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Predicting, Measuring, and Tailoring the Transverse Thermal Conductivity of Composites from Polymer Matrix and Metal Filler[1]

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The addition of conductive filler in a polymer matrix is an effective way to increase the thermal conductivity of the plastic materials, as required by several industrial applications. All quantitative models for the thermal conductivity of heterogeneous media fail for heavily filled composites. The percolation theory allows good qualitative predictions, thus selecting a range for some qualitative effects on the thermal conductivity, and providing a way to choose a range for some experimental parameters. The design of such composite materials requires a study of its thermal features combined with different mechanical, ecological, safety, technical, and economical restrictions. A specific small guarded hot plate device with an active guard, conductive grease layer, and controlled variable pressure was used for measurement of the transverse thermal conductivity on 15 mm sided samples of composite parts. Extensive thermal and composition measurements on filled thermoplastics show that the conductivity of the filler, its size and shape, and its local amount are, with the degree of previous mixing, the main factors determining the effective conductivity of composites. For injection-molded polybutylene terephtalate plates, the best filler is the short aluminum fiber. With fibers of 0.10 mm diameter, it is possible to obtain conductivities larger by factors of 2, 6, and 10 than those of polymer for aluminum contents of 20, 42, and 43.5 vol%, respectively.

KEY WORDS: aluminum fiber; filled polymer; thermal conductivity; thermoplastic compound.

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1. INTRODUCTION: THE CHALLENGE OF THERMALLY CONDUCTIVE POLYMERS

Thermally-conducting filled composite polymers (TCFCP) are heterogeneous materials containing at least two solid phases: a continuous insulating one—the matrix with a polymeric structure—and a disperse conducting phase. The last phase is introduced as filler during the elaboration of the composite; thus, the positions of inclusions in the end product are irregular. The conducting inclusions are more or less unequal in shape and size, as the technical nature of the whole problem does not allow well calibrated filler particles.

Such materials are intended to be used instead of simple polymers when good transfer of heat is required, as in automotive structure panels or for cases containing active electronics. Typical geometries of parts are plate-like, of variable thickness: 0.8 to 2 mm for electronics and electrotechnics, and 2 to 4 mm for mechanical or energetical applications.

The suitable thermal conductivity in the transverse direction of the plate is 1.3 to 2 $W \cdot m^{-1} \cdot K^{-1}$ for mechanical applications and 2 to 4 $W \cdot m^{-1} \cdot K^{-1}$ for electronic applications, instead of low conductivity values from 0.15 to 0.3 $W \cdot m^{-1} \cdot K^{-1}$ of unfilled technical polymers. The in-plane conductivity is less relevant for the end-user, although good values for this property can help to avoid hot points.

A practical difficulty for the creation of the TCFCP consists of preservation of the technical characteristics of the bare polymer. As the presence of filler leads to poor mechanical properties (inducing fragility, for example), great care must be taken into account to satisfy, by design of composite, not only good conductivity, but also the requirements of stability, innocuousness, mechanical quality and, last but not least, low price. An alternative to the filled polymers is the intrinsically conductive polymers, but their high cost and their lack of stability are the main drawbacks for their use.

The difficulties to produce true conducting TCFCP increase in the following order: inks, adhesives/mastics, rubbers, thermosets, and thermoplastics. The first two classes are already technically mature, the rubbers are often made conductive by blending with carbon black, but thermosets are seldom made conductive by filling. Finally, the commercialization of conductive thermoplastics, though repeatedly announced, has never became effective.

2. PREDICTION OF THE EFFECTIVE CONDUCTIVITY OF THERMALLY-CONDUCTING FILLED POLYMERS

Studies dedicated to the computation of the effective thermal conductivity $\lambda_{t,\mathrm{eff}}$ for composite materials are very numerous and periodically reviewed as, for example, by Uvarov [1] for analytical equations and by Privalko and Novikov [2] for calculations using numerical methods.

2.1. *Ab initio* Prediction Models

The most developed are the *ab initio* methods. In the simplest case, the composite volume is entirely occupied by two kinds of material, of known conductivities, λ_m and λ_f for matrix and filler inclusions, respectively. If the thermal field is continuous (there is no contact resistance between the two phases), it is possible in principle, to compute the $\lambda_{t,\mathrm{eff}}$ value from a complete knowledge of the spatial distribution of the matter, i.e., if in any given point of space the existing matter is either the polymer or the filler.

Any *ab initio* method does not start with the true spatial distribution of matter, since this is very difficult to measure. Instead, one makes use of simplified models of distribution. One can distinguish between deterministic and statistical methods.

The former assumes that the distribution is entirely known before the computation. The filling of space can be described with a spatially periodic structure or with a self-consistent technique.

- The deterministic methods assume that the composite is formed by a great number of identical heat flux tubes (separated by adiabatic walls) and that each flux tube is composed from a number of equivalent cells, separated by isothermal planes and each one containing an inclusion. The self-consistent method replaces the heterogeneous structure by a homogeneous "effective medium" with the same global properties, averaging fields and fluxes (Staicu et al. [3]).
- Another possible *ab initio* calculation uses statistical methods, implying the stochastic attribution of the space points to one phase or another, as Nicolai and De Baerdemaecker [4] suggest.

The statistical methods can be:

- Probabilistic: use of the probability function for simultaneous distribution between phases of **n**-points, depending on the distances between all the points
- variational, leading to upper and lower bounds for the λ_{eff} value
- percolational, introducing the concept of conductive breakthrough for each filler amount greater than the critical "percolation" threshold value (Dani and Ogale [5]).

2.2. Physical Prediction Models

These methods do not require a detailed knowledge of the composite structure. Instead, the list of arguments contains macroscopic (thus, measurable) properties of each phase, as the two conductivities λ_m and λ_f, of the composite itself (volumetric fractions ϕ_f and ϕ_m of filler and matrix, $\phi_f + \phi_m = 1$) or another property easier to measure than $\lambda_{t,\,eff}$. One can distinguish between semi-empirical and empirical relationships: the former do not contain any adjustable parameters, whereas the latter contains such parameters and thus some λ_t measurements are required.

The simplest equations contain as arguments only λ_m and λ_f and a volumetric fraction ϕ_f:

$$\lambda_{t,\,eff} = \lambda_m F(\lambda_f/\lambda_m, \phi_f) \tag{1}$$

either as asymmetric formulae (i.e., that distinguish the continuous phase from the disperse one) or as symmetric equations, which do not change form by replacing in Eq. (1) λ_f by λ_m, λ_m by λ_f, and ϕ_f by $\phi_m = 1 - \phi_f$. The symmetric equations generally have a larger range of validity than the asymmetric ones, but are not very accurate, as they do not take into account the different connectivity of phases. A well-known asymmetric equation is the Maxwell–Eucken equation [6], with the function F in Eq. (1) given by

$$F = (R_{ME} + 2)/(R_{ME} - 1), \qquad R_{ME} = (\lambda_f/\lambda_m + 2)/[\phi_f(\lambda_f/\lambda_m - 1)] \tag{2}$$

whereas the most popular symmetric relationships are those for the lower λ_L and the upper λ_U bounds of $\lambda_{t,\,eff}$ given by Hashin and Shtrikman [7], $\lambda_{L,\,HS} \leqslant \lambda_{t,\,eff} \leqslant \lambda_{U,\,HS}$:

$$\begin{aligned} \lambda_{L,\,HS} &= \lambda_m + \phi_f[(\lambda_f - \lambda_m)^{-1} + \phi_m(3\lambda_m)^{-1}], \\ \lambda_{U,\,HS} &= \lambda_f + \phi_m[(\lambda_m - \lambda_f)^{-1} + \phi_f(3\lambda_f)^{-1}] \end{aligned} \tag{3}$$

Other items in the argument list can be the aspect ratio of individual filler particles and the connectivity tendency, which is more or less defined empirically. The particle size does not belong to this list, so long as the model does not consider the thermal contact resistance. One can also find adjustable parameters, as by Phelan and Niemann [8] or by Nielsen [9] whose equation is at present the most used for the thermal conductivity of filled polymers.

Generally, the existing models are satisfactory for low filler contents and become inappropriate when the amounts of filler with large conductivities

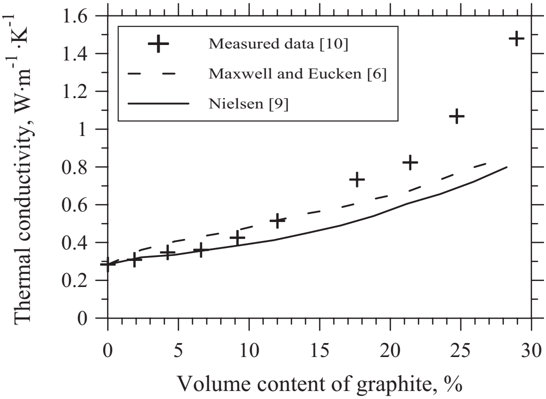


Fig. 1. Thermal conductivity of polyethylene filled with graphite.

exceed 20%. This is illustrated by Fig. 1 (according to Agari and Uno [10]) for the conductivity of graphite filled polyethylene.

3. SEARCH FOR MATERIALS AND FOR PROCESSING

3.1. Utility of Models for Thermal Conductivity

The utility of the different models and relationships for the selection of materials and processing conditions has to be considered from three angles:

- **Predictive features.** The existing models for $\lambda_{t,\mathrm{eff}}$ in heterogeneous mixtures are ineffective for predictions for TCFCP: the *ab initio* methods need precise knowledge of the material texture (which is never available or even quantifiable), whereas the so-called "physical" methods can be used for estimates of the conductivity only for systems with a ratio $\lambda_{t,\mathrm{eff}}/\lambda_m$ less than 3, being thus of little interest for TCFCP, where $\lambda_{t,\mathrm{eff}}$ must be 10 times greater than the matrix conductivity λ_m.

  The prediction of the physical models are not so sharp. Thus, for example, for a conductivity of composite of 2.2 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ (i.e., 10 times the conductivity of bare polymer) with PBT and Al of thermal conductivities of 0.22 and 180 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, respectively, the volumetric amount of filler for Maxwell–Eucken is 75 vol%, whereas the Hashin–Shtrikman models provide limits as different as 1.6 and 75 vol%. This does not compare very well with the experimental values of 43 vol% of aluminum.

- **Explanatory features.** On the other hand, some conductivity models are *explanatory*, providing justification of some features of TCFCP's thermal conductivity. For example, the percolation theories can explain why the $\lambda_{\mathrm{t,eff}}(\phi_{\mathrm{f}})$ dependence is weak at low filler content, but it becomes quickly strong when ϕ_{f} overtakes the percolation threshold, ϕ_{fc}. Nevertheless, the value of this threshold cannot be predicted.
- **Exploratory features.** Nearly all identified models for $\lambda_{\mathrm{t,eff}}$ are exploratory, i.e., they can be used to select a list of factors to modify the conductivity. The content of this list changes from one model to another, and thus, quantitative selections for each factor, to measure it or to control it, is rarely straightforward.

3.2. Tailoring a Composite with Desired Properties

Considering the difficulty of predicting the conductivity, the great number of factors to modify λ, and the great number of technical requirements imposed on each industrial product, it appears to be of great importance to select for each factor—quantitative or qualitative—one of the three following possibilities:

(a) vary the factor over a more or less great number of levels (for quantitative factors) or of modalities (for qualitative factors),
(b) keep the factor constant, or
(c) leave the factor uncontrolled.

The most important task in conceiving a product is to put each factor in one of these three classes above. The decision depends on the following points:

1. If the probability effect of a quantitative factor on λ is nonlinear, and/or it is easy to change the factor, the best choice is (a).
2. If the assumed effect is linear (and of known direction) and/or it is difficult to modify the factor, the best choice is (b).
3. If the factor has probably little effect, or the sign of its effect is unpredictable, or the factor correlates strongly with another factor, it is rational to choose (c).

For case (a), the optimum choice for selecting the value of the factor depends on the type of factor:

- For a quantitative factor, the optimum level is the one that ensures better conductivity without important degradation in the economical, safety, or environmental properties of the TCFCP; but

- if the factor is qualitative, the best choice is to select a modality for which a good $\lambda_{t,\,eff}$ is probably more difficult to realize than for most of the cases. This can ensure a larger range of validity conditions of fabrication of a TCFCP.

3.3. Uncontrolled, Fixed, and Varied Factors in the Experimental Study of TCFCP

The choice of uncontrolled or fixed factors, and in the first case, the choice of the modality or level, is presented in Table I. The numbers of uncontrollable factors is actually infinite.

Table I. Control of Factors Acting upon the Thermal Conductivity of Filled Polymers

	Controlled levels or modalities	
Factor description	Number	Value(s)
polymer composition: class	1	thermoplastic, in technical degree
polymer composition: subclass	1	PBT (polybutylene terephtalate)
filler composition: class	1	metal
filler composition: subclass	1	aluminum, in technical degree
filler content (average of the whole molded part)	5	10/15/20/30/40 vol%.
shape of filler particles	2	powder/fiber
diversity of shape	2	only one shape/ both (powder + fiber) shapes
size of filler particles	2	big/little: 90/150 μm but 180/300 μm, if the *filler shape* = powder
dispersity of the filler size	1	large (as resulting by the cheapest manufacturing)
mixer type	1	twin screw
mixing time	2	90/300 s
mixing temperature	0	see Section 3.3
mixing power	1	20% as higher as stipulate for pure PBT
forming process: class	1	molding
forming process: subclass	2	compression/ injection molding
forming installation	2	(mold no. 1/mold no. 2 from different workshops)
molding temperature	0	see Section 3.3
molding pressure	1	as for pure PBT
form of molding part: class	1	tabular
form of molding part: subclass	1	squared but circular, if the *forming process subclass* = compression
size of molding part	1	100 mm size
thickness of molding part	2	2/4 mm
mold alimentation	1	frontal (through the narrow side)
location of measurements	15	different positions within the molded part
thickness of sample (for physical measurements)	1	the whole thickness of the part
shape of the sample	1	squared
sample side	2	10/15 mm

One can observe that the *average* temperatures of mixing and molding are controlled factors but they are not important for the processing; it is the distribution of temperature that matters, and especially the maximum temperature whose control is not easy within industrial equipment.

4. MEASUREMENT METHODS

4.1. Thermal Conductivity

An experimental device was developed for measurements of small and average thermal conductivities (from 0.1 to 5 $W \cdot m^{-1} \cdot K^{-1}$) on small samples (maximum dimensions of $5 \times 15 \times 15\ mm^3$). The experimental procedure represents an extension of the guarded hot plate (GHP) method. A heat source and a heat sink (an electrical heater and two heat exchangers with thermostated baths) are located, respectively, on the bottom and top surfaces of the sample. This setup generates a temperature gradient in the thickness direction. The main characteristic of the experiment concerns the use of an active guard that allows the thermal flux, dissipated by the heat source, to pass entirely through the sample (Fig. 2a).

Parallelism between upper and lower plates of the experimental setup was achieved using guides for vertical displacement, that were controlled by a pneumatic jack in order to ensure an adjustable pressure P on both sides of the sample. In order to minimize the measurement errors, the following precautions have been taken:

- A thermal guard was wrapped around the sample for minimizing the heat losses to the surroundings. This ensures that the relative rate of the heat loss is less than 0.1%, for a 5 mm thick sample.
- Thermal resistances between the sample and heat source and between the sample and heat sink, were minimized by applying a thermal grease on the top and bottom faces of the sample.

For the latter item, the effect of thermal contact resistance on λ_t measurements was carried out by embedding three internal 80 μm thermocouples in a 4 mm thick sample and by varying the contact pressure P and the application (or not) of silicone grease on both sides of the sample. The results are presented in Fig. 2b, where *external* refers to the thermocouples installed in the heat sink and the electric heater. These thermocouples are usually used for the λ_t measurement with this noninvasive GHP method. For samples without silicone grease, λ_t values calculated from external and internal thermocouples differ by 20 to 30%, whereas this difference with silicone grease is in the range of measurement error

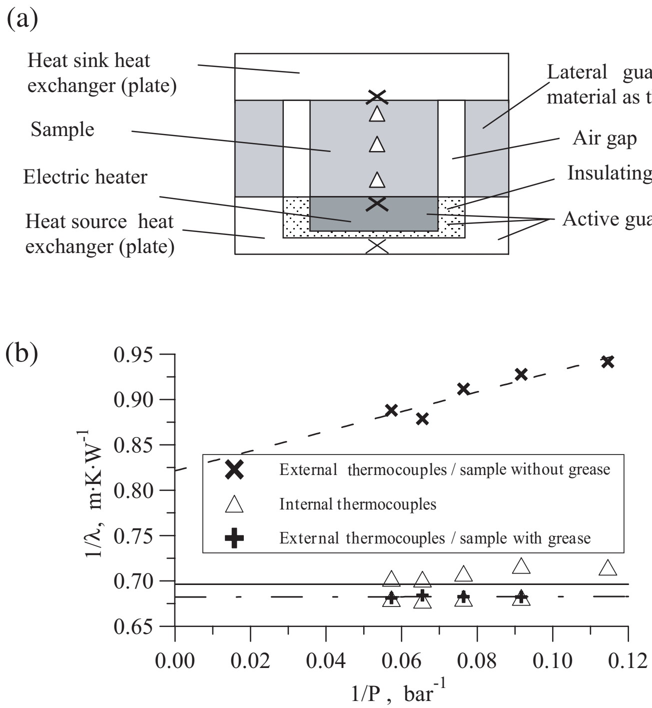


Fig. 2. (a) Thermal conductivity measurement setup and locations of internal (△) and external (×) thermocouples for the study of the effect of thermal contact resistance. (b) Effect of the thermal contact resistance between sample and instrumented setup on the thermal conductivity values.

(about 5%), independent of the pressure. This demonstrates the necessity to introduce silicone grease between samples and setup, in order to minimize an important measurement bias.

4.2. Electrical Conductivity and Compound Composition

For electrical conductivity measurements, 100 nm thick silver coatings on both faces of each sample were used as electrodes in order to obtain the bulk resistivity. This setup minimized biases caused by the electrical contact resistance and by water films on the samples.

The average composition of the injected parts is rather well known, but the content of filler particle depends on the location that is considered in the part. To study the sample inhomogeneity, samples were cut from the injected parts and their filler concentrations were measured by weighing the residual amount of material after 450°C pyrolysis of compound samples.

5. RESULTS AND DISCUSSION

5.1. Effects of Varied Factors on the Sample Conductivity

5.1.1. Filler Conductivity and Shape

By using a wide range of materials as filler in a previous set of measurements, we have noticed that ceramic fillers cannot provide a suitable increase of thermal conductivity without an unacceptable hardening of the compound. The only filling material which has really improved the thermal conductivity without significantly decreasing the mechanical properties is boron nitride, but the price of this filler is much too high to keep the compound competitive.

Within the type and proportion to be handled during the mixing, the addition of carbon black fillers does not result in a significant increase in the thermal conductivity, as shown in Table II. In this table, thermal conductivities and filler amounts are mean values for the molded part. The filler amounts differ between fillers; they represent 95% of the maximum amounts which can be incorporated into the polymer without mechanical damage for the mixer. For metallic fillers, it was shown that fibers give better results than powders. The mixing of fillers of different materials or shapes does not provide any significant improvement. Aluminum fibers are satisfactory as fillers, provided that they are thin enough, as will be shown in Section 5.2.

5.1.2. Compounding and Processing Conditions

The choice of compounding conditions has a great effect on the final quality of the compound, for example, by allowing a more or less controlled fiber/polymer proportion. Not enough tests were performed with various residence times and shear strengths during the mixing in order to

Table II. Thermal Conductivities of Injected Compounds with PBT and Various Types of Filler

Filler	carbon black (CB)	aluminum powder[a]	aluminum fiber ALF1[a]	aluminum fiber ALF2[a]	aluminum powder + ALF1 + CB
ϕ (vol %)	9	25	34	44	20[b]
$\lambda_{\mathrm{t,\,eff}}$ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	0.37	0.79	0.85	1.42	0.50

[a] Al. powder (aver. diam.: 300 μm), ALF1 fiber (diam.: 150 μm, length: 1.1 mm), ALF2 fiber (diam.: 90 μm, length: 1.1 mm).

[b] Composition: 9 vol% of aluminum powder, 9 vol% of ALF1 fiber, and 2 vol% of carbon black.

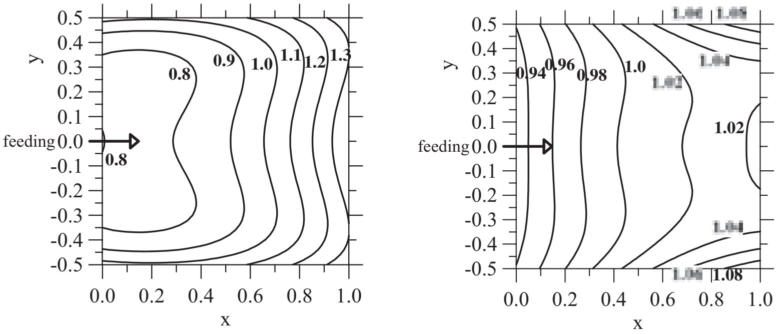
conclude on the effect of these two factors. For the molding process, we have found that the shape of the gate and the mold geometry are not too important for the *average* conductivity, but are of considerable importance for the orientation and distribution of fiber in the final parts and, therefore, for the *local* $\lambda_{t,\,eff}$ value, as will be illustrated later in Sections 5.2 and 5.3. Otherwise, by changing the thickness of the parts, $\lambda_{t,\,eff}$ values do not vary, i.e., there is no significant skin effect.

5.2. Local Variations of Filler Content

Minimizing the dispersion of $\lambda_{t,\,eff}$ is crucial to avoid hot points during the use of molded parts. In order to check the homogeneity of the parts, smaller samples were cut out of injected polymer parts filled with ALF1 thick fibers. It appears that the distribution of filler was very inhomogeneous; the measured filler content in the small samples has a mean value of 32.2% with a dispersion of 6.7% (Fig. 3). With thin fibers of ALF2, the dispersion of filler content was reduced to 1.6% (i.e., 4 times smaller), for a mean value of 43.1%.

5.3. Effect of the Filler Content on the Thermal and Electrical Conductivities

Experimental results for ALF1 and ALF2 aluminum fibers were used to plot the transverse thermal and electrical conductivities versus the



$\phi_{f,\,average} = 32.7\ \%$

PBT filled with thick (ALF1) fibers

$\phi_{f,\,average} = 34.8\ \%$

PBT filled with thin (ALF2) fibers

Fig. 3. Spatial distribution in the mold of the relative (i.e., divided by the average value) aluminum fiber content for thick ALF1 and thin ALF2 fibers. x is the flow direction during the feeding and y is the direction perpendicular to x in the plane of the molded part.

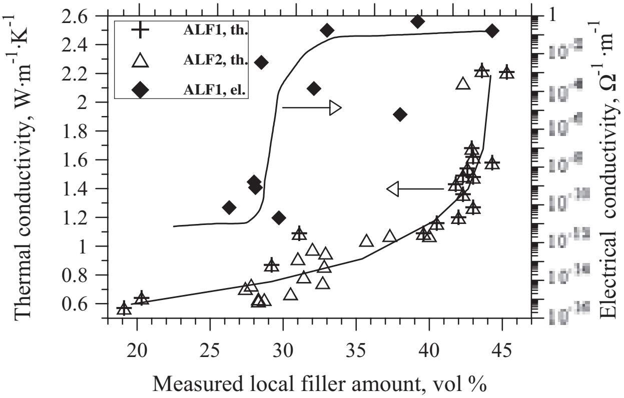


Fig. 4. Thermal and electrical conductivities versus measured local filler amount (compound with PBT and ALF1 fiber).

measured filler content (Fig. 4). One can notice a strong increase of λ_t between 40 and 45 vol% of filler, proving thus a typical percolation pattern for heat transfer. The percolation threshold for thermal conductivity (about 43 vol%) appears to be higher than the one (about 30%) for the electrical conductivity. This results probably from the difference between the two conductivity filler/matrix ratios: the ratio is only 3 orders of magnitude for λ_t and 18 or 19 orders of magnitude for λ_{el}.

6. CONCLUSION

For injection-molded flat pieces from filled polybutylene terephtalate (its thermal conductivity is 0.22 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ in unfilled state), the largest transverse thermal conductivity that we have obtained by adding filler is 2.2 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The conditions to obtain this (see also Table II) include the use of short aluminum fibers (square cross-sectional area of average side of 0.09 mm and average length of 1.1 mm) in a proportion of 43 vol%.

The nonuniformity of λ_t is still important; the relative standard deviation is near 30%, for an extent of the molded part of 100 mm. For coarse fibers, the nonuniformity of λ_t values is similar to that for thin fibers, since the larger nonuniformity of the filler amount for coarse fibers is compensated by a smaller sensitivity of λ_t to the amount of these fibers.

Possible ways to attain a further increase of the average thermal conductivity are as follows:

- Increasing the filler amount up to 50 vol%. This requires important changes in the process compounding and can be damaging for the mixing screw. One can, for example, recirculate the masterbatch, with a gradual introduction of metal filler, or introduce an important amount of a well chosen surfactant agent into the compound mixture.

- Changing the mold design, by locating the entrance gate on the broad side of the mold. The fibers will presumably become better oriented.
- Increasing the dispersion of fiber in the volume of the matrix, avoiding the clustering of fiber. This can be done either by a greater mixing intensity (thus increasing the power of the mixer), or by finding a good third component of the masterbatch, to better spatially distribute the filler. This component can be either the already discussed surfactant, or another thermoplastic, only partially miscible with the PBT and forcing the filler to prefer the interfacial region between the two polymers.
- Changing the connectivity of the conductive paths, by using a metallic sponge filler instead of the fibrous metal.

To reduce the nonuniformity of the λ_t distribution across the surface of the part, we suggest:

- Modification of the admission rate of filled polymer in the mold, by more precise control of the matter output, or of the viscosity of the polymer just before molding.
- Further decrease of the filler size, as the nonuniformity is presumably increasing with the inertia forces during the mold filling, and these forces are proportional to the weight of a fiber.

This decrease of the filler size leads to a risk: a reduction of the average conductivity, by increasing the effect of the thermal contact resistance TCR (at the polymer/metal interface) on the effective conductivity. Indeed, as Lipton and Vernescu [11] have shown, the appearance of a resistance at the phase contact reduces the effective conductivity of a composite, especially when the size of inclusion decreases.

This risk is not easy to evaluate, as the TCR is not well understood: the only measurements—our proper ones: Dupuis et al. [12]—seem to indicate that a 50% reduction in the fiber diameter does not reduce the average conductivity more than 10%. But this effect assumes that the contact resistance is not dependent on the curvature of the interface, and this hypothesis needs to be verified.

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