COUPLED THERMAL AND MOISTURE FIELDS WITH APPLICATION TO COMPOSITES[1]

András SZEKERES* and Jüri ENGELBRECHT**

*Department Applied Mechanics
Research Group of Continuum Mechanics, HAS
Technical University of Budapest
H–1521 Budapest, Hungary
**Institute of Cybernetics, EAS

Received: March 30, 1997

Abstract

The mathematical models of heat and moisture transfer have been presented and analysed. The coupling of fields is described by including the Dufour and Soret effects. For high-rate processes, a modification of models is proposed with relaxation effects taken into account. The possible applications in mechanics of composites are discussed.

Keywords: heat, moisture, coupling, composites.

1. Introduction

Heat and mass transfer have great importance in many natural and technological processes. In porous or absorptive materials the mass transfer may considerably change the properties of the whole material. Here in this report we concentrate upon heat and moisture transfer, bearing in mind composite materials. It goes without special proof that composite materials are nowadays widely used in many areas starting from large-scale products for home usage to high-technology structures for aircraft, cars, etc. On the one hand, the composite structures may be exposed to rapid temperature changes in a large scale. On the other hand, however, composites are characterised by a property to absorb moisture. Both of these effects have direct impact on the properties of composites, on internal stresses, and as a result, may cause failure due to the loss of stiffness or fracture.

In this report, the mathematical models of heat and moisture transfer are analysed. Actually, there exist several ways to model a physical problem, say the heat and moisture transfer. First, one could approach the problem from the practical side, learning how both heat and moisture cause degradation, delamination and how the properties of the material change with the changes of external fields [1 –7]. Second, one could start

[1]Based on the Research Report Mech 108/94, Institute of Cybernetics elaborated while the first author visited the Institute as a guest researcher.

from studying the physical mechanism that in this case means the study of heat conduction and moisture diffusion with needed attention to entropy requirements and basic rules of continuum mechanics [1, 2, 8 – 10]. In addition, the third way is to establish mathematical models ad hoc by using analogies and studying a special class of equations [11, 12].

Here we start from the second viewpoint, establishing the clear physical mechanism. Then we use the third approach and actually use analogies to propose modified mathematical models. The first viewpoint, the practical side will only be briefly illuminated, leaving proper analysis for the future.

In Section 2, the Fick's Law and its analogy to the Fourier Law are discussed. That means actually establishing the sound basis for heat and moisture transfer. Section 3 describes the coupling between heat and moisture transfer. The Dufour and Soret effects are described and the corresponding relations given. Section 4 deals with basic new ideas of this report. For high-rate dynamics, i.e. for large external field gradients, the relaxation effects should be taken into account. While different fields, i.e. temperature and moisture fields have been separately discussed earlier, e.g. [13, 14], then here the attention is paid to coupling. The new model contains several new physical constants, the essence of which is briefly discussed. The model follows the principle of equipresence. The next section, Section 5 is devoted to the brief analysis of these effects in composites from the practical side.

2. The Fick's Law and its Analogy to the Fourier Law

In continuum mechanics, the independent variables must first of all satisfy the conservation laws of mass, momentum and energy. A conservation law may be written in a general form

$$\rho_1 \dot{C} = \nabla \cdot \mathbf{J}^C + \sigma^C . \tag{2.1}$$

A simplest constitutive law for a variable C is

$$\mathbf{J}^C = -\alpha^C \nabla C . \tag{2.2}$$

Here $\mathbf{J}^C$ and σ^C stand for the flux and source term, respectively, corresponding to C, ϱ_1, and α^C are the coefficients; the upper dot denotes the material time derivative and ∇ the space derivative.

The *Eqs* (2.1), (2.2) could be applied for various independent variables like the specific volume v, the velocity $\mathbf{v}$, etc. Here we apply these equations for moisture and temperature.

(i) Moisture and the Fick's Law

Let $C = m$ that is the moisture concentration at a certain point of a solid. Then $\mathbf{J} = \mathbf{f}$ is the moisture flux, $\varrho_1 = 1$, $\sigma = 0$ and $\alpha = D_m$ is the moisture diffusion coefficient. With these notations, *Eqs* (2.1), (2.2) read

$$\nabla \cdot \mathbf{f} + \dot{m} = 0\,, \tag{2.3}$$

$$\mathbf{f} = -D_m \nabla m\,. \tag{2.4}$$

Substituting (2.4) into (2.3) we obtain

$$\dot{m} = D_m \nabla^2 m\,. \tag{2.5}$$

Eq. (2.4) is called Fick's First Law and *Eq.* (2.5) Fick's Second Law [9].

(ii) Temperature and the Fourier Law

Let $C = T$ that is the temperature at a certain point of a solid. The other notations are then: $\mathbf{J} = \mathbf{q}$ is the heat flux, $\rho_1 = \rho c_p$, where c_p is the specific heat with respect to the volume and ρ is the density; as above, σ is neglected and $\alpha = k$ is the coefficient of heat conduction. *Eq.* (2.1) emphasises then the conservation of energy

$$\nabla \cdot \mathbf{q} + \rho c_p \dot{T} = 0\,, \tag{2.6}$$

while *Eq.* (2.2) is the celebrated Fourier's Law

$$\mathbf{q} = -k \nabla T\,. \tag{2.7}$$

Substituting (2.7) into (2.6), the heat conduction equation yields

$$\dot{T} = D_T \nabla^2 T\,. \tag{2.8}$$

Here $D_T = k/\rho c_p$.

The similarity between the final results (2.5) and (2.8) is obvious, as well as between the (first) Fick's Law and the Fourier Law. It means actually that theoretical, numerical, and experimental problems of moisture and temperature diffusion can be treated in a similar way.

An interesting question arises about the simultaneous transport of moisture and temperature: are the effects caused by these phenomena coupled or not? The answer is given in the following section.

3. Coupling between Heat and Moisture Transport

There is an experimental evidence that temperature field affects the moisture transport, and, vice versa, moisture concentration affects the temperature field [1, 2]. First, the heat flux, caused by moisture concentration gradient

$$\mathbf{q} = -\alpha_T^m \nabla m \tag{3.1}$$

is associated with Dufour effect, while the corresponding flux is called the Dufour flux [2]. Second, the moisture diffusion due to temperature gradient

$$\mathbf{f} = -\alpha_m^T \nabla T \tag{3.2}$$

is associated with Soret effect with the corresponding flux being the Soret flux (2].

Here α_T^m, α_m^T are the coupling diffusion coefficients: diffusion-thermo and thermal-diffusion coefficients, respectively [1, 2, 9].

Suppose we add the Dufour and Soret fluxes to our basic equations in the previous section. The coupled fluxes can then be written in the following form

$$\mathbf{J}_i = -\alpha_{ij} \nabla C_j \tag{3.3}$$

and the coupled final equations (provided α_{ij}'s are constant)

$$\dot{C}_i = D_{ij} \nabla^2 C_j + \sigma_i \,, \tag{3.4}$$

where the summation convention over the repeated indices is used, $i, j = 1, 2$. The notation is obvious:

$$\mathbf{J}_1 = \mathbf{f}, \qquad \mathbf{J}_2 = \mathbf{q};$$

$$C_1 = m\,, \qquad C_2 = T\,;$$

$$\alpha_{11} = \alpha_m\,, \quad \alpha_{12} = \alpha_m^T\,, \quad \alpha_{21} = \alpha_T^m\,, \quad \alpha_{22} = k\,;$$

$$D_{11} = \alpha_m\,, \quad D_{12} = \alpha_m^T\,, \quad D_{21} = \frac{\alpha_T^m}{\rho c_p}\,, \quad D_{22} = \frac{k}{\rho c_p}\,.$$

It should be noted that *Eq.* (3.4) is the system of coupled hygro-thermal equations following the principle of equipresence. In addition, the Onsager's relation for α_{ij} can be added

$$\alpha_{12} = \alpha_{21}\,.$$

There are also restrictions on the coefficients due to the entropy condition [2]. The generalisation of the coefficients, like the dependence of thermal-diffusion coefficient on temperature [3] or on moisture concentration and on stress [4], makes the *Eq.* (3.4) more complicated but does not change its order.

Certainly, *Eqs* (3.3), (3.4) may theoretically be extended up to any number of fields.

4. High-Rate Dynamics: the Modification of Equations

The paradox of the heat conduction equation

$$\dot{T} = D_T \nabla^2 T \tag{2.8}$$

is well-known. Because of its parabolic character, *Eq.* (2.8) predicts the infinite speed of heat propagation which contradicts the physical principles. Already Maxwell has pointed out how to solve this paradox but contemporary understanding is based on ideas of Vernotte and Cattaneo who introduced relaxation time for the heat flux into the basic *Eq.* (2.7). We refer here to [15] as to an excellent recent review on this topic. Some of our earlier papers also concern this problem [16 – 18].

The basic (more or less formal) solution to this paradox is the following. Instead of *Eq.* (2.7) we use

$$\mathbf{q} + \tau_T \dot{\mathbf{q}} = -k \nabla T\,, \tag{4.1}$$

where τ_T is the relaxation time. Introducing (4.1) into (2.6), we obtain

$$\dot{T} + \tau_T \ddot{T} = D_T \nabla^2 T\,, \tag{4.2}$$

which is a hyperbolic equation, describing wave motion with a finite speed

$$c_T = \left(\frac{D_T}{\tau_T}\right)^{1/2}. \tag{4.3}$$

There are still debates about the value of the relaxation time [9, 15, 19, 20] and the mechanism of heat propagation. We leave this analysis here aside and concentrate more on the formal mathematical models.

The striking analogy between the basic models of moisture and heat transport (*Eqs* (2.5), (2.8)) leads logically to formal generalisations.

First, we are tempted to generalise the constitutive law (2.2)

$$\mathbf{J}^C + \tau^C \dot{\mathbf{J}}^C = -\alpha^C \nabla C\,, \tag{4.4}$$

where τ^C is a certain relaxation time. It means that the flux is considered to be inertial and the process of equilibrium from one state to another involves a characteristic relaxation time. The Deborah number

$$De = \frac{\tau^C}{t_{ch}}\,, \tag{4.5}$$

where t_{ch} is a certain external characteristic time, should be finite, not too small, not too large [21]. We understand the 'accuracy' of such a statement but given the problems around estimation of τ_T [15] and the wide range of t_{ch}, the value of De could be easily around 1.

Let us use this idea, at least formally, to generalise *Eq.* (2.4), i.e. moisture diffusion. Then, instead of *Eq.* (2.4) we have

$$\mathbf{f} + \tau_m \dot{\mathbf{f}} = -D_m \nabla m\,, \tag{4.6}$$

and instead of *Eq.* (2.5)

$$\dot{m} + \tau_m \ddot{m} = D_m \nabla^2 m\,. \tag{4.7}$$

What is the physical meaning of this equation? Certainly, the paradox of the infinite speed of the removed moisture transport is described by a hyperbolic equation. The idea of using such an equation for mass transfer including moisture transport in porous bodies belongs to LUIKOV [9]. However, the physical mechanism behind it is still not clear, as well as the real values of τ_m. The heat transfer and the corresponding relaxation time τ_T are related to transfer mechanism by phonons and electrons and are essentially dependent on the molecular structure of media. It is also shown that for high-frequency processes including propagation of shock waves thermal relaxation may have important role [15, 18]. For moisture transfer, as far as it is known to the authors, such estimations are absent. Nevertheless, it seems to be worth while to elaborate a theoretical basis for further research, that could be used in applications (see Section 5).

We propose now a formal generalisation of basic equations including the Dufour and Soret effects. First we introduce the relaxation time into the constitutive law. Then for i fluxes we have

$$\mathbf{J}_i s + \tau_{ij} \dot{\mathbf{J}}_j = -\alpha_{ij} \nabla C_j\,. \tag{4.8}$$

Substituting (4.8) into the conservation law, we obtain

$$\dot{C}_i + \tau_{ij} \ddot{C}_j = D_{ij} \nabla^2 C_j + \sigma_i + \tau_{ij} \dot{\sigma}_j\,. \tag{4.9}$$

In our case i, $j = 1, 2$ with $C_1 = m$, $C_2 = T$. The corresponding equations in these terms are the following.

(i) Constitutive laws

$$\begin{bmatrix} \mathbf{f} \\ \mathbf{q} \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \dot{\mathbf{f}} \\ \dot{\mathbf{q}} \end{bmatrix} = - \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix} \begin{bmatrix} \nabla m \\ \nabla T \end{bmatrix}, \tag{4.10}$$

$$\begin{cases} \mathbf{f} + \tau_{11}\dot{\mathbf{f}} + \tau_{12}\dot{\mathbf{q}} = -\alpha_m \nabla m - \alpha_m^T \nabla T, \\ \mathbf{q} + \tau_{21}\dot{\mathbf{f}} + \tau_{22}\dot{\mathbf{q}} = -\alpha_T^m \nabla m - k \nabla T. \end{cases} \tag{4.11}$$

(ii) Governing equations

$$\begin{bmatrix} \dot{m} \\ \dot{T} \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \ddot{m} \\ \ddot{T} \end{bmatrix} = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \begin{bmatrix} \nabla^2 m \\ \nabla^2 T \end{bmatrix} + \begin{bmatrix} \sigma_1 \\ \sigma_2 \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \dot{\sigma}_1 \\ \dot{\sigma}_2 \end{bmatrix}, \tag{4.12}$$

$$\begin{cases} \dot{m} + \tau_{11}\ddot{m} + \tau_{12}\ddot{T} = \alpha_m \nabla^2 m + \alpha_m^T \nabla^2 T + \sigma_1 + \tau_{11}\dot{\sigma}_1 + \tau_{12}\dot{\sigma}_2, \\ \dot{T} + \tau_{21}\ddot{m} + \tau_{22}\ddot{T} = \dfrac{\alpha_T^m}{\rho c_p} \nabla^2 m + \dfrac{k}{\rho c_p} \nabla^2 T + \sigma_2 + \tau_{21}\dot{\sigma}_1 + \tau_{22}\dot{\sigma}_2. \end{cases} \tag{4.13}$$

These are the formal results and some comments are in order. It is obvious that $\tau_{11} = \tau_m$ and $\tau_{22} = \tau_T$. Other two relaxation times $\tau_{12} = \tau_m^T$ and $\tau_{21} = \tau_T^m$ characterise coupling effects. When τ_m and τ_T have more or less clear physical background [9, 15], then the physical explanation of τ_m^T and τ_T^m is not clear yet. LUIKOV [9] has stressed the importance of the heat transfer process being inseparably linked with mass (i.e. moisture) transfer. This statement is certainly not sufficient, and the explanation seems to be related to the microstructure of the medium, where nonlocality and after-effects should be taken into account. All this needs further studies. From the formal viewpoint, the character of governing equations has been changed dramatically from parabolic to hyperbolic. Again, from the viewpoint of continuum mechanics, the model is complete, following strictly the principle of equipresence.

Every modification leads to an inevitable question – is it needed at all? Apart from getting rid of the paradox of infinite speeds, the real values of the coefficients may turn to be small and may not affect the final results. In the next Section, some ideas based on the behaviour of composites are briefly presented and discussed in order to justify modifications introduced above.

5. Heat and Moisture Transport in Composite Materials

The study of heat (temperature) and moisture transport in composite materials has gained more and more interest. First, the composites are widely used materials in high-technology including automotive engineering, aircraft structures, etc. Second, strength and stiffness are greatly influenced by heat and moisture parameters. The temperature changes may cause nonuniform thermal expansions and changes in material (physical) properties, and the same goes to the absorption of moisture by composites. As a result of external field, the internal stresses may grow and the stiffness and strength of a structure may be lowered.

Having established the importance of these physical phenomena for composite, we may still limit the analysis to using the simplest possible mathematical models and separate the influence of heat and moisture field (see Section 2). However, there are cases when the coupling effects cannot be neglected [1, 10]. For example, SIH et al. [10] analysed the influence of coupled heat and moisture fields on stresses in a composite plate, a surface of which undergoes a sudden change in temperature. The stresses due to heat–moisture coupling effect differ from the stresses calculated on the basis of uncoupled theory as much as 20 to 80% dependent on the gradient of the boundary condition. TAMBOUR [1] has also shown that the changes of the temperature distribution in a moist slab are essentially different for various moisture distributions. The differences depend very much on the gradients (the bigger the gradient, the more essential the influence is) and also on time. When time approaches to infinity, the equilibrium is the same either determined by the coupled or uncoupled theory. LEE and PEPPAS [4] have demonstrated stress accumulation due to moisture transport in epoxy composites used in graphite fibres. Evidence on coupling effects is given also in [1, 2].

A very important question is how to estimate the values of the parameters needed to specify the mathematical models. Some estimations are given by TAMBOUR [1]. Based on the rather heuristic statement, that the Soret and Dufour coupling coefficients 'are usually much smaller than the regular transport coefficients', we may establish

$$\frac{\alpha_T^m}{h_m} \ll D_m \,, \tag{5.1}$$

$$\frac{h_m \alpha_m^T}{c_{sm}} \ll D_m \,, \tag{5.2}$$

where c_{sm} is the specific heat of the moist solid and h_m is the moisture specific enthalpy determined by

$$h_m = \int_0^T c_m \mathrm{d}T \,. \tag{5.3}$$

Here c_m denotes the specific heat of moisture. In addition

$$\alpha_m^T = \frac{c_{sm}^2 D_m^2}{h_m k_{sm}}, \tag{5.4}$$

where k_{sm} is the thermal conductivity of a moist solid.

Just now we are not able to report much about the estimations on relaxations times. For heat transfer, the estimations are scattered (see [15]), more or less known for non-conductors but for metals the estimations vary. For moisture transport, the estimations are given by LUIKOV [9]. Due to the large variety of composite materials, new experimental evidence is needed, concerning the basic τ_T and τ_m as far as the coupling τ_m^T and τ_T^m estimations. One of the possible ways to get some experimental evidence is to use electromagnetic analogies [20].

We would like to point out one important area beside stress and fracture analysis of composites, where the theory presented above could be used. This is the synthesis (or 'tailoring') of the composites with prescribed thermomechanical properties [22 – 24). Given the load, the designer would like to design variables so that the structure deforms in a specified way. The general approach, envisaged in [24, 25] needs certain minimisation procedures to be used while some of thermomechanical properties are exactly given as targets, some, however, given in a certain range. It is clear that the mathematical model proposed in Section 4 is too complicated to be used for tailoring a certain composite. However, a simplified variant with τ_m and τ_T in action, could be effectively used when tailoring a composite under external field with large gradients. This is a problem for our further studies.

Endnote

This report is written as a result of an informal co-operation between Budapest TU, Oulu University and Institute of Cybernetics, Estonian Acad. Sci. The experience in thermoelasticity (BTU), mechanics of composite materials (OU) and in wave dynamics (IC) is so channelled into one direction. In 1993, one of the authors (A. SZEKERES) has spent a month in IC and three months in OU. The results of this co-operation deal with modified thermoelasticity and internal variables [26, 27] as well as tailoring of composites [28]. A. Szekeres would like to appreciate the possibility to work with colleagues also in 1994.

Acknowledgements

I (A. Szekeres) would also like to mention the background of this report. Namely, this is the next chapter of the, let us call it, 'Tallinn School of Thermodynamics of Complex Systems' which was based on the traditions of IC in the field of non-linear waves and of the Dept. of Technical Mechanics (BTU) in the field of thermoelasticty. Later the co-operation has been completed with researches on thermomechanics of composites which has old traditions in the Engineering Mechanics Laboratory (OU). I would like to thank both of my partners for the co-operation.

References

1. TAMBOUR, Y. (1984): On Local Temperature Overshoots due to Transport Coupling of Heat and Moisture in Composite Materials. *J. Composite Materials,* Vol. 18. Sept., pp. 478–494.
2. HARTRANFT, R. J. – SIH, G. C. (1980): The Influence of the Soret and Dufour Effects on the Diffusion of Heat and Moisture in Solids. *Int. J. Engng. Sci.* Vol. 18, pp. 1375–1383.
3. CHEN, R. S. – TU, C. Y. – TSAI, H. S. (1993): The Effect of Moisture upon the Optimal Temperature Path of the Visco-Elastic Symmetric Composite Laminates after Past Cure. *J. Composite Materials,* Vol. 27, No. 16/1993, pp. 1578–1597.
4. LEE, M. S. – PEPPAS, N. A. (1993): Models of Moisture Transport and Moisture-Induced Stress in Epoxy Composites. *J. Composite Materials,* Vol. 27, No. 12/1993, pp. 1146–1171.
5. VOYIADJIS, G. Z. – KATTAN, P. I. (1993): Damage of Fiber-Reinforced Composite Materials with Micromechanical Characterization. *Int. J. Solids Structures,* Vol. 30, No. 20, pp. 2757–2778.
6. TUCKER, W. C. – LEE, S.-B. – ROCKETT, T. (1993): The Effect of Pressure on Water Transport in Polymer. *J. Composite Materials,* Vol. 27, No. 8/1993, pp. 756–763.
7. TWARDOWSKI, T. E. – LIN, S. E. – GEIL, P. H. (1993): Curing in Thick Composite Laminates: Experiment and Simulation. *J. Composite Materials,* Vol. 27, No. 3/1993, pp. 216–250.
8. LEBON, G. – JOU, D. – CASAS-VAZQUEZ, J. (1992): Questions and Answers about a Thermodynamic Theory of Third Type. *Contemporary Physics,* Vol. 33, No. 1, pp. 41–51.
9. LUIKOV, A. V. (1968): Analytical Heat Diffusion Theory. Academic Press, New York and London.
10. SIH, G. C. – SHIH, M. T. – CHOW, S. C. (1980): Transient Hygothermal Stresses in Composites: Coupling of Moisture and Heat with Temperature Varying Diffusivity. *Int. J. Engng. Sci.* Vol. 18. pp. 19–42.
11. GRINDROD, P. (1991): Patterns and Waves. The Theory and Applications of Reaction-Diffusion Equations. Clarendon Press, Oxford.
12. FIFE, P. C. (1988): Dynamics of Internal Layers and Diffusive Interfaces. SIAM Publication, Philadelphia, Pennsylvania, 1988.
13. FUKUNAGA, H. – SEKINE, H. (1993): Optimum Design of Composite Structures for Shape, Layer Angle and Layer Thickness Distributions. *J. Composite Materials,* Vol. 27, No. 15/1993, pp. 1479–1492.

14. DUNN, M. L. – TAYA, M. – HATTA, H. – TAKEI, T. – NAKAJIMA, Y. (1993): Thermal Conductivity of Hybrid Short Fiber Composites. *J. Composite Materials,* Vol. 27, No. 15/1993, pp. 1493–1518.
15. CHANDRASEKHARIAH, D. S. (1986): Thermoelasticity with Second Sound: A review. *Appl. Mech. Rev.,* Vol. 39, No. 3, March (1986).
16. SZEKERES, A. (1980): Equation System of Thermoelasticity Using the Modified Law of Thermal Conductivity. *Periodica Polytechnica, Mech. Eng.,* Vol. 24, No. 3, pp. 253–261.
17. FARKAS, I. – SZEKERES, A. (1984): Application of the Modified Law of Heat Conduction and State Equation to Dynamical Problems of Thermoelasticity. *Periodica Polytechnica, Mech. Eng.,* Vol. 28, Nos 2–3, pp. 163–170.
18. ENGELBRECHT, J. (1983): Non-Linear Wave Processes of Deformation in Solids. Pitman, London.
19. MAURER, M. J. (1969): Relaxation Model for Heat Conduction in Metal. *J. Applied Physics,* Vol. 40, No. 13.
20. SZALONTAY, M. – SZEKERES, A. (1980): Experiments on Thermal Shock of Long Bars. *Periodica Polytechnica, Mech. Eng.,* Vol. 24, No. 3, pp. 243–251.
21. KESTIN, J. (1992): Local-Equilibrium Formalism Applied to Mechanics of Solids. *Int. J. Solids Structures,* Vol. 29, pp. 1827–1836.
22. PRAMILA, A. (1990): Extreme and Zeros of Coefficients of Thermal Expansion of a Balanced Symmetric Laminate. *J. Composite Materials,* Vol. 24, July 1990, pp. 786–794.
23. PRAMILA, A. (1992): Extreme of Some Thermoelastic Properties of Symmetric Laminates. *Periodica Polytechnica, Mech. Eng.,* Vol. 36, No. 2, pp. 125–134 .
24. AUTIO, M. – LAITINEN, M. – PRAMILA, A. (1993): Systematic Creation of Composite Structures with Prescribed Thermomechanical Properties. *Composites Engineering,* Vol. 3, No. 3, pp. 249–259.
25. FANG, C. – SPRINGER, G. S. (1993): Design of Composite Laminates by a Monte Carlo Method. *J. Composite Materials,* Vol. 27, No. 7/1993, pp. 721–753.
26. BEREZOVSKY, A. – ENGELBRECHT, J. – SZEKERES, A. (1993): On Thermodynamics of Complex Systems. *Proc. Estonian Acad. Sci. Phys. Math.,* Vol. 42, No. 4, pp. 350–352. Based on the Seminar held in the Institute of Cybernetics, Tallinn, on 3rd of May, 1993.
27. ENGELBRECHT, J. – SZEKERES, A. (1993): Modified Thermoelaslicity: Internal Variables and Heat Conduction. Research Report Mech. 88/93, Institute of Cybernetics, 'Tallinn.
28. AUTIO, M. – SZEKERES, A. (1993): Tailoring of Composites: Theoretical Questions and Thermomechanical Applications. Seminar held in the Engineering Mechanics Laboratory, Oulu University, on 3rd of December, 1993.