PAULINA JAKUBOWSKA[1),*)], TOMASZ STERZYŃSKI[2)]

Thermal diffusivity of polyolefin composites highly filled with calcium carbonate

Summary — The thermal diffusivity measurements are usually performed in order to determine the ability of polymeric materials to transport heat and to characterize the rate of heating and cooling of plastic products. In our investigations the so-called modified Angstrom method was used, and the investigations were conducted on four types of materials: blends of commercial polyolefins (PE-HD/*i*-PP) and three types of composites of PE-HD/*i*-PP/$CaCO_3$ where $CaCO_3$ was modified with calcium stearate or stearic acid and waxes or was unmodified. The content of $CaCO_3$ in all the blends was in the range between 48 and 64 wt. %. The results have been discussed in terms of the influence of calcium carbonate content, particles size and modification of the filler on the thermal diffusivity of highly filled polyolefin composites.

Keywords: thermal diffusivity, polyolefin composites, calcium carbonate.

DYFUZYJNOŚĆ CIEPLNA KOMPOZYTÓW POLIOLEFIN O WYSOKIM STOPNIU NAPEŁNIENIA WĘGLANEM WAPNIA

Streszczenie — Dyfuzyjność cieplna materiałów polimerowych określana jest zazwyczaj celem wyznaczenia ich zdolności do transportu ciepła i służy określaniu zdolności do nagrzewania oraz chłodzenia gotowych wyrobów wytworzonych z tworzyw polimerowych. W niniejszej pracy do badań dyfuzyjności cieplnej zastosowano zmodyfikowaną metodę Angstroma. Badaniom poddano cztery typy materiałów: mieszaninę poliolefin (PE-HD/*i*-PP) oraz trzy rodzaje kompozytów PE-HD/*i*-PP/$CaCO_3$, w których $CaCO_3$ był: modyfikowany stearynianem wapnia lub kwasem stearynowym oraz woskami lub nie był modyfikowany. Zawartość $CaCO_3$ we wszystkich rodzajach kompozytów mieściła się w granicach od 48 do 64 % mas. Określono zależność dyfuzyjności cieplnej od zawartości węglanu wapnia, rodzaju modyfikacji jego powierzchni oraz rozmiaru cząstek.

Słowa kluczowe: dyfuzyjność cieplna, kompozyty poliolefin, węglan wapnia.

In recent years the numerical models used as a tool to improve control and quality of polymer processing became more sophisticated, thus there is an increasing need for reliable data, concerning among others also their thermo-physical properties. Such thermal properties are usually measured when heat is supplied or removed from the material, and these data are very important in any project including the thermal environment [1—2]. The understanding of the heat transfer under steady or transient conditions is an essential point in any engineering design, as well as for the tailoring of thermal and mechanical behavior of materials [3].

THERMAL CONDUCTIVITY AND DIFFUSIVITY

The thermal conductivity (λ), thermal diffusivity (*D*), specific heat at constant pressure (c_p) and bulk density (ρ) are related by the following equation [3—7]:

$$D = \frac{\lambda}{\rho \cdot c_p} \tag{1}$$

Principally, the thermal diffusivity is representative for the heat propagation through a material, usually taken into consideration by non-steady state heat conduction, which frequently happens during heating and cooling of polymeric materials. This is a key property needed to determine the cooling time, by optimization of injection molding cycle time, and melt extrusion. In the analysis of most extrusion problems a constant value of thermal diffusivity is assumed, although it depends on pressure, temperature and macromolecular orientation [2, 5, 8, 9]. During cooling a temperature profile with a slope dependent on material's thermal diffusivity, profile dimensions, and thermal gradients, *etc.*, may be deve-

---

[1)] Poznan University of Technology, Institute of Chemical Engineering and Technology, Polymer Division, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland.

[2)] Poznan University of Technology, Institute of Material Technology, Polymer Division, ul. Piotrowo 3, 60-965 Poznań, Poland.

[*)] Author for correspondence; e-mail: Paulina.Jakubowska@put.poznan.pl

loped, leading to creation of a crystalline distribution profile on the product section that determines the final product properties [10]. Though, the thermophysical properties of polymers should be known to produce high-quality products, without or with a low level of residual stresses, thus warranting a high dimensional stability [11] of molded polymeric products.

The thermal diffusivity of commonly used polymeric materials, like polypropylene and polyethylene is relatively low, however for certain applications materials with enhanced thermal properties are required. By an addition of suitable fillers as aluminum powder, carbon fibers, graphite, aluminum nitrides or magnetite particles, the thermal diffusivity of polymers may be shifted from $D = 0.2$ mm^2/s for an unfilled polypropylene, up to a significantly higher thermal diffusivity of $D > 1.2$ mm^2/s [12]. Such polymer composites with a high thermal transport ability, relatively to the unfilled ones, become more and more important in a wide range of applications, like production of electronic packaging [13], *etc*.

DETERMINATION OF THE THERMAL DIFFUSIVITY

Currently, various techniques for the determination of thermal diffusivity are known from the literature. Transient methods are commonly used for the determination of heat transport in polymers at elevated temperature, due to its relatively short test duration, compared with steady-state methods; thereby allowing to reduce the specimen degradation. The following commonly used techniques may be cited: laser flash methods [3, 8, 9, 12, 14—18], laser heating [19], flash radiometry technique [20, 21], photothermal radiometry [22], photothermal mirage [23] and optical techniques — Rayleigh scattering [25, 26], photoacoustic spectroscopy methods [24, 28], unsteady state technique — step down perturbation method [10], transient methods, for example plane source technique or heat transfer in a semi-infinite solid [27, 29], nonlinear least-squares criterion [30], periodical methods [31] and finally hot-wire methods [2, 3, 32, 33] and temperature wave analysis [20, 34, 35].

The above mentioned techniques require mostly specific samples preparation and the measurement procedures are time consuming. In our investigations the so-called modified Angstrom method [38, 39] was used, characterized by a relatively effortless sample preparation, a short measurement time, simple experimental procedure and relatively simple measuring device, as only the determination of temperature and time are required.

HIGHLY FILLED POLYMERIC COMPOSITES

Over the last few years the development of new composite materials, because of its very attractive properties systems, has been extensively studied. One of the most commonly used fillers, applied in a high concentration is calcium carbonate. Although, a huge number of papers concerning composites of polyolefins with calcium carbonate in world-literatures were published, there are no data available about ternary composites where one polymer is a matrix, and the second one with $CaCO_3$ as a filler is added as a master batch. Such polymeric composites are used in the production of paper — like films. Moreover, up till now all investigations were performed for composites with the $CaCO_3$ content below or equal to 40 wt. %.

Thus, the aim of our studies was the determination of thermal diffusivity of highly filled polyolefin composites (HFPC), with $CaCO_3$ content in the range between 48 and 64 wt. % and the analysis of the heat transport in function of the filler content and filler surface modification. The investigations were conducted by the so-called modified Angstrom method.

EXPERIMENTAL

Materials

The following materials were applied in our investigations:

— a high density polyethylene (PE-HD) with trade name Tipelin FA 381-10 (produced by TVK Rt., Hungary), used as matrix in the investigated composites;

— an isotactic polypropylene (*i*-PP) with trade name Malen P F401 (produced by PKN Orlen, Poland);

— an *i*-PP based master batch Filolen FP-0800 (produced by EXFOLMO Chrostniki S.A., Greece), with 80 ± 2 wt. % of $CaCO_3$ (particle size of 3.7 μm);

— calcium carbonate ($CaCO_3$) — (Omyalite 95T produced by Omya, France) with modified surface, with a high chemical purity and ultrafine particles (1 μm);

— calcium carbonate with a name Omyacarb 2-VA (produced by Omya, France) which was a selected $CaCO_3$ with particle size 2.5 μm, chemical purity.

Preparation of composites

Three groups of composites of type PE-HD/*i*-PP/$CaCO_3$ varied by filler type, were prepared for the thermal diffusivity investigations. The concentrations of components in composites are summarized in Table 1.

Table 1. Composition of four types of PE-HD/*i*-PP/$CaCO_3$ composites

Group	Symbol of the sample	Type of master batch *i*-PP/$CaCO_3$ (20/80)		Content, wt. %		
		i-PP	$CaCO_3$	PE-HD	*i*-PP	$CaCO_3$
H	H1	Filolen FP-0800		40	12	48
	H2			35	13	52
	H3			30	14	56
	H4			20	16	64

M	M1	Malen P F401	Omya-lite 95T	40	12	48
	M2			35	13	52
	M3			30	14	56
	M4			20	16	64
N	N1	Malen P F401	Omya-carb 2-VA	40	12	48
	N2			35	13	52
	N3			30	14	56
	N4			20	16	64
R	R1	Malen P F401	—	77	23	—
	R4			56	44	—

Two mixtures of PE-HD with neat *i*-PP (R1 and R4) were also examined as a reference material.

The samples (10 × 40 × 2 mm) were produced in injection molding process (Battenfeld PLUS 35, Austria).

Methods of testing

SEM investigations

The scanning electron microscopy observations were performed on the cryogenic fracture surface with a deposition of a thin carbon layer, in vacuum duster Jeol JEE 4B, JEOL Company (Japan). The fracture surface images were registered with the scanning electron microscope (SEM) Vega 5135MM Tescan Company (Czech Republic), with a contrast of secondary electrons (SE) at the acceleration voltage 15 kV.

The thermal diffusivity measurement

The modified Angstrom method was used to determine thermal diffusivity values [38, 39]. The principle of this technique consists of heating of one end of the sample with a microheater, supplied with a sinusoidal variable voltage, as it is shown in Figure 1. The sinusoidal variable heat wave transits from one end of the sample to the other. The second end of the sample is in the ambient temperature and additionally in contact with a metal block which receives transited sinusoidal variable heat wave, and doesn't let the heat wave to go back. The temperature along the sample is registered with temperature sensors (Pt 1000 — RTD). In order to eliminate possible mutual perturbations, the sensors are located on both sides of the sample circumference, at uniform distances from the heating source. The measurements are performed in vacuum in order to avoid heat losses by convection and by radiation. An electrical microheater with a sinusoidal changing voltage, in the range 0—30 V, is used to heat the samples. In our case the measurements were performed at the heating voltage $U = 23$ V for 400 s. Based on the temperature run and shift of the temperature maximum, the values of the thermal diffusivity were evaluated. The results of measurement are registered by the Angstrom computer program.

The thermal diffusivity was evaluated (in m^2/s) according to the formula:

$$D = \frac{\pi \cdot l^2}{2 \cdot (t_2 - t_1) \cdot \ln \frac{\Delta T_1}{\Delta T_2}} \qquad (2)$$

where: l *— distance between the RTD sensors (in mm),* t_1, t_2 *— the period when the maximum temperature in individual sensors is achieved (in s),* ΔT_1, ΔT_2 *— the difference between the maximum temperature and ambient temperature (in deg).*

RESULTS AND DISCUSSION

The temperature measured by three RTD sensors [the first one placed between the microheater and the sample and the two other (T_1 and T_2) at a certain distance along the sample], were determined. As it was already shown before [38, 39], the amplitude of the temperature becomes lower with increasing distance from the microheater, and an evident shift of the temperature maximum may also be noted. Based on the difference in the temperature maximum, and on the shift of corresponding maximum, the temperature diffusivity was evaluated.

A dependence of the D value on the material composition and the type of calcium carbonate is presented in Figure 2 and 3. For the reference composite the D value increases with the increase of *i*-PP content, from $D = 1.29 \cdot 10^{-7} \pm 9.54 \cdot 10^{-8}$ m^2/s for the series R1 to $D = 6.36 \cdot 10^{-7} \pm 9.15 \cdot 10^{-8}$ m^2/s for the series R4. The introduction of a filler into the polyethylene matrix results in a higher D value of the composites, compared with the corresponding value of the reference material (Fig. 2). For example the value of D increases up to $7.87 \cdot 10^{-7} \pm 5.25 \cdot 10^{-8}$ m^2/s for the composites containing modified $CaCO_3$ (sample H1) and to $D = 1.28 \cdot 10^{-6} \pm 4.95 \cdot 10^{-8}$ m^2/s for the compo-

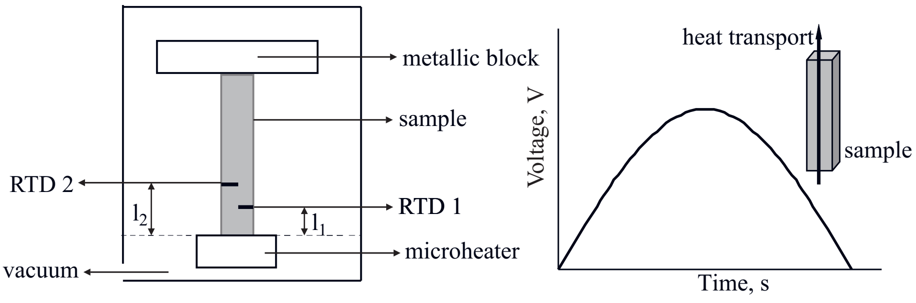

Fig. 1. Scheme of the apparatus for the modified Angstrom measurements of thermal diffusivity (RTD — resistance temperature detector)

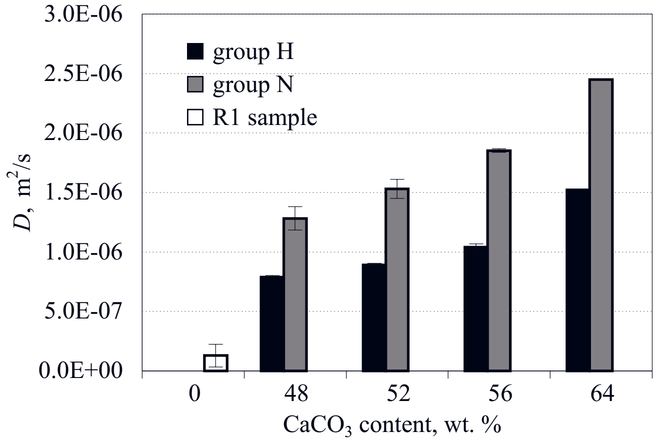

Fig. 2. Thermal diffusivity (D) of samples from group: R, H, N (description of samples according to Table 1) as a function of calcium carbonate content (R1 — reference material)

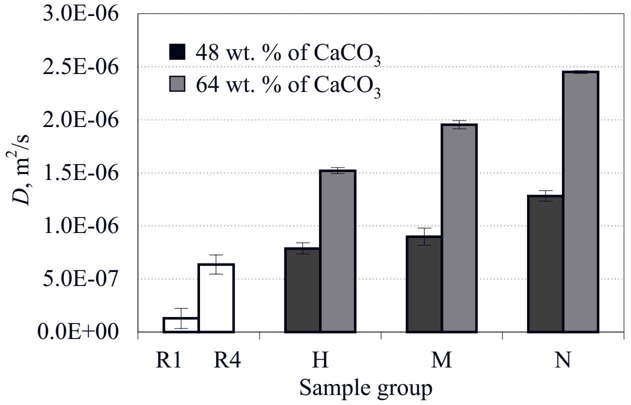

Fig. 3. Thermal diffusivity (D) of samples from group: R, H, M, N (description of samples according to Table 1) as a function of calcium carbonate modification (R1, R4 — reference materials)

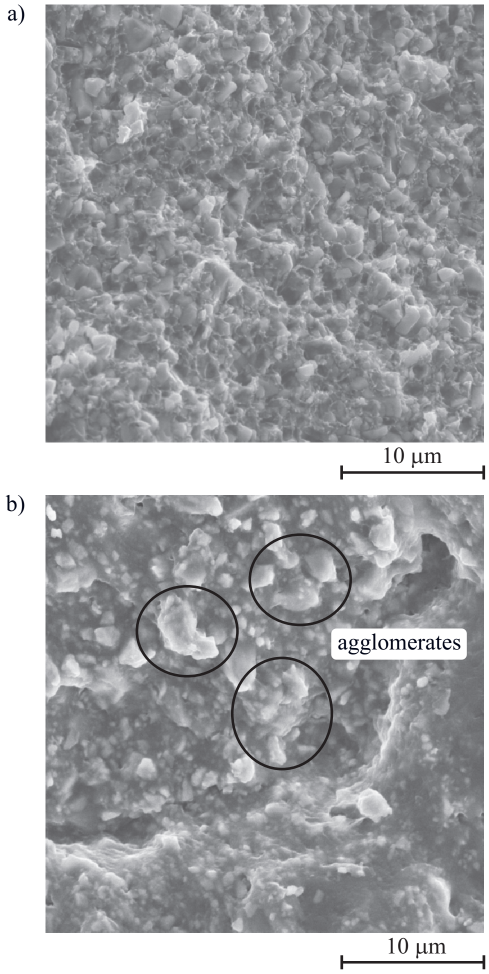

Fig. 4. SEM of PE-HD/i-PP/$CaCO_3$ composites with a) commercial Filolen FP-0800 concentrate (sample H1), b) concentrate prepared from Malen P F401 and Omyacarb 2-VA (sample N1)

sites produced from the same amount of non-modified $CaCO_3$ (sample N1).

It is worth to note that in all cases, independently on the $CaCO_3$ concentration (in our case 48 wt. % and 64 wt. %), the temperature diffusivity of the composites fulfills the following relationship (Fig. 3):

D of the samples H < D of the samples M < D of the samples N.

It may be suggested that the type of calcium carbonate, particularly its average grain dimension and the surface modification *i.e.* the ability to form agglomerates, play a decisive role in the heat transport along the composite materials. The highest D values were noted for the composites produced from non-modified $CaCO_3$ with an average grain dimension of 2.5 μm. In this case also the most important non-homogeneity of the structure was observed in SEM microphotographs, what is shown in Figure 4.

With an increased content of the powder filler in composites an increase of its D value was observed (compare Fig. 3), *i.e.* about 49 % for the composites from the group H, 54 % for the group M and 48 % for the group N [*e.g.* the difference between composites with the lowest (48 wt. %) and the highest (64 wt. %) $CaCO_3$ content]. This effect is probably due to much higher thermal diffusivity of calcium carbonate (about 5 times), compared to the thermal diffusivity of the polyolefin matrix.

CONCLUSIONS

The measurements of the thermal diffusivity with the modified Angstrom method proved the satisfactory quality of this relatively simple method in the determination of heat transport of polymeric materials and composites. Compared with other methods, this procedure seems to be very rapid, simple and convincing in the case of compression molded, injection molded and extruded samples, thus the presented results may provide an interesting approach for the industrial application also in processing of recycled composites.

It was confirmed that the use of calcium carbonate as a filler significantly influences the heat transport of the highly filled polyolefin composites. Such composites are an economically and ecologically interesting substitute for other materials. The comprehension of its thermal diffusivity dependence delivers the knowledge important to the determination of processing limits.

ACKNOWLEDGMENTS

This work was partly supported by the Ministry of Science and Higher Education (Poland) — Grant N N209 106837.

REFERENCES

1. Chang H. J., Morikawa J., Hashimoto T.: *J. Appl. Polym. Sci.* 2006, **99**, 1104.
2. dos Santos W. N.: *Polym. Test.* 2005, **24**, 932.
3. dos Santos W. N.: *Polym. Test.* 2007, **26**, 556.
4. Sikora R.: „Przetwórstwo tworzyw polimerowych. Podstawy logiczne, formalne i terminologiczne", Wydawnictwo Politechniki Lubelskiej, Lublin 2006.
5. Żenkiewicz M.: „Tworzywa wielkocząsteczkowe. Polimeryzacja — właściwości — badania", Wydawnictwo Akademii Bydgoskiej, Bydgoszcz 2002.
6. Ram A.: „Fundamentals of Polymer Engineering", Plenum Press, New York 1997.
7. Rosato D. V., Rosato M. G.: „Plastics Design Handbook", Kluwer Academic Publishers, USA 2001.
8. dos Santos W. N., Agnelli J. A. M., Mummery P., Wallwork A.: *Polym. Test.* 2007, **26**, 216.
9. Iguchi C. Y., dos Santos W. N., Gregorio Jr. R.: *Polym. Testing* 2007, **26**, 788.
10. Papa J., Albano C., Bare W., Navarro O., Galarraga D., Zannin F.: *Eur. Polym. J.* 2002, **38**, 2109.
11. Zhang Ch., Salama I. A., Quick N. R., Kar A.: *Int. J. Thermophys.* 2007, **28**, 980.
12. Konieczna M., Markiewicz E., Jurga J.: *Polym. Eng. Sci.* 2010, **50**, 1613.
13. Weidenfellera B., Hoferb M., Schilling F. R.: *Composites Part A* 2005, **36**, 345.
14. Hay B., Filtz J. R., Hameury J., Davée G., Rongione L., Enouf O.: *Int. J. Thermophys.* 2009, **30**, 1270.
15. Schoderböck P., Klocker H., Sigl L. S., Seeber G.: *Int. J. Thermophys.* 2009, **30**, 599.
16. dos Santosa W. N., Mummery P., Wallwork A.: *Polym. Test.* 2005, **24**, 628.
17. Agari Y., Ueda A., Omura Y., Nagai S.: *Polymer* 1997, **38**, 801.
18. Agari Y., Shimada M., Ueda A.: *Polymer* 1997, **38**, 2649.
19. Wang Y., Wright N. T.: *Int. J. Thermophys.* 2005, **26**, 1849.
20. Kurabayashi K.: *Int. J. Thermophys.* 2001, **22**, 277.
21. Tsutsumi N., Kizu S., Sakai W., Kiyotsukuri T.: *J. Polym. Sci., Part B. Polym. Phys.* 1997, **35**, 1869.
22. Choy C. L., Yang G. W., Wong Y. W.: *Pulsed Photothermal Radiometry* 1997, 1621.
23. Salazar A., Sanchez-Lavega A.: *Int. J. Thermophys.* 1998, **19**, 625.
24. Jothi Rajan M. A., Vivekanandam T. S., Ramakrishnan S. K., Ramachandran K., Umapathy S.: *J. Appl. Polym. Sci.* 2004, **93**, 1071.
25. Venerus D. C., Schieber J. D., Iddir H., Guzman J., Broerman A.: *Int. J. Thermophys.* 2001, **22**, 1215.
26. Venerus D. C., Schieber J. D., Iddir H., Guzman J. D., Broerman A. W.: *J. Polym. Sci., Part B. Polym. Phys*. 1999, **37**, 1069.
27. Agarwal R., Saxena N. S., Sharma K. B., Thomas S., Sreekala M. S.: *J. Appl. Polym. Sci.* 2003, **89**, 1708.
28. Jothi Rajan M. A., Mathavan T., Vivekanandam T. S., Umapathy S.: *J. Appl. Polym. Sci.* 2006, **100**, 3756.
29. Rusu M., Sofian N., Rusu D.: *Polym. Test.* 2001, **20**, 409.
30. Boudenne A., Ibos L., Fois M., Gehin E., Majeste J. Ch.: *J. Polym. Sci., Part B. Polym. Phys*. 2004, **42**, 722.
31. Krupa I., Boudenne A., Ibos L.: *Eur. Polym. J.* 2007, **43**, 2443.
32. Zhang X., Fujii M.: *Polym. Eng. Sci.* 2003, **43**, 1755.
33. Zhang X., Hendro W., Fujii M., Tomimura T., Imaishi N.: *Int. J. Thermophys.* 2002, **23**, 1077.
34. Hashimoto T., Morikawa J., Kurihara T., Tsuji T.: *Thermochim. Acta* 1997, **304/305**, 151.
35. Song M., Hourston D. J., Grandy D. B., Reading M.: *J. Appl. Polym. Sci.* 2001, **81**, 2136.
36. Kozłowski M., Kozłowska A., Frąckowiak S.: *Polimery* 2010, **55**, 726.
37. Prociak A.: *Polimery* 2008, **53**, 195.
38. Prociak A., Pielichowski J., Sterzyński T.: *Polym. Test.* 2000, **19**, 705.
39. Prociak A., Sterzyński T., Pielichowski J.: *Polym. Eng. Sci.* 1999, **39**, 1689.

Received 6 X 2011.