

SELF-CONSISTENT SCHEME TO PREDICT THE THERMAL CONDUCTIVITY OF COMPOSITES BY FINITE PARTICLE CONCENTRATION

Kliment Hadjov, Dimitar Dontchev

University of Chemical Technologies & Metallurgy, 1756 Sofia, E-mail: klm@uctm.edu

ABSTRACT. In this work we propose a new model to predict the thermal conductivity of composites with enhanced particle concentrations. The model is based on the self-consistent scheme. The proposed model is evaluated using great number of published experimental data on the thermal conductivity enhancement of particulate composites at great concentration, covering broad ranges of phase thermal conductivity ratios and particle volume fractions. A comparison with a differential medium model is made. Using the self consistent scheme, upper and lower bounds for such particulate composites are presented.

МЕТОД НА САМОСЪГЛАСУВАНЕТО ЗА ПРЕДСКАЗВАНЕ НА ТЕРМОПРОВОДИМОСТТА НА КОМПОЗИТИ ПРИ ГОЛЯМО НАПЪЛВАНЕ

Климент Хаджов, Димитър Дончев

Химикотехнологичен и Металургичен Университет, 1756 София, E-mail: klm@uctm.edu

РЕЗЮМЕ. В тази работа се предлага нов хомогенизационен модел за предсказване на термопроводимостта на композити с повишена концентрация на включванията. Моделът е базиран на метода на самосъгласуването и е сравнен с многобройни публикувани експериментални резултати за повишаване на термопроводимостта на композити с голямо напълване. Сравнението обхваща голям диапазон на проводимости на фазите, тяхното отношение и напълване. Направено е сравнение с модела на диференциалното нарастване на напълването. Представени са горна и долна граници на коефициента на ефективната термопроводимост за такива композити.

Introduction

To make efficient use of composite materials the variation of physical properties with the kind and concentration of fillers should be known. One important property of particulate composites is the thermal conductivity.

General framework

The Maxwell equation to the effective conductivity of two phase spherical particulate composite without interaction between particles can be expressed as follows (Maxwell, 1904)

$$K_{eff,M} = K_m \left(1 + \frac{f}{1/(\alpha - 1) + (1-f)/3} \right). \quad (1)$$

Here K_m , K_p and f are the thermal conductivity of the matrix, the particles and the particle volume fraction respectively, $\alpha = K_p / K_m$.

An other equation concerning the case of finite particle concentration (with interaction between particles) is the Bruggeman's one (Bruggeman, 1035)

$$K_{eff,B}(f) = \frac{K_m}{4} \left((3f - 2)(\alpha - 1) + \alpha + \sqrt{((3f - 2)(\alpha - 1) + \alpha)^2 + 8\alpha} \right), \quad (2)$$

Using the so called self consistent scheme, it can be shown (Hashin, 1968) that equation (1) represent the lower Hashin-Strickmans bound for inclusions with arbitrary shape. Thus, the Maxwell equation (1) is the best possible for a statistically homogeneous and isotropic two phase composite if $K_p > K_m$. The Bruggeman model has no limitations on the concentration of inclusions and can be used for particles percolation in suspensions or when the particle concentration is sufficiently high (Wang, 2003). Following (Hashin, 1968) and (Wang, 2003) it could be expected that if $K_p > K_m$, the values of $K_{eff}(f)$ should lie between equation (1) and the Bruggeman's one - equation (2). In other words, equation (2) represent the upper bound concerning only spherical inclusions. In this case the above equations (1) and (2) can be regarded as lower (without interaction) and upper (with maximal interaction between particles) bounds of the effective conductivity for composites containing spherical inclusions in the case

$K_p > K_m$. For such a composites, real conductivity enhancement curves must be placed between the curves described by equations (1) and (2) - Fig. 1.

Using the self consistent scheme (particle with radius a surrounded by matrix material with radius b , both embedded in the effective medium) employed by Hashin (1968), to the homogenized thermal conductivity curve, placed between curves (1) and (2), we can write the following quadratic equation

$$A k(c, f)^2 - B k(c, f) - C = 0 \quad (3)$$

where:

$$\begin{aligned} A &= 2(2 + c) + \alpha(1 - c), \\ B &= 2(1 + 2c) + \alpha(1 - 4c) + 9(c - 1)f, \\ C &= 2(1 - c) + \alpha(1 + 2c), \\ \alpha &= K_p / K_m, k = K_{eff} / K_m, c = (a / b). \end{aligned}$$

Equation (3) has always real opposite sign roots [3]. Because of $c \leq 1$, the positive solution of eq. (3) is obviously

$$k(c, f, \alpha) = \frac{B(c, f, \alpha)}{2A(c, f, \alpha)} + \frac{\sqrt{B(c, f, \alpha)^2 + 4A(c, f, \alpha)C(c, f, \alpha)}}{2A(c, f, \alpha)} \quad (4)$$

If $c = f$, equation (4) coincides with equation (1) – the lower bound. If $c = 1$, equation (4) coincides with equation (2) – the upper bound. Thus, for

$$f < c < 1, \quad (5)$$

equation (4) lie between the above mentioned bounds – fig. 1.

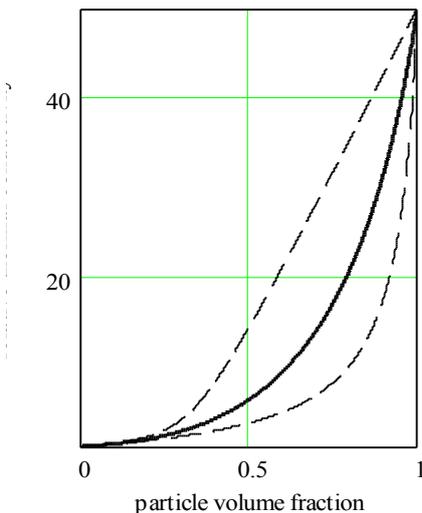


Fig. 1. Relative thermal conductivity enhancement via particle volume fraction. Lower (equation (1)) and upper (equation (2)) bounds with dashed lines. Continuous thick line – equation (4) with parameter c between f and 1.

We need now to estimate this dimensionless parameter c in order to obtain reasonable curves to predict the thermal conductivity of particulate composites with interaction between particles, which take place in the case of enhanced particle volume fractions. From fig. 1 one can see that for lower volume fractions both equations (1) and (4) coincide. Thus, for lower fractions c must be near to f and for very great volume fractions c must lie near to 1. Moreover from fig. 2 one can see that for lower volume fractions both equations (1) and (2) coincide. Thus, the relation $c(f)$ must be a concave function as $c = f^n$ and in the beginning (for lower fractions) this function can be very declined in order to move for greater fractions near the horizontal limit of 1 – fig. 2. The parameter c must be also α dependent. From the experimental curves listed below, it is clear that for lower conductivity ratios α , the thermal conductivity enhancement curves lie near to the Maxwell equation (1) and vice versa for greater α these curves move near to equation (2). Thus, the n parameter must be a convex function of α such as $n(\alpha) = 1 - a \cdot \exp(k/\alpha)$ – see fig. 3.

As has been showed in [5], the saturated conductivity rate of inclusion to matrix increases with the volume fraction of the dispersed phase raising. The conductivity of inclusion has a saturated value for improving the conductance of composite at a certain fraction. It means the effective conductivity of composite cannot be improved considerably when the conductivity ratio comes over this transition point at a definite volume percentage.

Let us finally assume the following equation to describe the relation between the parameter c , the volume fraction f and the conductivity ratio α

$$c(f, \alpha) = f^{(1 - a \exp(k/\alpha))} \quad (6)$$

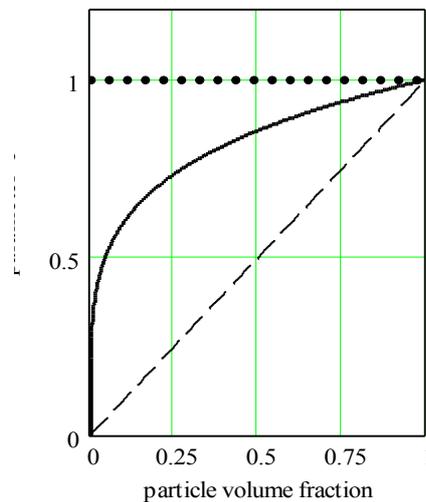


Fig. 2. Parameter c as a function of the particle volume fraction. Dotted line $c = 1$ (upper bound in fig. 1), Dashed line $c = f$ (lower bound in fig. 1), thick line- eq.6 with $f < c < 1$.

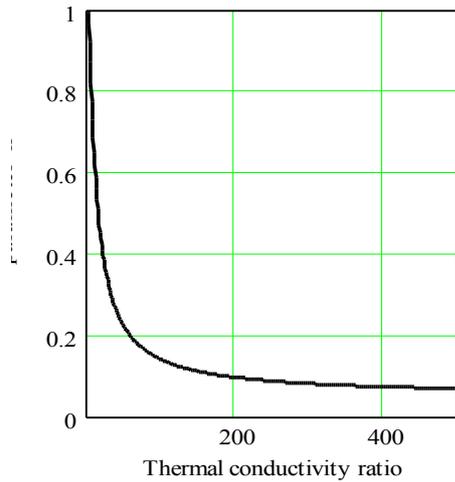


Fig. 3. Parameter n as a function of the thermal conductivity ratio α : $n(\alpha) = 1 - a \cdot \exp(k/\alpha)$.

The new proposed equation (4) together with equation (6) can be used to predict the thermal conductivity enhancement of concentrated particulate composites. By fitting the theoretical curves (4) together with equation (6) and the experimental data demonstrated in sets (1-13), to the parameters a and k in equation (6) we obtain the following values: $a = 0.95$ and $k = 70$, which could be valid for any composite phases with spherical particles.

Bellow we compare our model with different experimental data concerning thermal conductivity enhancement of two phase particulate composites in the case of great volume fractions. In these figures we have shown the differential medium approach curves proposed in [6], which can be taken in the form

$$\left(\frac{K_{eff}}{K_m}\right) \left[\frac{K_p - K_m}{K_p - K_{eff}} \right] = \left(1 - \frac{f}{f_{max}}\right) f_{max} \quad (7)$$

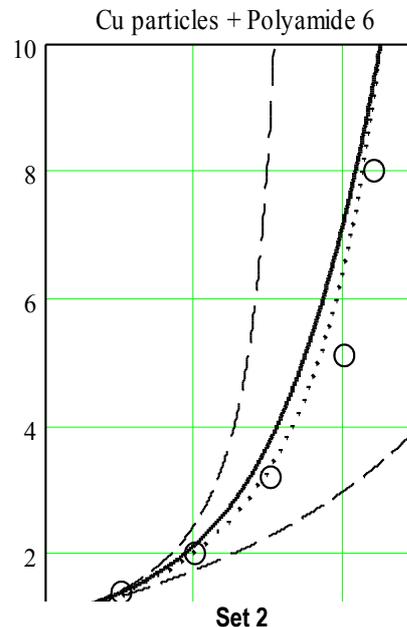
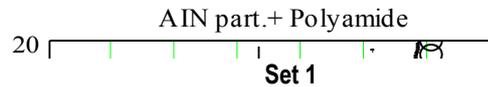
Here f_{max} is the maximum packing volume fraction of particles introduced in equation (7) in order to take into account the overlap effect. For random packing of spherical particles $f_{max} = 0.637$.

Comparisons

Thirteen sets of data concerning the thermal conductivity enhancement of particulate composites at great concentration covering broad ranges of thermal conductivity ratio $\alpha = K_p / K_m$ are considered in order to evaluate our model. In the following we also compare the predictions of our model (equation (4) together with (6)) with the model proposed in (Pal, 2007) - (equation (7)), assuming $f_{max} = 0.637$ (random packing of particles). The lower and upper bounds according to equations (1) and (2) are also shown. In table 1 we have describe the various composites considered in the present work.

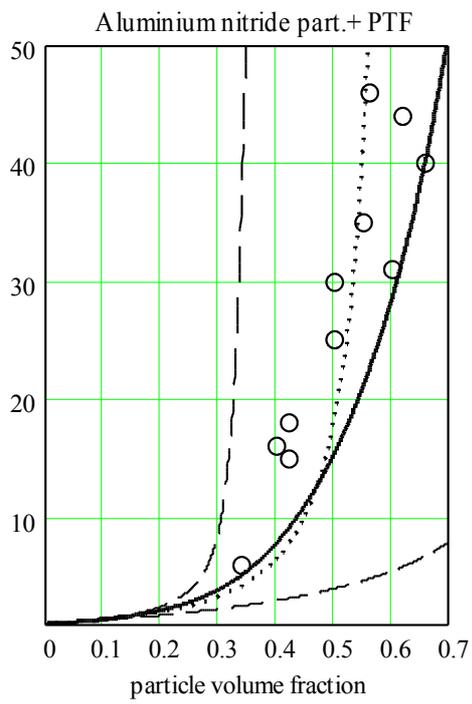
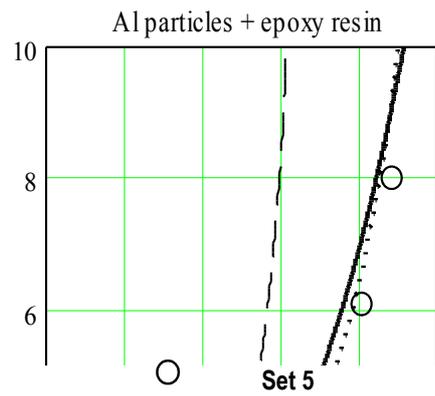
Table 1. Characteristics of the composites presented here

Set	filler	matrix	α	references
1	Alum. nitride	Polyamide	909	Wang, 2004
2	Cuprum	Polyamide 6	1200	Tavman, 1996
3	Alum. oxide	Polystyrene	290	Pal, 2007
4	Alum. nitride	Polyvinylidene fluoride	1666	Pal, 2007
5	Aluminium	Epoxy resin	1068	Pal, 2007
6	Aluminium	Parafine oil	200	Pal, 2007
7	Aluminium	Polyethylene	737	Tavman, 1996
8	Aluminium	Polypropylene	992	Pal, 2007
9	Cuprum oxide	Epoxy resin	42	Pal, 2007
10	Glass	Polystyrene	7	Nielsen, 1974
11	Graphite	Polytetrafluoroethylene	643	Cai, 2005
12	Glass	Polyethylene	3.15	Nielsen, 1974
13	Selenium	Polypropylene glycol	37	Baxley, 1966

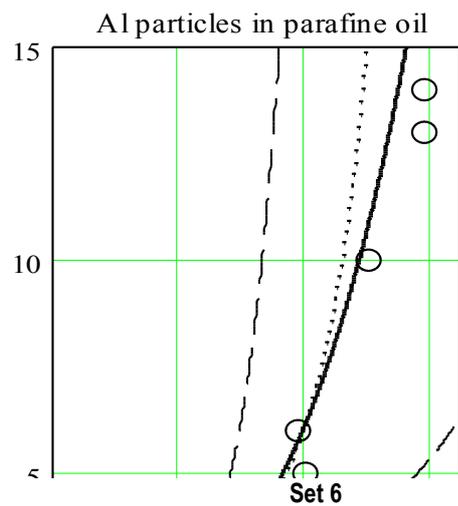




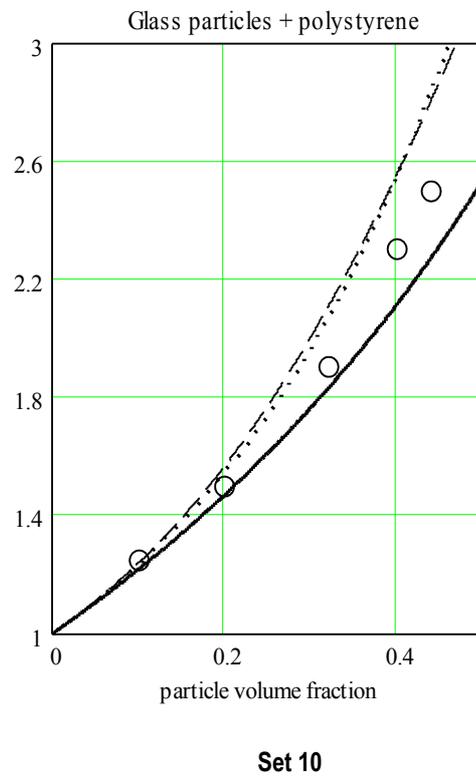
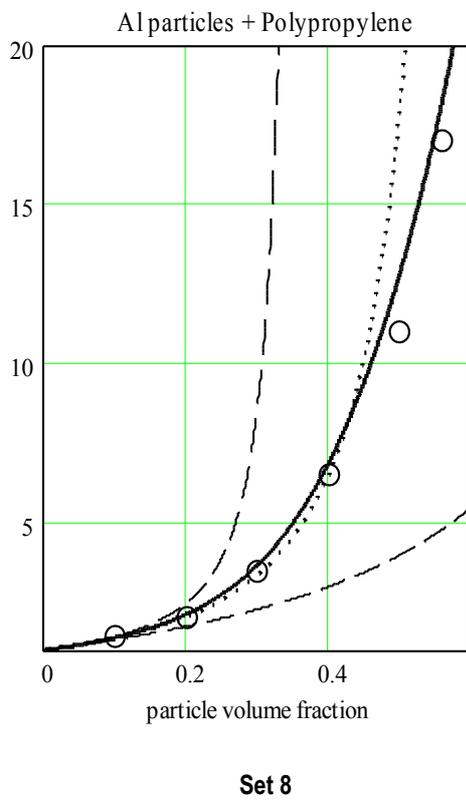
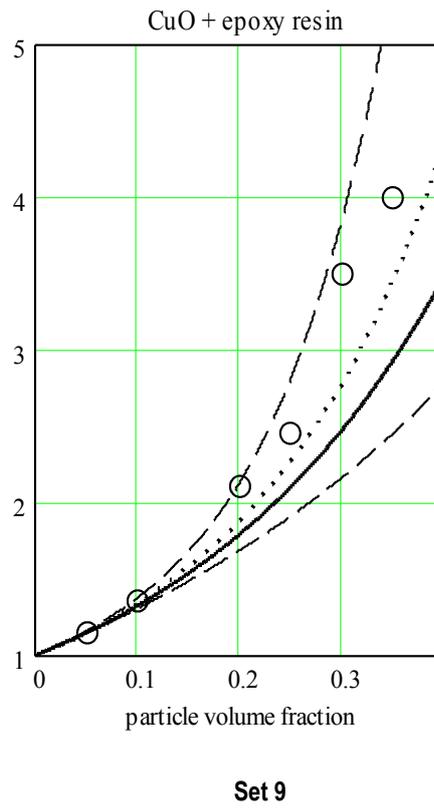
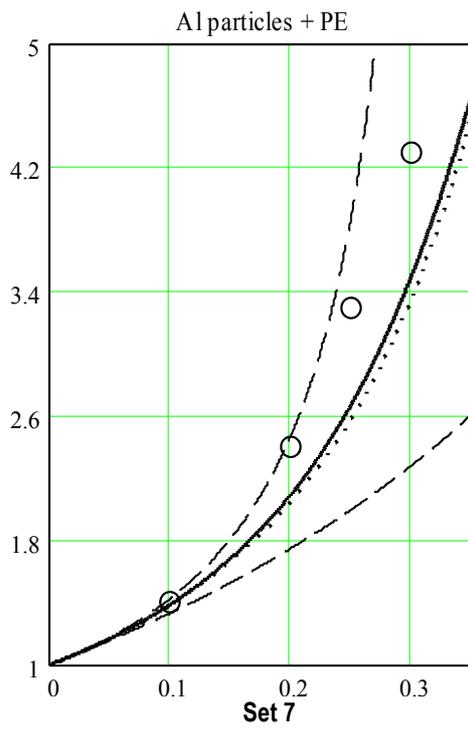
Set 3

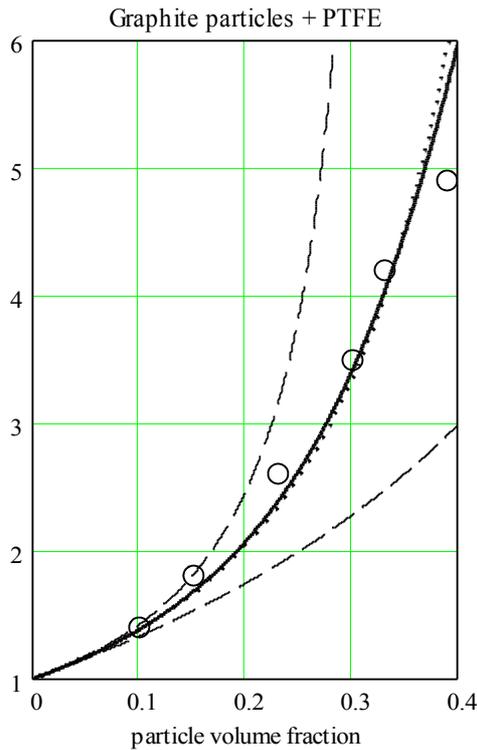


Set 4

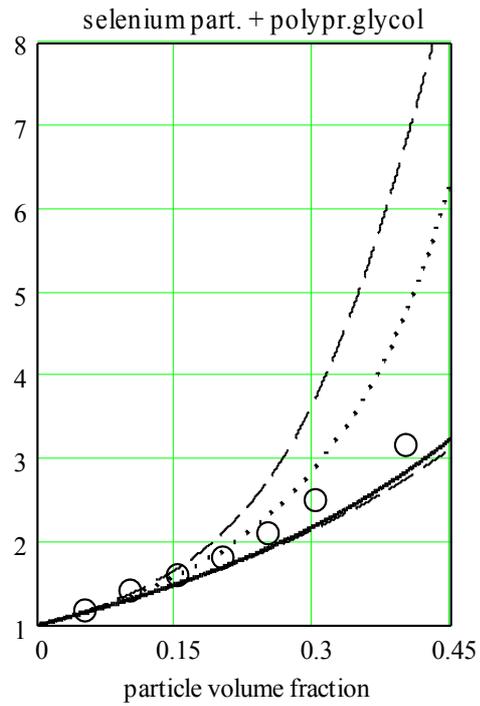


Set 6





Set 11



Set 13

In the above figures (sets from 1 to 13), the thick line concerns our model - equations (4) and (6), the dotted line concerns equation (7) and the dashed lines concern the lower and upper bounds according to equations (1) and (2) respectively.

Discussion

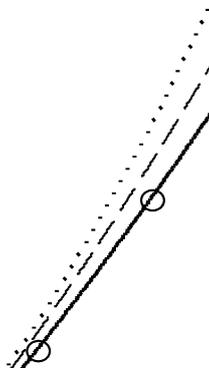
As one can see the proposed c-function - equation (6) in the self consistent scheme - equation (4) can well predict the thermal conductivity enhancement of particulate composites taking into account the interaction between spherical inclusions which is encountered by great volume fractions of inclusions. Our equation agrees a little better than equation (7) proposed by Pal (2007) and based on the so called differential medium approach. Some disagreement with the experimental data - set 9, can be explained by the nonspherical inclusion shape (Nielsen, 1974). In sets 10 and 12 our equation coincides practically with the Maxwell one because of the lower thermal conductivity ratio α .

Acknowledgements

Financial support by the AUF (project No 6316 PS 821 / 2008) is greatly acknowledged.

This work was supported also by the Scientific Research Section of the UCTM - project No 10518 / 2008.

Set 12



References

- Baxley A.L., Couper J.R. 1966. Thermal Conductivity of Two-Phase Systems, part IV, *Research Report Series No.8*, University of Arkansas (Ed), Arkansas, 239 p.
- Bruggeman D.A.G. 1935. , Berechnung verschiedener physikalische Konstanten von heterogenen Substanzen, *Annalen der Physik*, 24, 636-679.
- Cai W., Tu S., Tao G. 2005. Thermal Conductivity of PTFE Composites with Three-dimensional Randomly Distributed Fillers, *J. of Thermopl. Comp. Mater.* vol. 18, 241-253.
- Hashin Z., 1968. Assesment of the Self consistent Scheme Approximation: Conductivity of Particulate composites, *Journ. Comp. Materials*, vol.2, 3, 284-300.
- Maxwell J. A. 1904. *Treatise of Electricity and Magnetism*, Clarendon, 3rd ed., Oxford, 275 p.
- Nielsen L. 1974. The Thermal and Electrical conductivity of Two-Phase Systems, *Ind. Eng. Chem.Fundam.*,13,17-20.
- Pal R. 2007. New Models for Thermal conductivity of Particulate Composites, *Journ.of Reinf. Plastics &Comp.*, vol 26, 7, 643-651.
- Tavman I. 1996. Thermal and Mechanical Properties of Aluminium Powder-Filled High density Polyethylene composites, *J. Appl. Pol. Sci.* 62, 2161-2167.
- Wang B.X. at al., 2003, *Int.Journ. Heat&Mass Trans.* 46, 2665-2672.
- Wang J., Yi X., 2004, *Comp.Sci.&Tech.*, 64, 1623-1628.
- Yin Y., Tu S.T. 2002. Thermal conductivities of PTFE composites with Random distributed Graphite Particles *Journ. Reinf. Plast. & Comp.* vol.21, 1619-1627.

Recommended for publication by Editorial board