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Title: ***Accurate Simultaneous Measurements of Thermal Conductivity and Specific Heat of Rubber, Elastomers, and Other Materials*** for the 12th Brazilian Rubber Technology Congress

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ABSTRACT

Thermal properties – thermal conductivity, specific heat, thermal diffusivity, thermal effusivity - of rubber, elastomers, and other materials are very important parameters for their practical applications.

The most widely used for thermal conductivity measurements of insulation materials is the Heat Flow Meter Method (ASTM C518, ISO 8301, EN 1946-3, etc.). It has been modified and significantly improved by LaserComp, Inc. to be used to test materials of moderate thermal conductivity such as rubber and elastomers.

Using special Two-Thickness procedure a much higher accuracy of thermal conductivity measurements has been achieved due to total exclusion of the distorting effect of thermal contact resistance.

In computerized instruments such as LaserComp's FOX50 the heat flow meters' signals are recorded versus time which gives information about volumetric specific heat of the sample. The calculation is derived from amount of the heat flow per square area absorbed by sample after switching instrument's plates' temperature set points from one (after reaching thermal equilibrium condition) to another (until reaching new thermal equilibrium condition). Accurate experimental corrections for heat absorbed by the heat flow meters and for edge heat losses are applied to get the best accuracy.

Thermal diffusivity and thermal effusivity are calculated using the measured values of thermal conductivity and volumetric specific heat. Density of the samples is a very easy parameter to measure - after that the mass specific heat also can be calculated.

Experimental checks using several materials with known thermal properties - Pyrex 7740, Vespel SP1, Pyroceram 9606, and Perspex were done, as well as rubber samples. Measurements errors in normal conditions do not exceed 3%.

INTRODUCTION – REGULAR HEAT FLOW METER METHOD

The Heat Flow Meter Method (ASTM C518, ISO 8301, EN 1946-3, etc.) is the most widely used traditional comparative steady-state method to measure thermal conductivity of thermal insulation materials (i.e. materials of low thermal conductivity). Flat-parallel sample is sandwiched between two isothermal plates (see Fig.1). Each plate has a temperature sensor and a heat flow meter (HFM) – transducer converting the heat flow into electric voltage. The general principle of the heat flow meter instruments is based on one-dimensional equation for Fourier law in steady state:

$$q = \Delta T/(x/\lambda) = S_{cal}\, Q \qquad [W/m^2] \qquad (1)$$

where q is heat flux (W/m^2) flowing through the sample, λ is its thermal conductivity ($W\ m^{-1}\ K^{-1}$) of the sample, x is sample's thickness (m), Q is electric output of the heat flow meter, and S_{cal} is calibration factor of the heat flow meter. Physically, calibration factor S_{cal} is a heat flux necessary to create 1 μV (or sometimes 1 mV) electric voltage (signal) on the transducer's output.

This Fourier law expression looks similar to the well-known Ohm's law, where heat flux q is analogous to an electric current, temperature difference ΔT – to voltage difference, and thermal resistance $R_{sample} = x/\lambda$ - to electric resistance.

For low conductivity materials the thermal contact resistances plus the two heat flow meters' resistances (for both sides of the sample) $2R$ are negligible in comparison with the samples' thermal resistances x/λ:

$$2R << x/\lambda \qquad [m^2K\ W^{-1}] \qquad (2)$$

and simple formulas (3) and (4) are valid:

$$S_{cal} = \Delta T/[(x_{cal}/\lambda_{cal})Q_{cal}] \qquad [(W/m^2)/\mu V] \qquad (3)$$

Calibration sample with reliable the rmal conductivity values (usually issued and certified by metrological institutions like NIST, IRMM, NPL, etc.) should be used to calibrate heat flow meter instrument.

After that samples of unknown thermal conductivity can be measured:

$$\lambda_{test} = S_{cal}\, x_{test}\, Q_{test} / \Delta T \qquad (4)$$

$$\lambda_{test} = \lambda_{cal}\, (x_{test}/x_{cal})(Q_{test})/ Q_{cal}) \qquad (4a)$$

where ΔT is temperature difference between the plates (i.e. between the temperature sensors) – same for calibrations and tests, Q are signals of the heat flow meters (transducers).

Calculation formulas (3) and (4) used in the Heat Flow Meter Method (ASTM C518, ISO 8301, EN 1946-3, etc.) are simple, but they are accurate only in case of samples of low thermal conductivity, i.e. when thermal contact resistance is negligible in comparison with the sample's thermal resistance. For samples of intermediate thermal conductivity like rubber, for example, those regular formulas become not very accurate both for calibrations of the Heat Flow Meter instruments and for tests, and the errors depend on ratio of the contact and the sample's thermal resistances [1, 2] which is not negligible anymore.

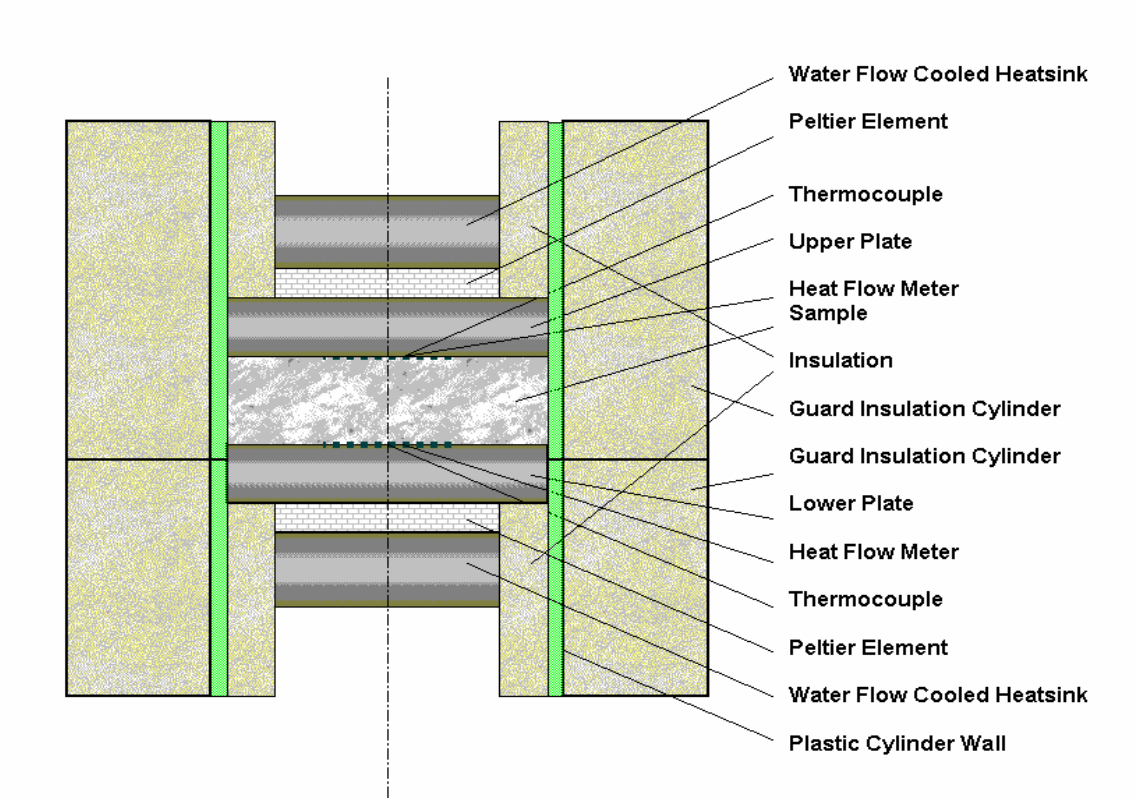

Figure 1 – Simplified drawing of the FOX50 Heat Flow Meter instrument, LaserComp, Inc. (not all parts are shown).

The thermal contact resistance R is equal to temperature difference δT [K] between two contacting surfaces divided by heat flux q [W/m^2]:

$$R = \delta T / q \qquad [\mathrm{m^2 K\ W^{-1}}]$$

and depends on the types of adjoining materials, their surface roughness, and the interface pressure. Although the subject has been studied for a long time, still very little is known about the complex mechanism of heat transfer at the contact between two bodies [3-5].

TWO THICKNESS METHOD

When testing materials of intermediate thermal conductivity (~0.1 <λ< ~20 W/mK), and, a fortiori, in case of higher conductivity materials, the thermal contact resistance plus HFM's resistance $2R$ can not be neglected. It must be excluded, otherwise significant errors may result – especially in case of thin samples and/or of higher thermal conductivity when the thermal resistance $2R$ may even exceed the sample's thermal resistance x/λ.

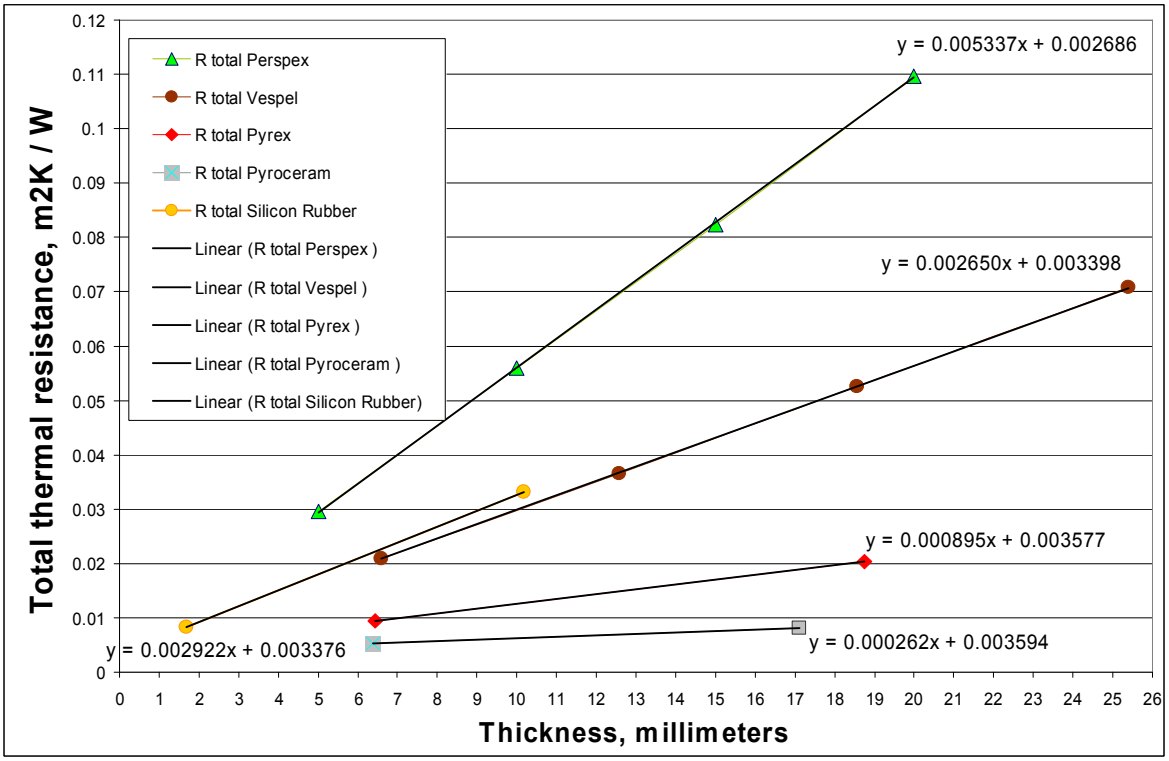

Figure 2 – Total thermal resistance vs. thickness in millimeters for several calibration samples and solid silicon rubber (Cohrlastic ® 700) at 25^0C mean temperature. Extrapolations down to zero thickness give values of the thermal contact resistance 2R. Reciprocals of the slopes (divided by 10^3) give accurate values of thermal conductivity λ.

Blunt and very labor-consuming way to exclude thermal contact resistance is using thermocouples placed directly into grooves machined on the sample to measure temperatures of the sample's surfaces.

Use of thermo conductive grease can only diminish thermal contact resistance but not to eliminate it and HFMs' thermal resistance.

Total thermal resistance $R_{total} = (x/\lambda) + 2R$ should be used in denominator of the Eq. (1). Corrected relation between the heat flux q and all other parameters now is:

$$q = \Delta T / [(x/\lambda) + 2R] = S_{cal}\, Q \qquad (1a)$$

Electric signal Q of the heat flow meter is proportional to the heat flux q, which in steady state condition is equal to temperature difference ΔT divided by the total thermal resistance - sum of thermal resistance of the sample x/λ and two thermal surface resistances $2R$, which includes contact resistance between adjoined surfaces and all thermal resistance between temperature sensors and samples' surfaces.

An accurate and effective way of excluding the thermal contact resistance is the Two Thickness Method [1]. By using at least two samples of the same material with

different thicknesses x_1 and x_2 a system of two equations containing two unknown values can be solved:

$$S_{cal}\, Q_1 = \Delta T / (x_1/\lambda + 2R) \quad (1b)$$

$$S_{cal}\, Q_2 = \Delta T / (x_2/\lambda + 2R) \quad (1c)$$

where Q_1 and Q_2 are signals from the heat flow transducers, x_1 and x_2 are thicknesses of thin and thick samples. We assume that the thermal contact resistances for both samples are the same. Solution of the system of the two Eqs. (1b) and (1c) for calibrations is:

$$S_{cal} = \Delta T\, \lambda_{cal}\, (Q_1 - Q_2)/[Q_1 Q_2 (x_2 - x_1)] \quad (5)$$

$$2R_{cal} = (x_2 Q_2 - x_1 Q_1)/[\lambda_{cal}\, (Q_1 - Q_2)] \quad (6)$$

Ideally, all the calibration runs should give the same values of the calibration factor no matter which method or what reference material was used for calibration, because calibration factor is a physical property of the heat flow meter.

For calibrations of the LaserComp's FOX50 Heat Flow Meter instruments four materials with known thermal conductivity [6-9] – Pyrex 7740, Pyroceram 9606, Vespel® DuPont™ SP1, and Perspex are used (accuracy of the values is believed to be about 2-3%; ~5% for Pyroceram):

TABLE I. THERMAL CONDUCTIVITY OF CALIBRATION MATERIALS, (W/mK)

T, ^{0}C	Perspex [8]	Vespel	Pyrex 7740 [5]	Pyroceram 9606, TPRC
0	0.1860	0.365	1.063	4.15
20	0.1885	0.371	1.086	4.04
40	0.1909	0.377	1.115	3.94
60	0.1933	0.386	1.145	3.85
80	-	0.389	1.175	3.78
100	-	0.396	1.203	3.71
For high temperature versions of the FOX50 HFM Instrument:				
150	-	0.411	1.270	3.58
200	-	0.426	1.330	3.49
250	-	0.441	1.391	3.42
300	-	0.457	1.452	3.34

Correct value of thermal conductivity can be calculated using the Two-Thickness procedure and following formula – solution of the system of the two Eqs. (1b) and (1c):

$$\lambda = S_{cal}\, Q_1 Q_2 (x_2 - x_1)/[\, \Delta T\, (Q_1 - Q_2)] \qquad (7)$$

$$2R = (x_2 Q_2 - x_1 Q_1)\, \Delta T/[(Q_1 Q_2 S_{cal}(x_2 - x_1)] \qquad (8)$$

It can be calculated from the slope (reciprocal value) of the graph of the total thermal resistance against thickness of the samples as well (see Fig.2 and Fig.3).

Two-thickness and Multi-thickness procedures of calibrations and tests [1] effectively eliminate thermal contact resistance errors. These procedures are used in LaserComp's FOX50 Heat Flow Meter instrument and WinTherm50 software both designed to obtain the best possible accuracy for thermal conductivity measurements of such samples.

In computerized systems the heat flow meters' (transducers') signals can be recorded versus time. The recorded signals can give additional information about other important thermal properties of the samples –volumetric specific heat and thermal diffusivity.

Volumetric specific heat can be calculated simply from amount of the heat flow per square area absorbed by sample after switching instrument's plates' temperature set points from one (after reaching thermal equilibrium condition) to another (until reaching new thermal equilibrium condition) .

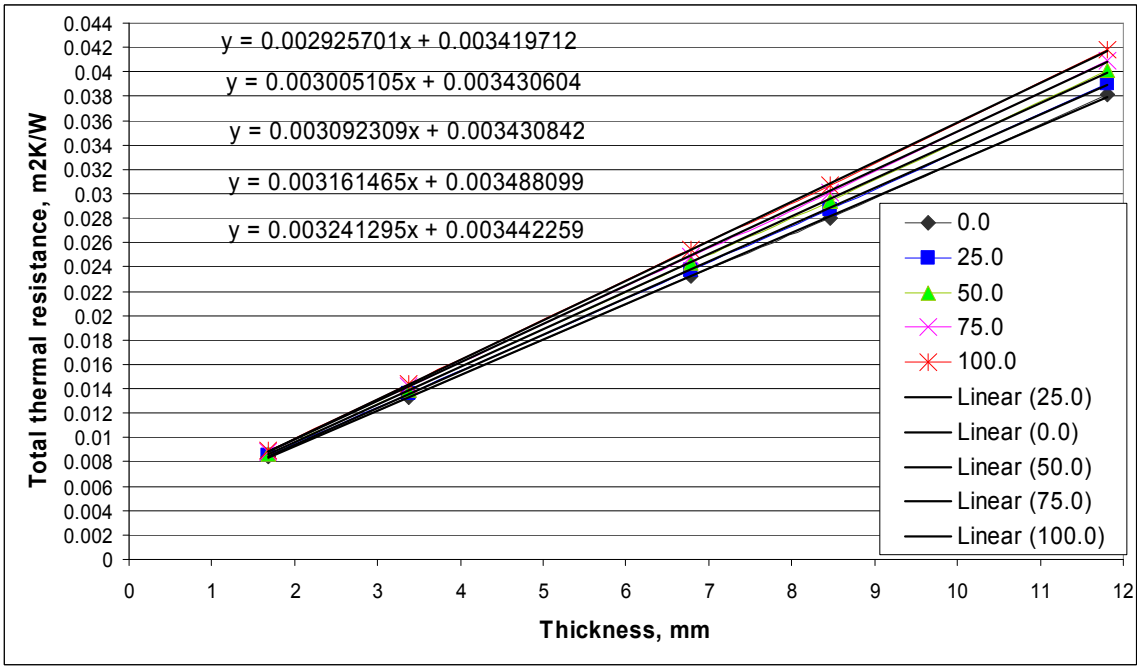

Figure 3 – Total thermal resistance vs. thickness in millimeters for samples of solid silicon rubber (COHRlastic ® 700 – 1, 2, 4, 5, and 7 layers) at different meant temperatures. Extrapolations down to zero thickness give values of the thermal resistance 2R. Reciprocals of the slopes (divided by 10^3) give values of thermal conductivity λ.

VOLUMETRIC SPECIFIC HEAT MEASUREMENTS PROCEDURE USING HFM INSTRUMENTS

Heat Flow Meter (HFM) instruments are routinely used for thermal conductivity λ (W m^{-1} K^{-1}) measurements only, although their heat flow meters' signals recorded versus time contain information about other important thermal properties of the samples – volumetric specific heat $C_p\rho$ (J m^{-3} K^{-1}) (ρ is density in kg m^{-3}), thermal diffusivity $a=\lambda/C_p\rho$ (m^2s^{-1}), and thermal effusivity $\varepsilon=(\lambda\, C_p\rho)^{1/2}$. Some efforts in this direction were already undertaken (see e.g. Nicolau, et. al. [10], Bae [11]). If any two of the four mentioned thermal properties - λ, $C_p\rho$, a, and ε - are known, then other two can be calculated, i.e. full set of the four thermal properties can be determined. We developed and tried new procedure to get second of these additional thermal properties (which are described below) – volumetric specific heat, using our LaserComp's FOX Heat Flow Meter instruments and their modified software algorithms, by calculating amount of heat absorbed by the sample from instrument's plates.

The heat flow meters' readings QU_i (upper plate) and QL_i (lower plate) are proportional (and direction-sensitive) to the heat flow's densities (W/m^2) in or out of the two sides of the sample, multiplied by the time interval τ between the readings, and then summed give us the total amount of heat absorbed by the sample (per unit of square area). I.e. the heat flow meter instruments can work like calorimeters. HFM signals at the final equilibrium condition QU_{equil} and QL_{equil} should be subtracted from each of the readings otherwise the total sum will never reach its plateau, and will keep slowly drifting because of the practically inevitable small edge heat losses (or, in case of low temperatures, gains):

$$H = \sum_{i=1}^{N} [SU_{cal}(QU_i - QU_{equil}) + SL_{cal}(QL_i - QL_{equil})]\tau$$

where SU_{cal} and SL_{cal} are the two HFMs' (upper and lower) calibration factors.

This sum H also contains amount of heat absorbed by the two heat flow meters themselves, which, as was proven by our experiments, is not negligible, and should be excluded to get accurate values of the $C_p\rho$. Heat capacity of the heat flow meters $C_p`\rho`2\delta x$ can be found from the energy conservation equation:

$$C_p\rho\, x + C_p`\rho`2\delta x` = H/\Delta T$$

where ΔT is temperature change, $C_p`\rho`$ and $2\delta x`$ is specific heat and thickness of the two heat flow meters, using different ways: 1) simply running specific heat test with no sample (closed plates should have same temperatures simultaneously increased or decreased) – all the heat is absorbed by the heat flow meters only; 2) running specific heat tests using thin sample of material of known specific heat; 3) running two (or more) the same material samples of two (or more) different thicknesses – thin x_1 and thick x_2 – for whom we have system of 2 equations with 2 unknowns:

$$C_p\rho\, x_1 + C_p`\rho`2\delta x` = H_1/\Delta T$$

$$C_p\rho\, x_2 + C_p`\rho`2\delta x` = H_2/\Delta T$$

Solving this system of 2 equations we can find both the volumetric specific heat of the samples:

$$C_p\rho = (H_2 - H_1) / [(x_2 - x_1)\ \Delta T]$$

and heat capacity of the two heat flow meters (per their square area):

$$C_p`\rho`\ 2\delta x` = (H_1 x_2 - H_2 x_1) / [(x_2 - x_1)\ \Delta T]$$

Or, in case of no sample between the plates (i.e. HFM's heat capacity measurements):

$$C_p`\rho`\ 2\delta x` = H / \ \Delta T$$

then to be excluded as the apparatus constant (which is temperature dependent) to get correct specific heat of a single sample test:

$$C_p\rho = (H/\Delta T - C_p`\rho`\ 2\delta x`) / x$$

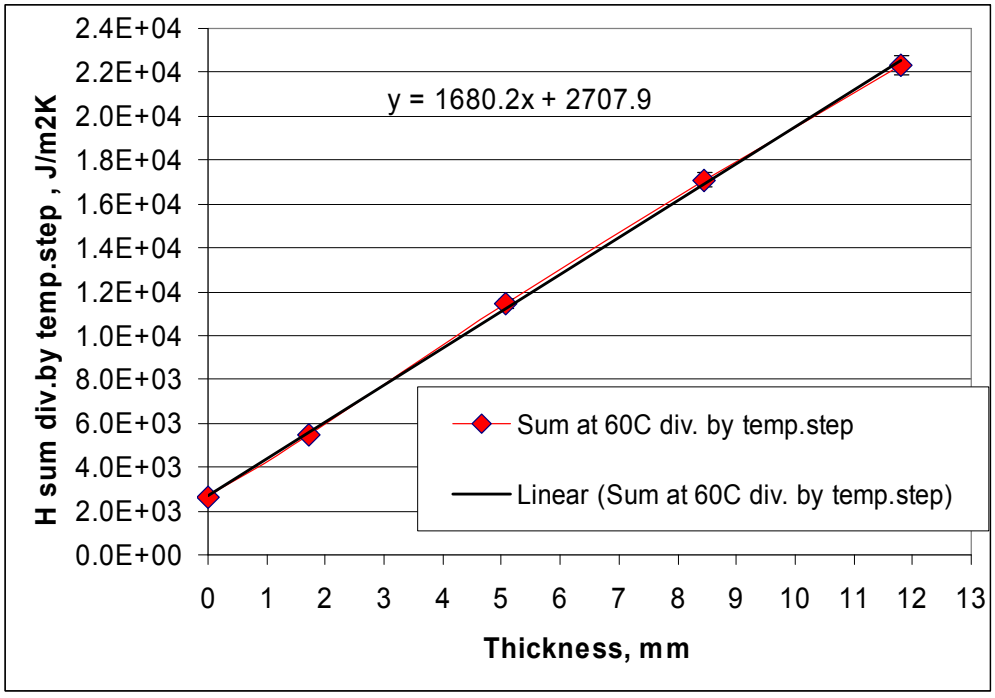

Figure 4. Graph of the H sum divided by temperature step (20^0C) vs. thickness in millimeters for COHRlastic ® Silicon Rubber (1, 3, 5 and 7 layers) for temperature change from 50^0C to 70^0C. Slope equals the volumetric specific heat $C_p\rho$ divided by 10^3. Point at zero thickness is measured heat capacity of the HFMs (per square area).

As experimental checks proved, the most accurate way to determine the HFMs' heat capacity C_p`$\rho$` $2\delta x$` is the first one - direct measurements with run of temperature change with closed instrument's plates and with no sample. After that the specific heat can be accurately determined using the latter formula.

Special versions of WinTherm50 (for intermediate thermal conductivity samples) (and WinTherm32 - for thermal insulation samples) software used by the LaserComp's FOX Heat Flow Meter instruments have been developed for the volumetric specific heat $C_p\rho$ measurements in addition to the routinely measured thermal conductivity. Specific heat measurements can be done simultaneously with the regular thermal conductivity tests. Temperature jump in this case is difference between mean temperatures of the two consecutive set points. For example, if plates' temperatures (set points) are 10^0C and -10^0C (mean 0^0C), 35^0C and 15 (mean 25^0), then temperature jump is 25^0C and the resulting specific heat value should be referred to the mean temperature of the two mean temperatures – i.e. to 12.5^0C.

Tests of several materials with known volumetric specific heat values recently were done [12] to prove that this new method gives correct and reliable results. Our results agree within 3-5% with literature data for Expanded Polystyrene, for 1450b - Standard Reference Material for thermal conductivity, for Vespel, for Pyrex 7740, for Pyroceram 9606, and for Stainless Steel 304. Volumetric specific heat measurements results of the COHRlastic ® 700 silicon rubber (Saint-Gobain Performance Plastics, durometer 70) are presented on Graph 3.

Two more important thermophysical properties – thermal diffusivity a, and thermal effusivity ε can be calculated from thermal conductivity and volumetric specific heat:

$$a = \lambda / C_p\rho \qquad [m^2\ s^{-1}]$$

$$\varepsilon = (\lambda C_p\rho)^{1/2} \quad [W\ s^{1/2}\ m^{-2}\ K^{-1}]$$

Thermal diffusivity is more generally applicable than thermal conductivity in most heat transfer problems. Thermal effusivity is a measure of material's ability to exchange thermal energy with its surroundings.

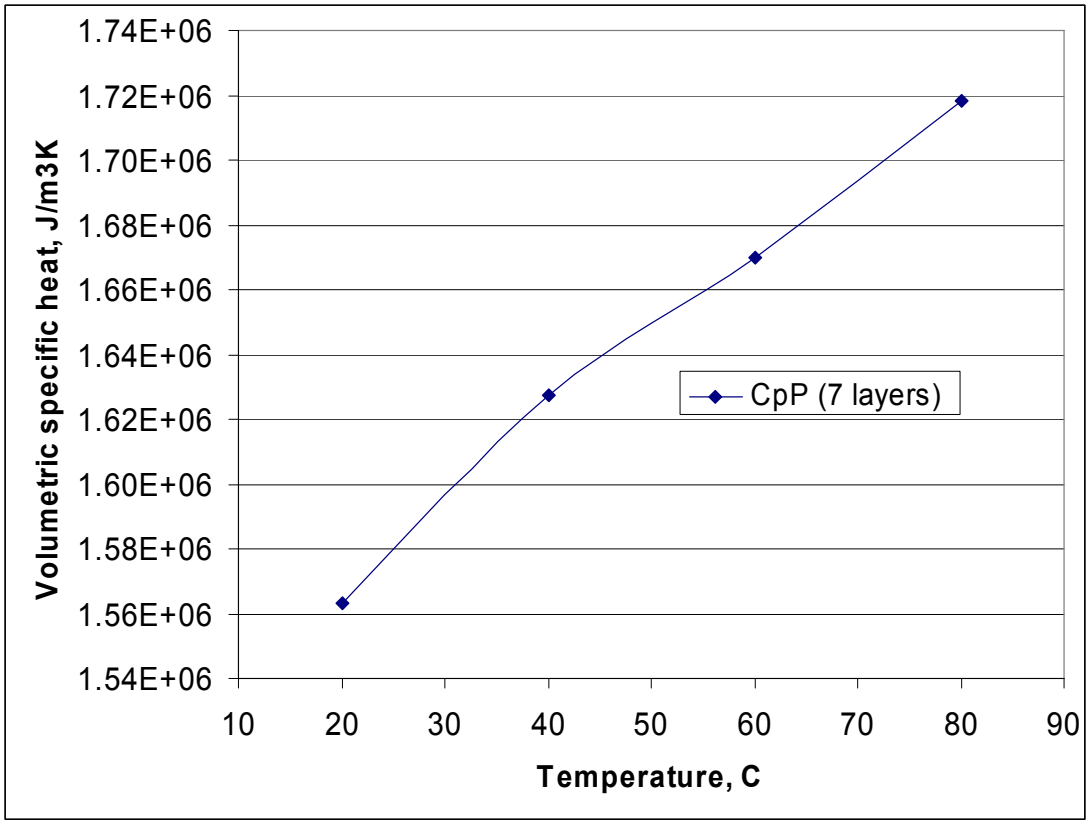

Figure 5. Volumetric specific heat $C_p\rho$ of COHRlastic ® 700 Silicon Rubber measured by FOX50 Heat Flow Meter instrument vs. temperature

CONCLUSIONS

Two Thickness procedures of calibrations and tests used in the LaserComp's FOX50 Heat Flow Meter instrument and its "WinTherm50" software provide excellent accuracy of thermal conductivity tests of materials like rubber, elastomers, glasses, ceramics, plastics, polymers, etc. It was shown that old simple formulas used in regular heat flow meter instruments give wrong results for such materials because of the presence of thermal contact resistance and thermal resistance of the heat flow meters. The Two-Thickness procedure of calibrations and tests provides significantly improved accuracy of thermal conductivity measurements compared to existing procedures. E.g. ASTM E1530 (Standard Test Method for Evaluating Thermal Resistance to Thermal Transmission of Materials by the Guarded Heat Flow Meter Technique) presents only one-digit accuracy (e.g. Pyroceram thermal conductivity is 4 W/mK, Pyrex – 1 W/mK, etc.), whereas the Two-thickness tests usually have three-digit accuracy (i.e. 3 reliable digits).

The FOX50 Two Thickness Analysis enables the User to perform this procedure simply and easily by merely entering a second sample of the same material at a different thickness into the FOX50 when the first sample's test has finished. LaserComp has performed hundreds of Two Thickness Analyses and our data has shown the very real and significant advantages of this Procedure.

Possibilities of the traditional Heat Flow Meter method have been significantly extended by using recorded signals of the heat flow meters versus time and presented algorithms to calculate additional important thermophysical properties – volumetric specific heat. Then two more thermophysical properties – thermal diffusivity and thermal effusivity can be calculated from thermal conductivity and volumetric specific heat, so full set of all four thermal properties now can be obtained using LaserComp's FOX Heat Flow Meter instruments with new updated versions of their software.

REFERENCES

1. Brzezinski, A., and A. Tleoubaev. 2002. "Effects of Interface Resistance on Measurements of Thermal Conductivity of Composites and Polymers," in *Proceedings of the 30th Annual Conference on Thermal Analysis and Applications (NATAS),* K. J. Kociba, ed. Pittsburgh: B&K Publishing, pp.512-517.
2. Tleoubaev, A. and A. Brzezinski, 2007. "Errors of the Heat Flow Meter Method Caused by Thermal Contact Resistance" presented at the Thermal Conductivity 29 / Thermal Expansion 17 Conference, June 2007, Birmingham, Alabama.
3. Holman, J. P. 1997. *Heat Transfer*, 8th Edition, New York, etc.: McGraw-Hill Book Company, pp. 56-59.
4. Kubičár, L. 1990. *Pulse Method of Measuring Basic Thermophysical Parameters*, *(Wilson and Wilson's Comprehensive Analytical Chemistry:* v.12, Pt.E), New York, etc.: Elsevier, pp. 44-62.
5. Fletcher, L. S. 1993 *Experimental Heat Transfer, Fluid Mechanics and Thermodynamics,* , pp. 195-206.
6. Powell, R.W., C. Y. Ho, and P. E. Liley. 1966. *Thermal Conductivity of Selected Materials*, National Standard Reference Data Series – NBS, Vol 8, 25 November.
7. Hulstrom. L. C., R. P. Tye, and S. E. Smith. 1985 "Round-Robin Testing of Thermal Conductivity Reference Materials," in: *Thermal Conductivity 19*, D. W Yarborough, ed. New York: Plenum Press, pp.199-211.
8. Filla, B. J., and A. J. Slifka. 1999. "Thermal Conductivity Measurements of Pyroceram 9606 Using a High-Temperature Guarded-Hot-Plate" in: *Thermal Conductivity 24*, P. S. Gaal and D. E. Apostolescu, eds. Lancaster: Technomics, pp. 85-96.
9. Tye, R. P., and D. R. Salmon. 2001. "Thermal Conductivity Certified Reference Materials: Pyrex 7740 and Polymethylmethacrylate" in *Thermal Conductivity 26,* R. B. Dinwiddie and R. Mannello, eds. Lancaster: DES*tech* Publications, pp. 437-451.
10. Nicolau, V.P., S. Guths, and M. G. Silva. 2002. "Thermal Conductivity and Specific Heat of Low Conductivity Materials Using Heat Flux Meters," in *The 16th European Conference on Thermophysical Properties,* Imperial College, London.
11. Bae, S.C. 1989. "Transient Measurements of Insulation Materials," in *Thermal Conductivity 20*, Proceeding of the 20th International Thermal Conductivity Conference, Oct.1987, Blacksburg, Virginia. D. P. H. Hasselman and J. R. Thomas, Jr., eds. New York: Plenum Press, pp.389-401.
12. Tleoubaev, A. and A. Brzezinski, 2007. "Thermal Diffusivity and Volumetric Specific Heat Measurements Using Heat Flow Meter Instruments" presented at the Thermal Conductivity 29 / Thermal Expansion 17 Conference, June 2007, Birmingham, Alabama.