Using of cross-linking protein hydrolysates for preparing of thermo-insulating panels from printed circuit boards waste

Dagmar Janáčová, Hana Charvátová, Pavel Mokrejš, Vladimír Vašek,
Antonín Blaha, Karel Kolomazník, Gordana Paravanová

Abstract—The paper describes possibility to use recycled printing circuit boards plastic materials to manufacturing of thermo-insulating panels. It describes methods used for finding of an optimal composition of adhesive mixture made of hycol and crotonaldehyde as crosss-linking agent. In the second part are presented results obtained by laboratory testing of thermo-insulating properties of panels made of plastic meal stucked together by the prepared adhesive mixture.

Keywords—Printed circuit boards waste, hycol, crotonaldehyde, thermo-insulating panels, thermal conductivity determination, cross-linking degree.

I. INTRODUCTION

The electronic waste recycling became a necessity with consumer electronics development in the recent years because the price reducing of electronics leads to its massive consumption and currently to reducing of its life time. The used up electronics usually ended at dumps of the solid and hazardous waste.

At our workplace we targeted the used up possibility of the electronic waste usage especially coming from

H. Charvátová, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: charvatova@fai.utb.cz)

D. Janáčová, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic; phone: +420 576 035 274; fax: +420 576 032 716; e-mail: janacova@fai. utb.cz

K. Kolomazník, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: kolomaznik@fai.utb.cz)

P. Mokrejš, Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: mokrejs@ft. utb.cz)

A. Blaha, Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: blaha@ft. utb.cz)
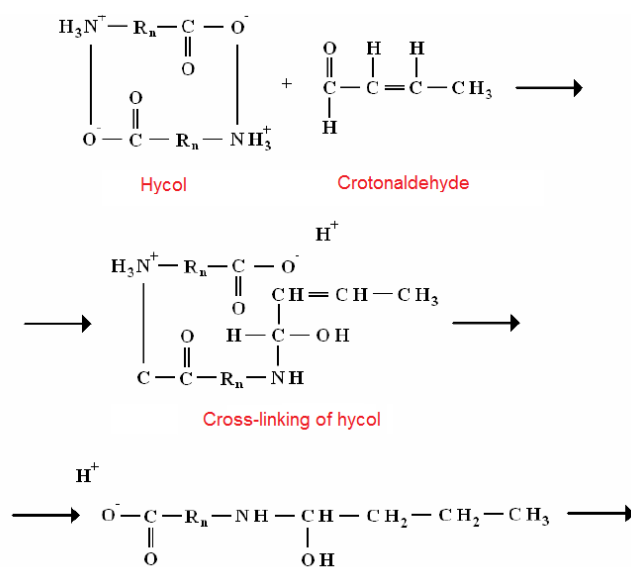
G. Paravanová, Tomas Bata University in Zlín, University Institute, Centre of Polymer Systems, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: paravanova@cps. utb.cz)
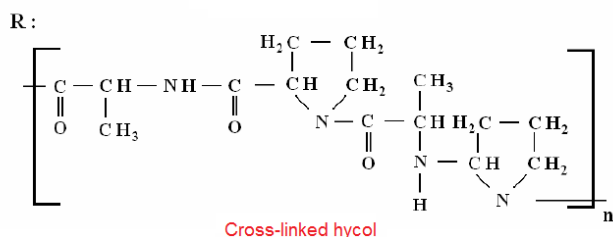
computer technology as a source of valuable raw material because these products contain a lot of worth components so as materials which are malignant for environment. From this point of view, we deal with personal computer recycling.

From this account we deal with finding of an optimal method of separation of plastic boards from conductive ways of printed circuit boards which are basic parts of all computers [1], [2]. The separated plastic material we would like to use for manufacturing of thermo-insulating panels.

II. PREPARING OF ADHESIVE MIXTURE FOR STICKING OF PLASTIC MELT

Main aim of our research is to made panels which will be thermo-insulating and stable to climatic influences and will be not unhealthy. Furthermore manufacturing of the panels have to be economically advantageous.

On this account we have tested properties of hycol as an alternative adhesive of panels. Hycol is a protein hydrolysate. It is a recycling product of solid tanned waste treatment produced by enzymatic hydrolyze in leather industry. But the problem which we had to solve was its solubility in water. This disadvantageous of hycol we tried to eliminate by cross-linking by use crotonaldehyde as cross-linking agent [4]. The cross-linking process can be described by following chemical reactions [4]:

Cross-linked hycol

Fig. 2 Tested samples with 30 % of crotonaldehyde at the beginning of dissolving in distilled water. Time of cross-linking: 5 minutes (left sample), 8 minutes (middle sample), 10 minutes (right sample).

III. TESTING OF AN OPTIMAL COMPOSITION OF ADHESIVE MIXTURE BY DISSOLUTION IN WATER

The laboratory testing consisted in finding of an optimal weight ratio of of crotonaldehyde in prepared adhesive mixture so the stucked together panels will be waterproof.

Preparing of tested mixtures

The tested samples were prepared from Hycol, crotonaldehyde and phthalic acid, which was used as stabilizer. The weight composition of the mixtures we show in Table 1.

Table 1. Material composition for tested adhesive mixtures

Ingredients	Weight ratio with regard to dry matter of hycol [%]
Hycol (30 weight % of dry matter)	-
Phthalic acid	1
Crotonaldehyde	0 - 50

The prepared mixtures with various content of crotonaldehyde were dried to constant weight under laboratory conditions. After them they were put into the kiln at temperatures 180°C for 5 minutes, 8 minutes and 10 minutes. The cross-linked samples were put into distilled water and their dissolving for 24 hour was tested.
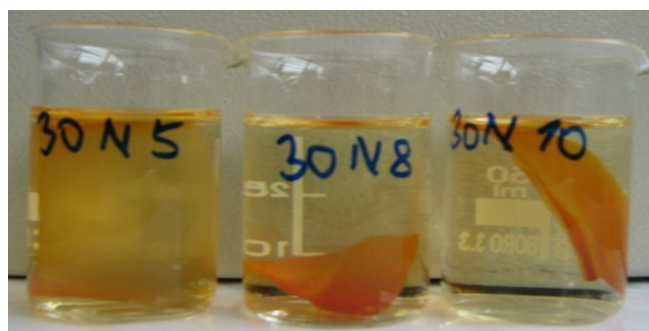

Fig. 3 Tested samples with 30 % of crotonaldehyde after 24 hours of dissolving in distilled water. Time of cross-linking: 5 minutes (left sample), 8 minutes (middle sample), 10 minutes (right sample).

This method enables to determine dissipation factor, that is the ratio of the power loss in a dielectric material to the total power transmitted through the dielectric, the imperfection of the dielectric. Equal to the tangent of the loss angle [5]:

$$D = \frac{\varepsilon''}{\varepsilon'} = \tan \delta = \frac{1}{2\pi f C_p R_p} \qquad (1)$$

where

f - frequency of applied voltage in cps,
C_p - equivalent parallel capacity,
R_p - equivalent parallel resistance,
δ - loss angle.

Aim of our testing was to verify an optimal time of cross-linking determined by above described method. We supposed that optimal time of cross-linking can be proved by change of dissipation factor of molecules of the tested mixtures.

The tested samples were prepared according the table 1. After them, they were dried to constant weight under laboratory. The measuring apparatus was prepared in conjunction of Department of Electronics and Measurements of Faculty of Applied Informatics at Tomas Bata University in Zlin. The measuring instrument was connected with software for evaluation of the measured data and with system of electrodes with tested sample (Fig. 4) [5].

Fig. 1 Tested samples before cross-linking: weight ratio of crotonaldehyde: 30 %

Dielectric spectroscopy measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity [5].

Computer with software Aligent VeePro

Measuring instrument Agilent 4263B

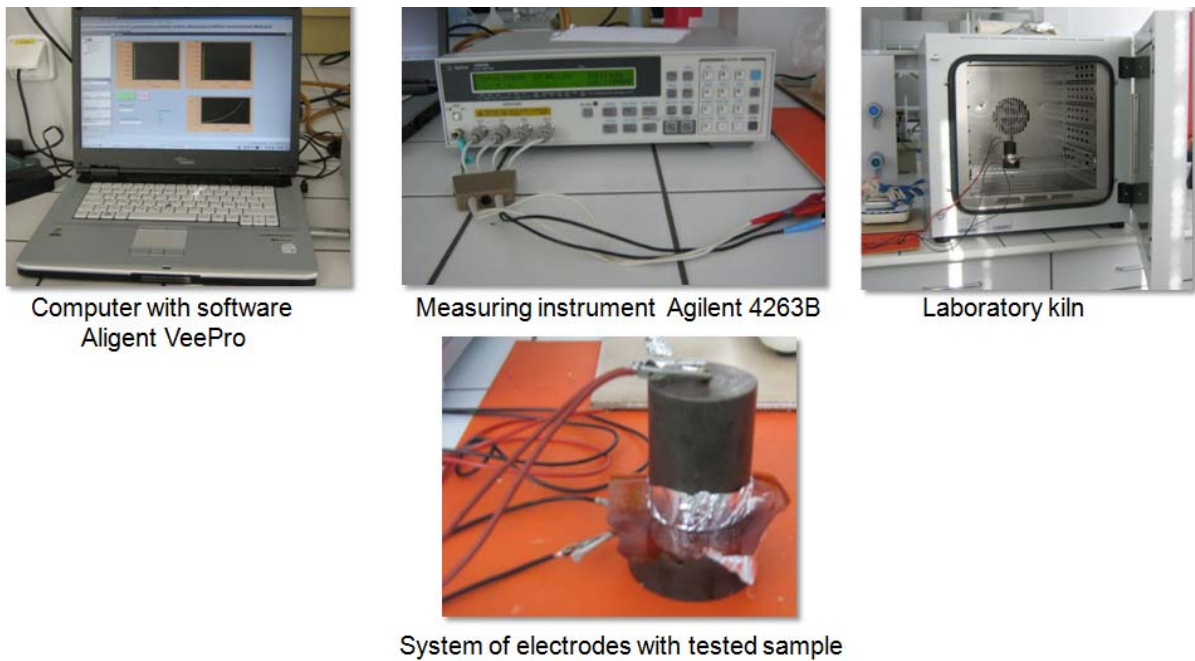Laboratory kiln

System of electrodes with tested sample

Fig. 4 Scheme of laboratory apparatus for determination of a dissipation factor in tested adhesive mixtures

First we searched an optimal temperature for cross-linking For this purpose we put samples into the kiln at 25 °C and measured dissipation factor during heating to temperature 230 °C. The obtained results are depicted in Fig. 5. But the measured data were inaccurate. In most of tested samples, the maximal values of dissipation factor were at temperatures about 180°C and 230 °C and minimal values were at temperature about 180 °C. Therefore we choose temperatures 140°C and 180 °C for other testing of cross-linking process.
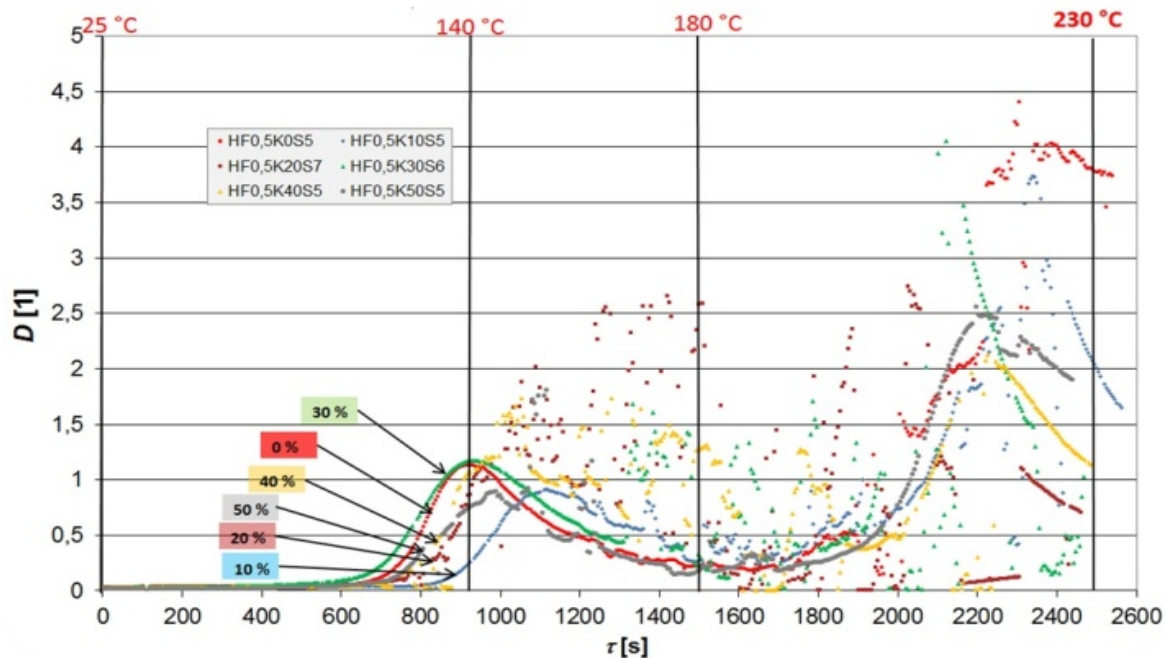

Fig. 5 Dependence of dissipation factor on temperature in the kiln. Mass ratios of crotonaldehyde in tested samples : 0% , 10%, 20%, 30%, 40%, 50 %.

For testing of an optimal time of cross-linking, we put the electrodes with samples into the kiln for 1 hour. The Fig. 6 and Fig 7 show determined data at tested temperatures 140 °C and 180 °C. But the obtained results didn´t prove dependence between content of crotonaldehyde and optimal time of cross-linking. The measured data were inaccurate as

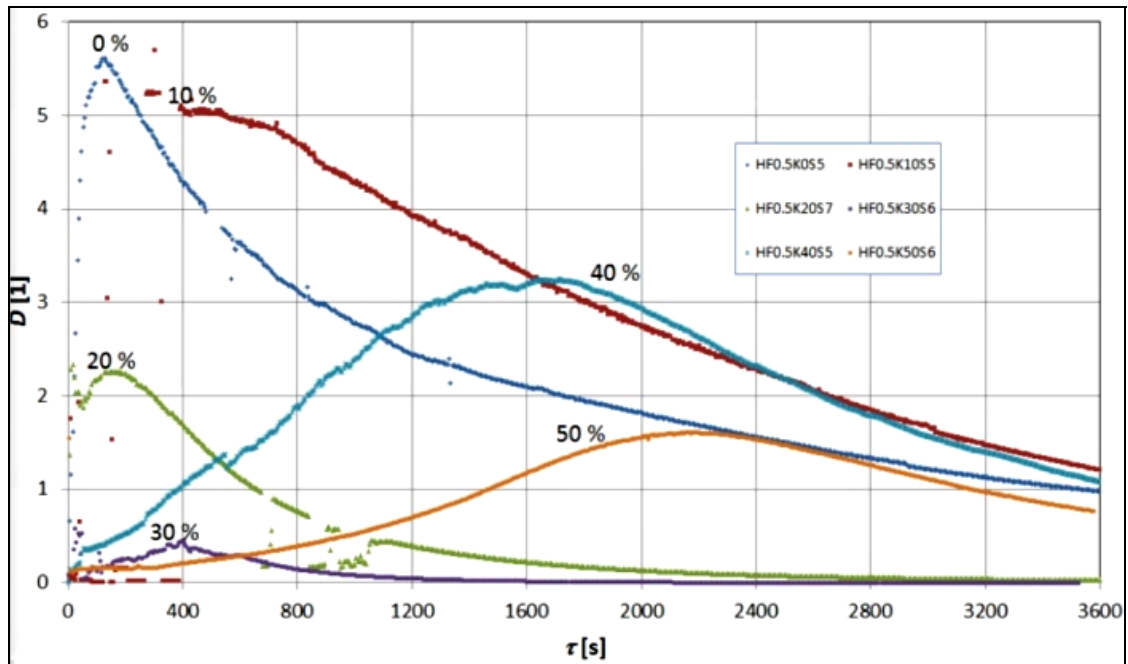by previous testing of optimal temperature of cross-linking.

Fig. 6 Measuring of dissipation factor during cross-linking at temperature 140 °C. Mass ratios of crotonaldehyde in tested samples: 0% , 10%, 20%, 30%, 40%, 50 %.
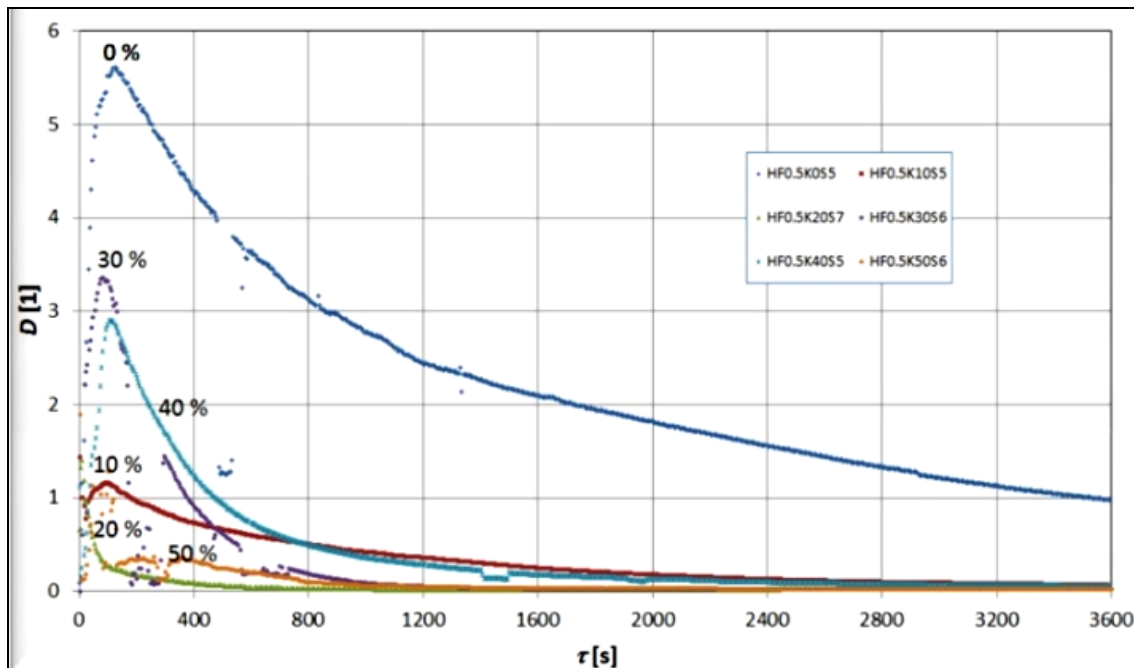

Fig. 7 Measuring of dissipation factor during cross-linking at temperature 180 °C. Mass ratios of crotonaldehyde in tested samples: 0% , 10%, 20%, 30%, 40%, 50 %.

IV. PREPARING OF THERMO-INSULATING PANEL SAMPLES

With regard to above presented results, we prepared adhesive mixture of the composition:
- hycol with 30 weight % of dry matter,
- crotonaldehyde of weight ratio 30 % with regard to dry matter of hycol,
- Phthalic acid of weight ratio 30 % with regard to matter of hycol.

We compounded the mixtures with plastic melts with granulity until 0.5 mm to 3 mm. After them, we pressed the samples by laboratory press at temperature 150°C in specially prepared form (Fig 8 and Fig.9). The thermo-insulating panel samples after pressing are shown in Fig. 10.

Fig.8 Form for manufacturing of thermo-insulating panel samples

Fig. 9 Laboratory press for manufacturing of thermo-insulating panel samples
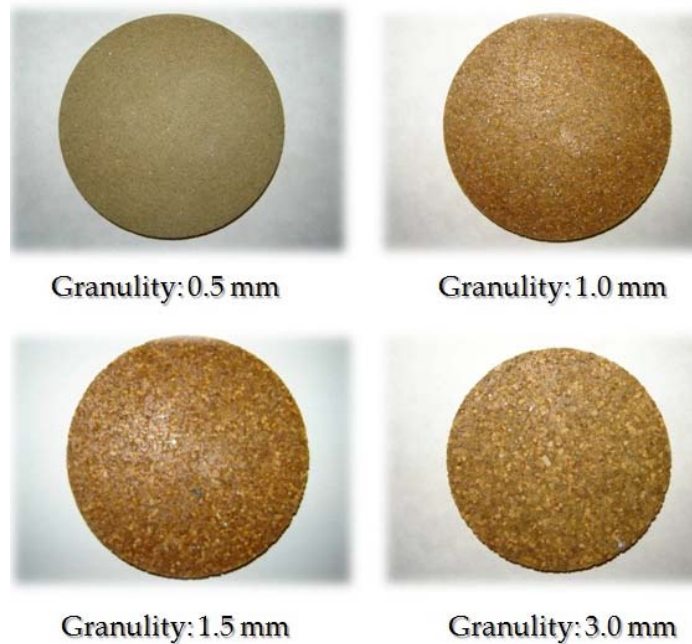

Granulity: 0.5 mm

Granulity: 1.0 mm

Granulity: 1.5 mm

Granulity: 3.0 mm

Fig. 10 Thermo-insulating panels samples after pressing

V. THERMAL CONDUCTIVITY OF THERMO-INSULATING PANEL SAMPLES MEASURING

The thermal conductivity of prepared panels we measured by apparatus according to Fitch (Fig. 11). The principle was measuring of thermal conductivity by non-stationary method. By these method, temperature is scanned by modified modulus Control Web 2000 (Fig. 12). Data are transferred by transmission system ADAM 5 through the communication into the personal PC. The measured temperature increases to steady-state value. The obtained file can be evaluated by software NeReg02 (Fig. 13 and Fig. 14).

Mathematical model describing dependence of measuring roller temperature on time is based on thermal balance equation (2):

$$-K \frac{dt}{d\tau} = \frac{S\lambda(t-t_1)}{\delta} + B(t-t_1) \qquad 0 < \tau < \tau_m \qquad (2)$$

Where

K – Thermal capacity of measuring roller, [J.K^{-1}];
S – Area of sample, [m^2];
λ – Thermal conductivity of material, [W.m^{-1}.K^{-1}];
t – Scanned temperature of measuring roller, [°C];
t_1 – Temperature of tempering board, [°C];
δ – Thickness of sample [m];

B – Heat loss coefficient, [J.K^{-1}.s^{-1}];
τ – time, [s];
τ_m – Orientation time of measuring, [s].

The heat loss coefficient B can be computed by equation (3):

$$B = \alpha \cdot S_z \tag{3}$$

Where
S – Area on which losses occur, [m^2];
a – Heat transfer coefficient, [W.m^{-2}.K^{-1}].

Right side of the equation (2) describes heat flow through the sample of block into the measuring roller. It includes also heat loss caused by convention of air around the measuring equipment.

Left side of the equation (2) describes accumulation of heat in the measuring roller as time change of temperature.

Analytical solution of equation (2) is given by equation (4):

$$t = t_1 - \left(t_1 - t_2(0)\right) \cdot e^{\left(-(A_1 + A_2)\tau\right)} \tag{4}$$

Where parameters A_1 and A_2 can be computed by equations (5) and (6):

$$A_1 = \frac{S\lambda}{\delta K} \tag{5}$$

$$A_2 = \frac{B}{K} \tag{6}$$

and

$$A_3 = A_1 + A_2 \tag{7}$$

Where
A_1 – Parameter of measuring equipment, [s^{-1}];
A_2 – Parameter describing heat loss into the surroundings, [s^{-1}].

For data evaluation, as dependence of measuring roller temperature on time, we used above described mathematical model. Parameters a_1, a_2, a_3 we determined by non-linear regression

$$t = a_1 + a_2 \cdot e^{a_3 \tau} \tag{8}$$

Thermal conductivity can by obtain from parameter a_3:
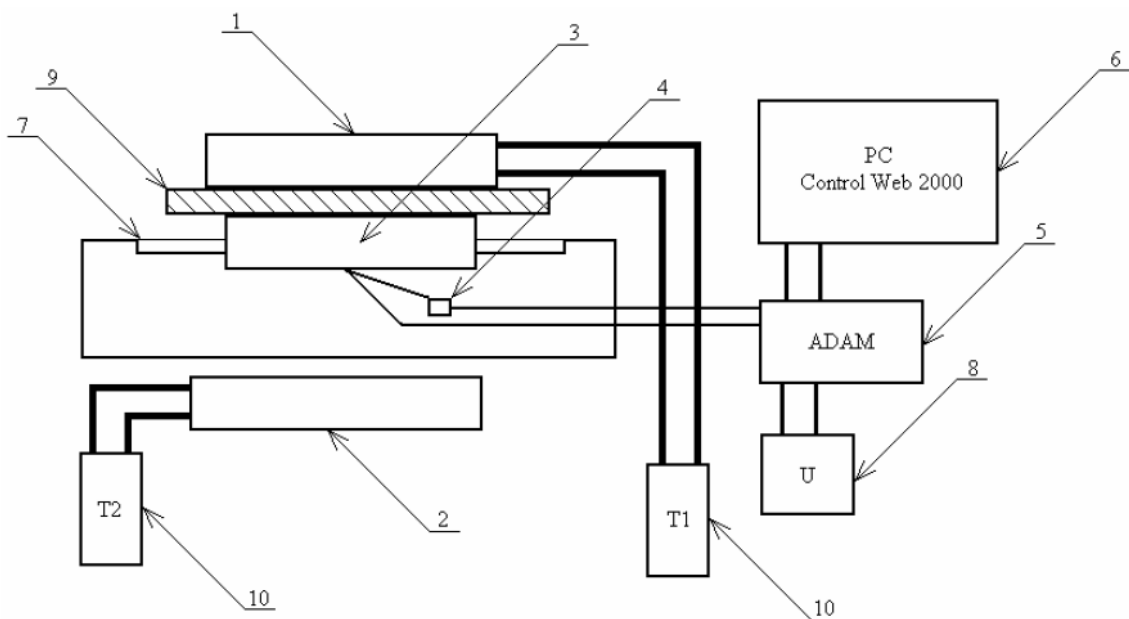
$$a_3 = -\left(A_1 + A_2\right) = -A_3 \tag{9}$$

Fig. 11 Scheme of apparatus according to Fitch

1 - Tempering temperature board for temperature t_1, 2 – Tempering temperature board for temperature t_2, 3 - Measuring roller, 4 –Thermocouple, 5 – System ADAM, 6 – Personal computer, 7 – Insulating cover of measuring roller, 8 – Stabilized direct-current generator, 9 – Measured sample, 10 – Thermostat
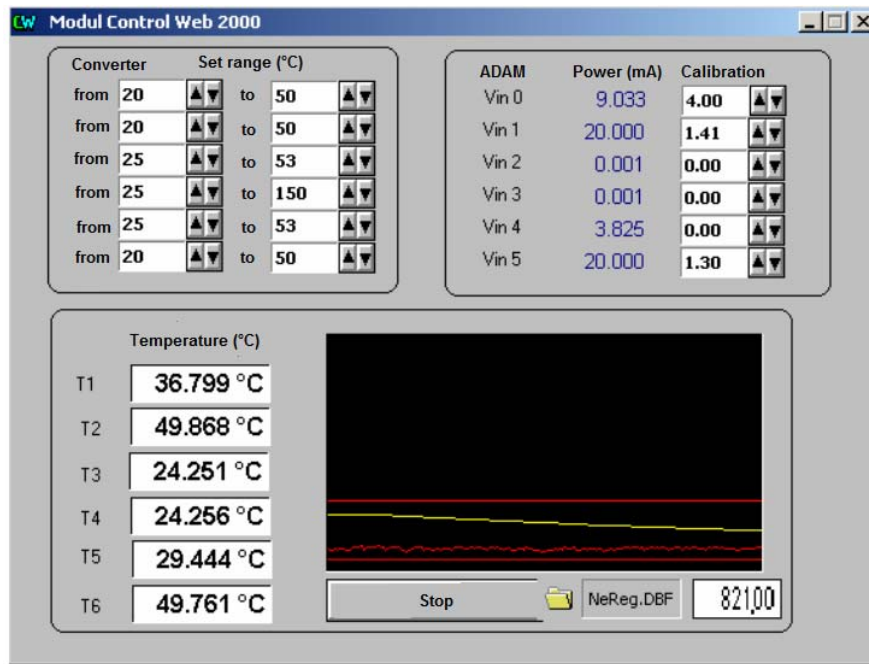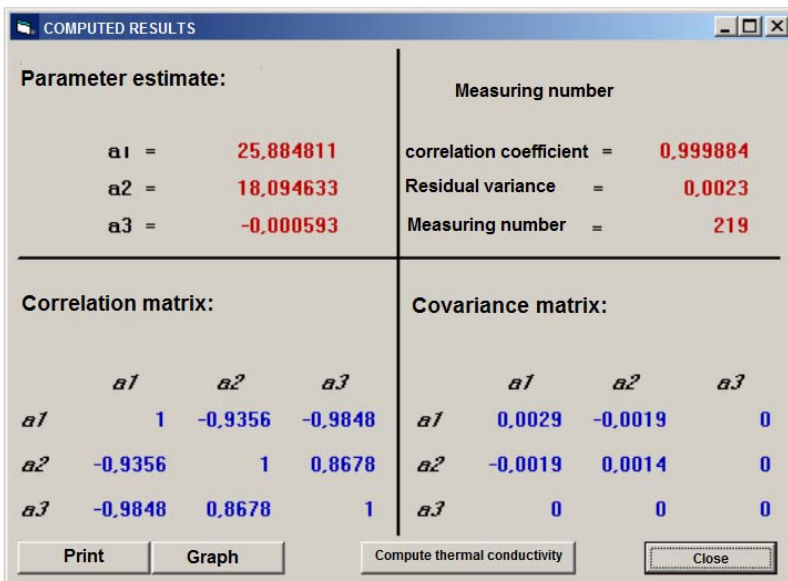
Fig. 12 Control web 2000 user interface

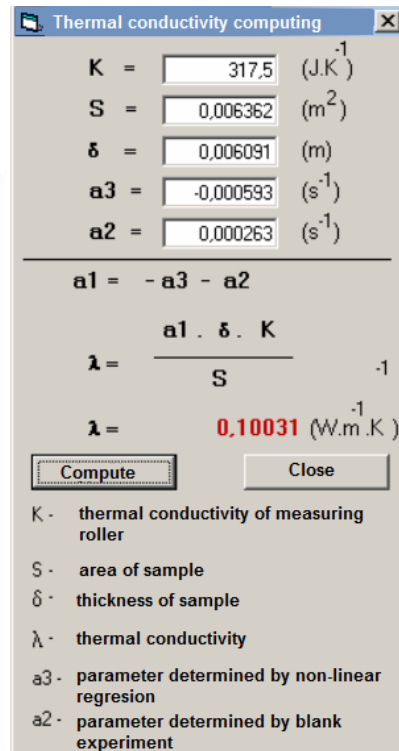Fig. 13 Window for data evaluation

Fig. 14 Window for thermal conductivity computing

The measured data are shown in table 2. The obtained results proved good thermo-insulating properties of the tested samples. The highest value of thermal conductivity was measured in samples of coarse melt. The samples by medium, fine and very fine granulity had approximately comparable thermal conductivity value.

Table 2 Determined values of thermal conductivity in the thermo-insulating panel samples

Tested sample	Granulity of the sample [mm]	Average thickness of the sample [mm]	Temperature of measuring roller [°C]	Ambient temperature [°C]	Thermal conductivity [$W.m^{-1}.K^{-1}$]
Coarse melt	3.0	6.72	41-30	27.9	**0.14171**
Medium melt	1.5	6.03	41-30	25.9	**0.10723**
Fine melt	1.0	6.09	41-30	27.3	**0,11207**
Very fine melt	0.5	5.98	41-30	29.2	**0.10867**

VI. CONCLUSION

In the paper we tested properties of adhesive mixture prepared for sticking of the plastic melt from printed circuit boards waste. The obtained results proved possibility to use hycol as an alternative adhesive. We eliminated its solubility in water by addition of crotonaldehyde. The optimal concentration of crotonaldehyde was 30 weight % with regard to dry matter of hycol.

The obtained results of thermal conductivity in prepared thermo-insulating panels proved good thermo-insulating properties. The highest value of thermal conductivity was measured in samples of coarse melt (about 14 $W.m^{-1}.K^{-1}$). The samples by medium, fine and very fine granulity had approximately comparable thermal conductivity value (about 11 $W.m^{-1}.K^{-1}$).

REFERENCES

[1] D. Janáčová, H. Charvátová, O. Šuba, K. Kolomazník, V. Vašek, "Treatment of Electronic Waste" in *International Carpathian Control Conference 2009*, Zakopané, Poland, 2009.

[2] D. Janáčová, et al., "Separation of Printed Circuit Board by Temperature Shock", in *Proceedings of the 5th WSEAS Conference on Heat Transfer, Thermal Engineering and Environment HTE'07*, WSEAS (Ed.), Athens, August 25 – 27, 2007.

[3] A., B. Lykov, *Teoria teploprovodnosti*, Moskva, Vysšaja škola. 1967

[4] T. Goňa, *Optimalizace síťovací reakce proteinových hydrolyzátů pro přípravu termo-izolačních panelů z recyklovaného plastu*, Diploma work. Tomas Bata University in Zlín, Zlín, 2011.

[5] M. Navrátil, *Instrumentation and diagnostics of polymer composites*, Doctoral Thesis. Tomas Bata University in Zlín, Zlín, 2070.

[6] L. Sýkorová, O. Šuba, M. Malachová, J. Černý, "Temperature Field Simulation of Polymeric Materials During Laser Machining Using COSMOS / M Software", in *13th WSEAS International Conference on Automatic control, modelling & simulation (ACMOS'11), WSEAS Press*, Lanzarote, Canary Islands, 2011.

[7] O. Šuba, L. Sýkorová, Š. Šanda, M. Staněk, "Modelling of Thermal Stresses in Printed Circuit Boards", in *13th WSEAS International Conference on Automatic control, modelling & simulation (ACMOS'11)*, WSEAS Press, Lanzarote, Canary Islands 2011.

[8] D. Janáčová, et al. "Modeling of temperature fields inside two layers board copper – plastic materials during treatment", *Proceedings of the 6th WSEAS International Conference on Engineering Education - Recent Advantages in Engineering Education*. Dondon P (Ed.), 2009, Rodos, Greece.

[9] D. Janáčová, et al. "Modeling of non-stationary heat field in a plane plate for assymetric problem", in *14th WSEAS International Conference on Systems. Latest Trands on Systems*.Volume II, WSEAS Press (GR), Rhodes, 2010

[10] L. Vašek, V. Dolinay, „Simulation Model of Heat Distribution and Consumption in Municipal Heating Network", in *14th WSEAS International Conference on Systems. Latest Trands on Systems*.Volume II, ,WSEAS Press (GR), Rhodes, 2010, p.439-442.

[11] M. Goosey, R. Kellner, A Scoping Study: End-of-Life Printed Circuit Board [online]. Available: http://www.cfsd.org.uk/seeba/TD/reports/PCB_Study.pdf

[12] H. S. Carslav and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford: Clarendon Press, 2008.

[13] V. Míka, *Fundamentals of chemical engineering*, Praha: STNL, 1977. (in Czech)

[14] H. Charvátová, et al. *Thermophysical properties of the selected substances.* Tomas Bata University in Zlín, Faculty of Applied Informatics, Zlín, 2009. (in Czech)

[15] F. Garvan, The Maple Book, New York: Chapman & Hall/CRC, 2002.

Dagmar Janáčová is an Associate Professor in the Department of Automation and Control Engineering, Faculty of Applied Informatics, of Tomas Bata University in Zlín. Her research activities include: modeling of treatment processes of natural polymers, transport processes, recycling of tannery wastes, and optimization and ecological approach of tannery processes. She has received the following honors: Diploma of England, XXIII IULTCS Congress, London, 11–14 September, 1997; Gold Medal - EUREKA EU Brussels 1997; Special Prize, Ministry of Agriculture, Belgium, 1997.

Hana Charvátová is a research worker at the Department of Automation and Control Engineering, Faculty of Applied Informatics, of Tomas Bata University in Zlín. Her research activities include recycling technology and modeling of natural and synthetic polymers treatment.

Pavel Mokrejš is an Associate Professor in the Department of Polymer Engineering, Faculty of Technology of Tomas Bata University in Zlín. His research activities include: treatment of liquid and solid waste form tannery industry, treatment of leather waste from shoe industry, utilization protein hydrolysates, biodegradable casings and films, and isolation of proteins from untraditional sources.

Vladimír Vašek is a Professor in the Department of Automation and Control Engineering,Faculty of Applied Informatics, of Tomas Bata University in Zlín. His research activities include: microcomputer applications in technology processes, computer monitoring and control systems, and discrete deterministic controllers approach of tannery processes. He has received the following honors: Diploma of England, XXIII IULTCS Congress, London, 11–14 September, 1997; Gold Medal - EUREKA EU Brussels 1997; Special Prize, Ministry of Agriculture, Belgium, 1997.

Antonín Blaha is an Associate Professor in the Department of Polymer Engineering, Faculty of Technology, of Tomas Bata University in Zlín. Zlín. His research activities include modeling of biopolymers treatment, chemical engineering transport processes, optimization and ecologization of tanning processes.

Karel Kolomazník is a Professor in the Department of Automation and Control Engineering, Faculty of Applied Informatics, of Tomas Bata University in Zlín. His research activities include: modeling of biopolymers treatment, chemical engineering transport processes, recycling of proteins, optimization and ecologization of tanning processes, and turning of vegetable and animal fats into biodiesel. He has received the following honors: Germany, American, England Leather Associations, XXIII IULTCS Congress, Friedrichshafen, May 15–20, 1995; England, XXIII IULTCS Congress, London, 11–14 September, 1997; USA, ALCA 1997, Annual Meeting, Regent Resort, NJ; Gold Medal - EUREKA EU Brussels 1997.

Gordana Paravanová is a research worker in the Center of Polymer Systems, University Institute, of Tomas Bata University in Zlín. Her research activities include natural and synthetic polymers treatment, deformation behaviour of polyelectrolytes modified ceramic compounds testing.