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Development of thermally conductive polymer materials and their investigation

András SUPLICZ[1, a], József Gábor KOVÁCS[1, b]

[1]Department of Polymer Engineering, Budapest University of Technology and Economics, Budapest H-1111, Hungary

[a]suplicz@pt.bme.hu, [b]kovacs@pt.bme.hu

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Abstract. In the recent years a remarkable development can be observed in the electronics. New products of electronic industry generate more and more heat. To dissipate this heat, thermally conductive polymers offer new possibilities. The goal of this work was to develop a novel polymer based material, which has a good thermal conduction. The main purpose during the development was that this material can be processed easily with injection molding. To eliminate the weaknesses of the traditional conductive composites low-melting-point alloy was applied as filler. Furthermore in this work the effect of the filler content on thermal conductivity, on structure and on mechanical properties was investigated.

Introduction

Recently the developments in technology result smaller devices with higher performance. Thanks to this advance the heat dissipation in the electronic packaging, mainly in the microelectronics is an important issue. Beside this the heat dissipation has a great influence on the lifespan. It is well known that the reliability of devices is exponentially dependent on its operating temperature, so a small difference in operating temperatures (about 10–15°C) can halve the lifespan of the devices [1-5].

It is well known that the polymer materials are good thermal insulators as their thermal conductivity varies between 0.1 and 0.5 W/(m·K). Generally conductive polymer composites are obtained dispersing conductive fillers into insulating polymer matrix. These fillers are mainly graphite, carbon black, and carbon fibers, ceramic or metal particles. They can increase the thermal behavior of polymers significantly. Furthermore the thermal properties depend on several factors: the filler concentration, the ratio between the properties of the components, the size and the shape of the filler particles, the manufacturing process and the filler matrix interactions. Nowadays the polymer based composite materials which have high thermal conductivity attract more and more attentions. Interest in using polymers for other electrical applications has increased due to their advantageous properties such as resistance to chemicals, weight and processability. Thermally conductive polymer composites offer new possibilities for replacing metal parts in several applications, such as electric motors, power electronics, heat exchangers, microelectronics, and many others [4, 5].

The thermal properties of thermoplastic polymers filled with metal or ceramic particles were investigated by different researchers [6-10]. It is important, that compromises have to be found regarding the amount of filler. Higher filler contents usually have a negative influence on the mechanical properties and also on processability due to the increase of melt viscosity. Many

researchers studied the thermal and mechanical properties of polymer/low melting point alloy composite materials [11-14]. It was pointed that the filler content can be increased significantly without decreasing the processability by using low melting point metal alloys because these alloys are in liquid phase under processing conditions.
In our work the aim was to prepare an injection moldable composite material with thermoplastic polymer matrix and low melting point alloy filler. We measured the tensile strength and modulus, the thermal conductivity and the melt flow rate of the composite material as a function of the filler content. Furthermore its microstructure was also analyzed.

Materials and methods

In this research the low-melting point alloy was a commercially available solder, containing 60 wt% tin (Sn) and 40 wt% lead (Pb) (Metalloglobus Kereskedelmi és Fémöntő kft., Hungary). The melting temperature of the alloy is between 183 and 190°C. The solder was obtained as wire so in first step it was chopped (diameter: 1.5 mm; length: 2.5 mm) with a LabTech pelletizer. The polymer was Tipplen H 145 F polypropylene (Tiszai Vegyi Kombinát, Hungary). Polypropylene was selected, because it is a common polymer, and H145 F has good flowing properties ($MFR_{(230°C/2.16\ kg)}$ = 25 g/10 min). The Sn-Pb alloy granules were added to the PP in 10 and 30 wt% and mixed mechanically. Then it was fed into the Arburg Allruonder 370S 700-290 advance injection molding machine and 80x80x2 mm specimens were produced (Fig. 1.). The melt temperature was 200°C and 230°C, the mold temperature was 40°C, while the injection rate was 50 cm^3/s.

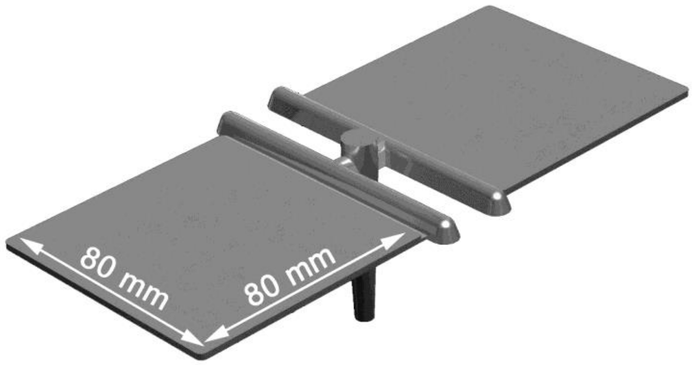

Fig. 1. Injection molded specimen for thermal conduction measurement

During the injection molding process, the injection pressure was observed. Tensile tests were carried out on Zwick Z020 universal testing machine using 5A type specimens according to EN ISO 527-1:1993 standard. The tensile specimens were machined from the injection molded parts and the test speed was 2 mm/min for each measurements.
In this research the thermal conductivity was measured according to transient hot plate method. The lower plate of the apparatus was cooled by four Peltier cells. The upper plate was heated by heating wire. This AlCr wire was 850 mm long, its diameter was 1 mm, and nominal resistance was 1.5 Ω. The temperature was measured with 2-2 termistors on each side (Fig. 2.). The point of the process is to reach a steady state condition in heat flow, thus simplifying the measurement to a one-dimensional case to use the Fourier's law (Eq.1) [15]:

$$q(x,t) = -\lambda \cdot \nabla T(x,t)\,, \qquad (1)$$

where q [W] is the transmitted heat flux, λ [W/(m·K)] is the thermal conductivity and T [K] is the temperature. The test temperature was 50°C.

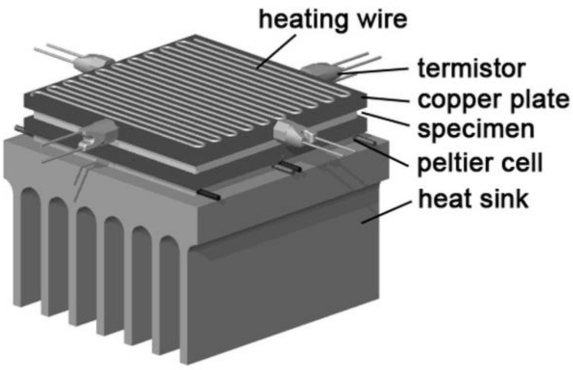

Fig. 2. Thermal conductivity measurement system

To characterize the processability and compare the flow behavior of the composite materials, their melt flow rate was determined on CEAST 7027.000 capillary rheometer. The measurement was performed according to the EN ISO 1133:2005 standard.

Result and discussion

During injection molding, the injection pressure changed significantly by varying the filler content and the melt temperature. At 200°C the pressure was 450 bars at the case of unfilled PP. Adding nominal 10 and 30 wt% Sn-Pb solder, the injection pressure decreased to 350 and 300 bars. Raising the melt temperature to 230°C the injection pressure decreased to 300 and 200 bars. It means that the low melting point alloy can help the flow of the polymer melt.
Because the solder has higher density (~7.4 g/cm^3) than the polypropylene (~0.95 g/cm^3) the mechanical mixing of the matrix and filler is insufficient to get homogenous mixture. So the real filler content of the specimens changed in a wide range and should be calculated after injection molding. The real filler content varied between 10 and 70 wt% (~1.5-22 v%) At smaller filler content the filler distribution is near homogenous and the solder has long, fiber-like form thanks to the shear stress as can seen on Fig. 3. Furthermore the microscopic investigation can confirm that there are filler particles in the core layer of the injection molded specimen. At higher filler content there are also aggregates of solder on the surface of the specimen and the so called segregation [16, 17] can be seen clearly (Fig. 3.).

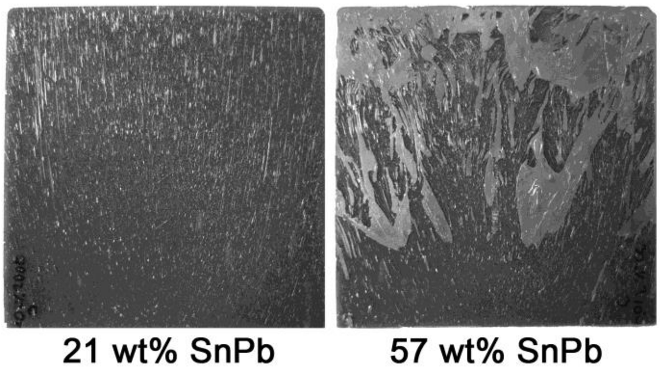

Fig. 3. Dispersion of the Sn-Pb alloy in injection molded samples

According to the tensile test, the filled materials have lower tensile strength and modulus of elasticity than the unfilled PP as can be seen on Fig. 4. The tensile strength of the virgin polypropylene is about 30 MPa. Adding 59 wt% (~14.6 v%) alloy, the strength decreased to 20 MPa. The unfilled polypropylene has 1.6 GPa modulus of elasticity. Increasing the filler content, the decrease of the modulus is not so significant. The composite which contains 59 wt% Sn-Pb has

1.35 GPa modulus of elasticity. Although the filler took fiber shape, the filled materials still have lower mechanical properties, because there is weak adhesion between the two materials.

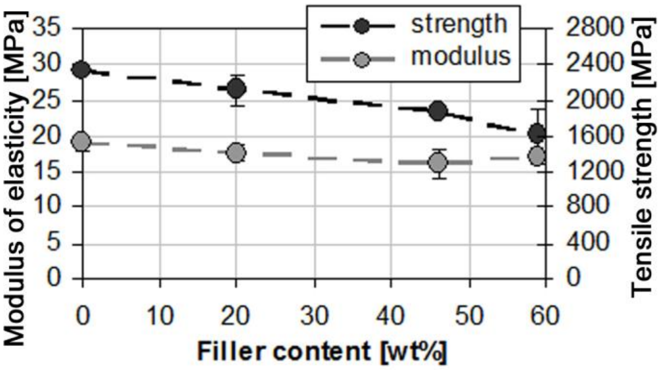

Fig. 4. Tensile strength and modulus of elasticity of the PP/SnPb compound

The result of the thermal conduction test can be seen on Fig. 5. The figure shows, that raising the filler content, the thermal conductivity raises too. A significant change on the diagram starts at about 50 wt% (~11 v%). This content means a percolation threshold where Sn-Pb particles start to form a continuous conductive net. As result the 0.22 W/(m·K) thermal conduction of unfilled PP changed to 0.45 W/(m·K) adding 68 wt% (~20 v%) Sn-Pb low-melting point alloy.

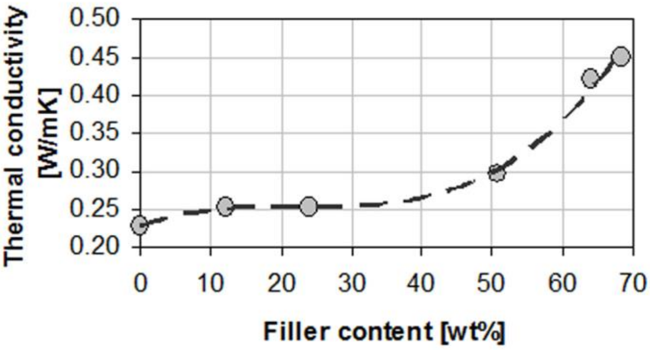

Fig. 5. Thermal conductivity of the PP/Sn-Pb compound as a function of the alloy content

According to the standard, the melt flow rate of the composite material was determined at 0, 30 and 48 wt% Sn-Pb content. In contrast to the metal or ceramic particle fillers, the low melting point alloy increase the MFR value as it can be seen on Fig 6. The MFR of the virgin PP is 28.6 g/10 min. Adding 30 and 48 wt% (5 and 10 v%) Sn-Pb this value changed to 34.3 then 37 g/10 min. It means that the low melting point alloy mends the flowing behavior and can help to fill the cavity of the injection mold. Beyond that, the uniform dispersion of the low melting point alloy is an important issue which requires further researches.

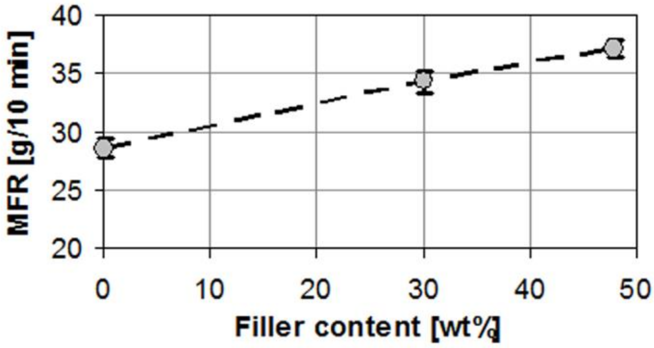

Fig. 6. Melt flow rate of the PP/Sn-Pb compound as a function of the alloy content

Summary

In this experiment the thermal conductivity of polypropylene was increased using Sn60Pb40 low-melting point solder. The solder was in liquid phase during injecting the mixture into the mold, thus the injection pressure decreased and the melt flow rate increased as a function of the filler content and the melt temperature. It means that the low melting point alloy can minimize the filling pressure during injection molding. The solder takes elongated shapes during the process. Because of the low adhesion of the matrix and the filler the mechanical properties decreased as a function of the filler content. On the other hand the thermal conductivity almost doubled to 0.45 W/(m·K) by adding 68 wt% (~20 v%) Sn-Pb.

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