES OF STYRENE BUTADIENE RUBBER FILLED WITH PINE TREE PARTICLES MEASURED BY THE TRANSIENT PLANE SOURCE TECHNIQUE

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Abstract

A batch of specimens based on a system of a rubber matrix mixed with various concentration of fine pine tree particles, were investigated by studying the variation in thermophysical properties. The pine tree particles were added into a styrene-butadiene rubber matrix in different quantities (0, 10, 20, 40 and 60 wt. %). The thermophysical properties behaviour with increasing pine tree particles concentration was found to be different from the originally expected behaviour.

Thermophysical properties of materials are very sensitive to any kind of the change of the material structure and thus we can distinguish relatively small changes in material structure. The particle-rubber interface surfaces as well as the inter-contacting particle-particle interface surfaces should be important parameters when modelling the thermal conductivity behaviour. The results of the thermophysical measurements of styrene butadiene rubber filled with pine tree particles will be used for construction and analysis of a new model of thermal transport in similar materials.

Introduction

New materials bring new problems into science. 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. The purpose of this work is to investigate the thermophysical properties behaviour of a well-defined composite material consisting of a matrix filled with particulate powder filler.

The Hot Disk Thermal Constants Analyser – sometimes referred to as the Transient Plane Source (TPS) or Gustafsson Probe [1] – 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 double spiral is placed inside an infinite and initially isothermal sample. By passing a step-wise electrical current through the spiral, heat is generated in the source and immediately dissipates into the sample. Simultaneously, the transient temperature response of the double spiral is recorded by following the resistance increase as a function of time. The relation between temperature and resistance increase is governed by the temperature coefficient of resistivity of the double spiral material.

A typical temperature increase versus time is depicted in Figure 2 (left). Typically, the total temperature increase during an experiment is between 0.2 K and 5 K – depending on the particular sample and sensor configuration used. A basic experimental setup is illustrated in Figure 1.

Figure 1 – Experimental setup of the Hot Disk Thermal Constants Analyser. The sensor is made of nickel in a form of a bifilar spiral, electrically insulated by Kapton or Mica.

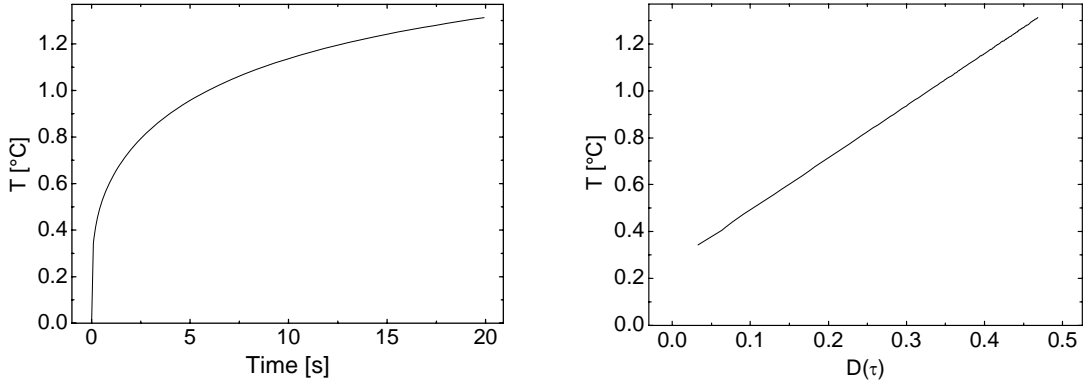
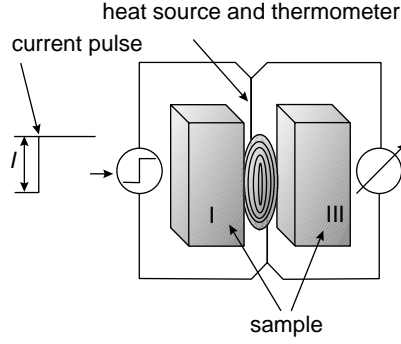


Figure 2. The transient temperature response is recorded as a function of time (left). In analysis of data the transient temperature response is linearly correlated with the dimensionless time function $D(\tau)$, according to relations 1-6 (right).

The theory of the method is characterised by a temperature function, *cf.* Equation 1, which is a solution of the partial differential equation with the boundary and initial conditions indicated above. The thermal transport parameters thermal conductivity λ and thermal diffusivity a are estimated using an appropriate model-fitting technique for the experimentally measured temperature versus time points. The average temperature increase of the double spiral can be expressed as:

$$\overline{\Delta T(\tau)} = \frac{P_0}{\pi^{3/2} r \lambda} D(\tau) \quad (1)$$

where the $D(\tau)$ function is a characteristic time-function of the probe:

$$D(\tau) = \frac{1}{[m(m+1)]^2} \times \quad (2)$$

$$\int_0^{\tau} \sigma^{-2} d\sigma \left[\sum_{l=1}^m l \sum_{k=1}^m k \exp\left\{-\frac{l^2 + k^2}{4m^2 \sigma^2}\right\} I_0\left(\frac{lk}{2m^2 \sigma^2}\right) \right]$$

$$\tau = \sqrt{t/\theta} \quad (3)$$

$$\theta = \frac{r^2}{a} \quad (4)$$

$$P_0 = R_0 I_0^2 \quad (5)$$

$$R(t) = R_0 [1 + \alpha \overline{\Delta T(\tau)}] \quad (6)$$

where R_0 is the initial electrical resistance of the double spiral, I_0 is the step-wise heat current, α is the temperature coefficient of resistivity, r is the radius of the outer concentric

circle of the double spiral and m is the number of concentric rings of the double spiral. A detailed description of the TPS or Gustafsson probe technique can be found in [1].

The ideal model presupposes that the heat source is placed in a sample of infinite dimensions. In practice, all real samples have finite dimensions. However, by restricting the total time of the transient, the experiment can still be treated as having been performed in an infinite medium, which means that the ideal theoretical model is still valid (linear part in Figure 2, right).

In our case for the evaluation we were able to use the data up to $D(\tau_{\max})=0.5$, corresponding to a real time vs. characteristic time ratio of $t_{\max}/\theta = 0.9$ (Figure 2 right).

The evaluation procedure involves the theory of the experimental method, the theoretical analysis of the sensitivity coefficients and difference analysis of experimentally measured temperature response. The analysis of the sensitivity coefficients [2, 3] gives the basic conditions for determining the time period suitable for the model fitting.

A common methodology for Contact Transient Methods (CTM), incorporating the TPS technique, have previously been published in *e.g.* [3, 4, 5]. These papers on experimental evaluation methodologies describe how a transient recording for a CTM should be evaluated. One of the advantages with the TPS technique is that it is possible to extract all thermophysical parameters – thermal conductivity, thermal diffusivity, and specific heat from one single transient recording.

Experiments

Thermophysical properties of styrene-butadiene rubber matrix filled by pine tree particles in concentration of 0, 10, 20, 40 and 60 wt. % were investigated. The composite mixtures of styrene-butadiene rubber (Krallex 1500, Kaucuk Kralupy, Czech republic) and pine tree particles of mesh 150 were prepared by mixing the components in laboratory mixer Brabender PLE 331 in a 30 ml mixing chamber at 70 °C for 14 minutes. During the mixing, vulcanization system was also added containing 5 phr ZnO, 3,5 phr Sulfenax CBS (vulcanization accelerator), 2 phr stearin and 3,5 phr sulphur. After mixing, the blend was compression molded at 150 °C for 35 minutes to thermoform the mixture and to cure the material. Photo of a series of specimen is in Figure 3.

The total porosity of the composite samples is lower than 3%. A set of composite specimens were prepared in a form of slabs having dimensions 50x75 mm and thickness 2 and 1 mm. Prepared slabs were stucked together to form a specimen set of 3+3 mm thick.

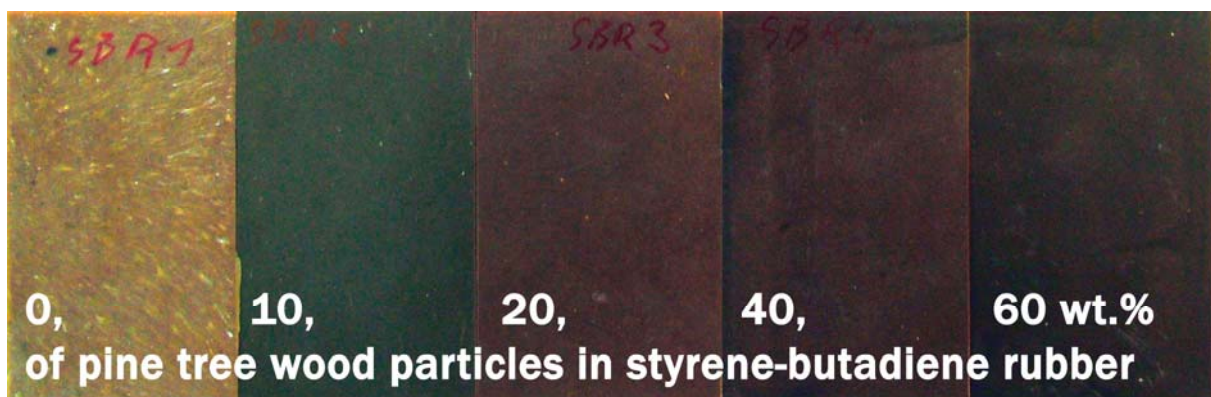


Figure 3. Photo of the styrene-butadiene rubber samples with different content of pine tree wood particles.

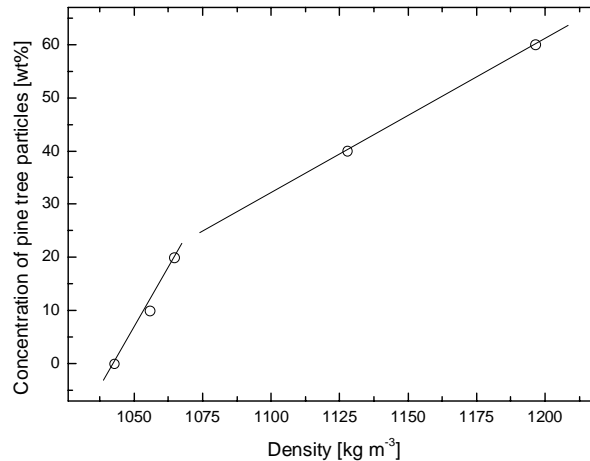


Figure 4. Concentration of pine tree particles vs. composite density.

The densities of the specimens were determined from the specimen dimensions and their weight. The densities of the investigated specimens are plotted in Figure 4. 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.

Sensor probes having a radius of 2.0 and 3.3 mm were used for the measurements. The probe was clamped in between two 3 mm thick slabs according Figure 1. The experiment was recorded during 20 seconds for a step-wise heat input with power ranging from 0.0075 up to 0.02 W. An example of the temperature response is plotted in Figure 2. Relations 1-6 were used for data evaluation by a model-fitting procedure. The temperature response becomes linear when plotted versus a dimensionless time function (Figure 2, right).

The transient recordings were evaluated in an optimal time-region, a procedure discussed previously in [3] where the time-region for data evaluation was found for total measurement times t_{\max} in a range $0.33 \leq t_{\max}/\theta \leq 1$, cf. [3]. The results are plotted in Figure 5.

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 $0.11 \text{ m}^2\text{s}^{-1}$ value for specific heat is $1699 \text{ Jkg}^{-1}\text{K}^{-1}$ and value for thermal conductivity is $0.195 \text{ Wm}^{-1}\text{K}^{-1}$. In comparison, for natural pine tree wood the values of $0.15 \text{ m}^2\text{s}^{-1}$ for thermal diffusivity, $1773 \text{ Jkg}^{-1}\text{K}^{-1}$ for specific heat and $0.12 \text{ Wm}^{-1}\text{K}^{-1}$ for thermal conductivity were measured by Pulse Transient Technique [6].

The initial assumption was that when increasing the concentration of a material having an initially lower conductivity than the rubber matrix, the conductivity of the final composite will decrease. Similar effect was observed considering the mixing rule for the specific heat. Both the natural pine tree wood as well as the rubber matrix has similar value of specific heat so the final value according the mixing rule should be similar. The results show the different 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. 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 4 and 5, 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

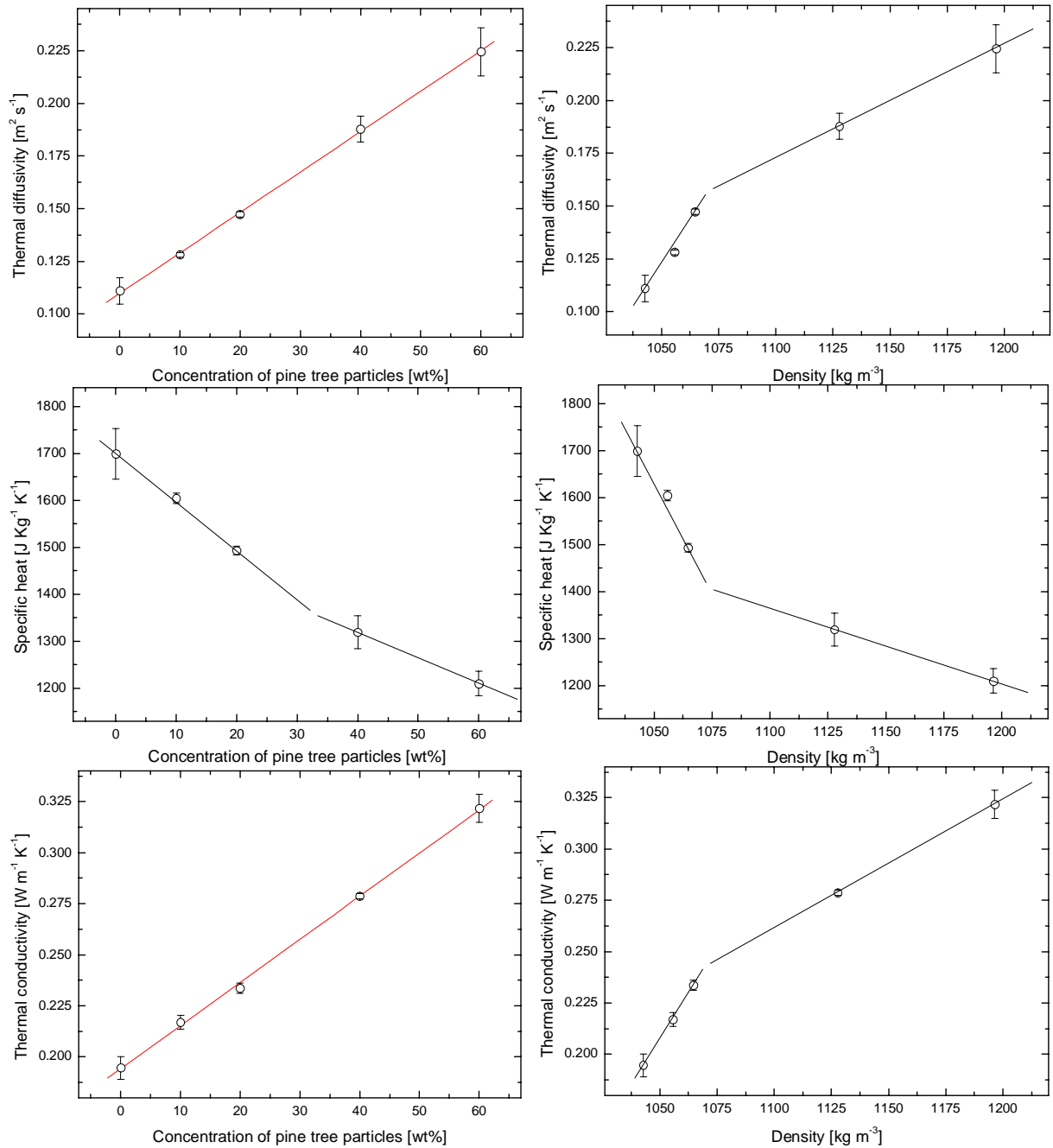


Figure 5. The dependence of the thermal diffusivity, specific heat and thermal conductivity on the concentration of pine tree particles in composite (left) and the dependence of all parameters on density (right). The value of specific heat (measured by pulse transient method [6]) for natural pine tree wood board was $1773 \text{ Jkg}^{-1}\text{K}^{-1}$, thermal conductivity $0.12 \text{ Wm}^{-1}\text{K}^{-1}$ and thermal diffusivity $0.15 \text{ m}^2\text{s}^{-1}$.

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.

The analysis of these experimental results shows that the thermophysical properties are strongly dependent on the concentration of pine tree particles. The values of thermal conductivity of the composite samples are higher than that 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 where the free volume (porosity) is minimal.

The value of thermal diffusivity for natural pine tree wood is somewhere in a middle of the range of measured values for investigated composites. Absence of pores in composite is the reason of improved heat transfer.

There were observed two regions of the dependency of thermophysical parameters on density - below and above 1070 kg m^{-3} (plotted in Figure 5, right). The break points correspond to value of about 25 weight % of pine tree particles. This effect should be caused by an increase on percolation effect when pine tree particles become inter-connecting in the composite.

Conclusions

A couple of 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 was found to increase with an increasing concentration of pine tree particles while the specific heat is decreasing.

A sudden change in dependency with density was found around 1070 kg m^{-3} , which was believed due to several reasons. The first one is the percolation effect, *i.e.* a change in the mechanisms of conducting heat transport when the particles in the matrix become interconnecting. 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.

In future work, more understanding on the mechanisms of heat transfer is hoped to be achieved for these interesting composites.

The thermophysical properties results will be used for construction and analysis of new models for description of thermal transport in these materials.

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