Enhanced thermal properties of poly(lactic acid)/MoS$_2$/carbon nanotubes composites

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In this work, few-layered molybdenum disulfide (MoS$_2$) was functionalized with metal oxide (M$_x$O$_y$) nanoparticles which served as a catalyst for carbon nanotubes (CNT) growth in the chemical vapour deposition (CVD) process. The resulting MoS$_2$/M$_x$O$_y$/CNT functionalized nanomaterials were used for flame retarding application in poly(lactic acid) (PLA). The composites were extruded with a twin-screw extruder with different wt% loading of the nanomaterial. Full morphology characterization was performed, as well as detailed analysis of fire performance of the obtained composites in relation to pristine PLA and PLA containing an addition of the composites. The samples containing the addition of MoS$_2$/M$_x$O$_y$/CNT displayed up to over 90% decrease in carbon oxide (CO) emission during pyrolysis in respect to pristine PLA. Microscale combustion calorimetry testing revealed reduction of key parameters in comparison to pristine PLA. Laser flash analysis revealed an increase in thermal conductivity of composite samples reaching up to 65% over pristine PLA. These results prove that few-layered 2D nanomaterials such as MoS$_2$ functionalized with CNT can be effectively used as flame retardance of PLA.

Greater use of conventional petroleum based commodity resins in various applications have led to inevitable rise of its ecological footprint. Various new eco-friendly biodegradable polymers were developed in order to counteract this effect. With its biodegradability, low emission of greenhouse gas and low production energy PLA currently stands as one of popular alternatives for conventional polymer materials 1. Due to its high degree of transparency, good mechanical properties, low toxicity and ability to process using equipment as well as relatively low cost and large production volume it shows high potential for packaging, household and biomedical applications. Nevertheless, other potential applications such as in electronics or automotive industry require PLA grades with high impact strength, better processing ability and improved flame retardant behaviour 2. In order to meet that demand novel methods of modification need to be developed and applied.

A common way of improving flame retardancy of polymer is through combining its matrix with flame retardant filler. In the past improved flame resistance was achieved by introduction of halogenated flame retardants (HFR). Nowadays, it faces severe restrictions in Europe and North America due to the release of toxic substances and large amounts of smoke during combustion 3. Instead, halogen-free flame retardant formulations function more commonly now as an environmentally friendly alternatives for HFR. These include intumescent flame retardants 4, phosphorus- and nitrogen-containing micro- and nanoparticles 5–8, inorganic substances and silica derivatives 9 which can be used either individually or in combination 10 to achieve optimal flame retardant performance.

Polymer/layered inorganic materials composites have high potential for improving thermal properties of polymers. Molybdenum disulfide is a member of a family of transition metal dichalcogenides (TDM). Structurally its crystals are characterized as hexagonal layered configurations. Atoms in the layer are bonded with strong covalent bonding, while layers are packed together to form a sandwich structure with weak Van der Waals forces similarly to graphite or boron nitride 11. With their unique electrical, optical, thermal and mechanical properties MoS$_2$ nanosheets can be potentially used for application as fillers for improving properties of polymers. Being a representative of layered inorganic materials MoS$_2$ is expected to disperse and exfoliate in polymers, which results in the physical barrier effects that inhibits the diffusion of heat and gaseous decomposition products 12,13. Molybdenum, a transition metal element, promotes the formation of charred layer during the combustion which

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acts as a physical barrier that slows down the heat and mass transfer. In order to achieve high-performance homogenous dispersion of MoS₂ nanosheets in the polymer hosts and proper interfacial interactions need to be established. Similarly to metal oxide/graphene hybrid materials addition of metal oxide/MoS₂ nanoparticles might prevent the aggregation of MoS₂ flakes during preparation of polymer nanocomposites and result in improved flame retardant performance. In addition they can also lead to improved char generation due to catalytic activity of metal oxide as well as suppressed smoke production and reduced toxicity due to catalytic conversion of carbon oxide (CO). Another possible alternative to the use of conventional flame retardants are carbon nanotubes (CNT). These can be introduced into the polymer matrix in pristine form of a small diameter (1–2 nm) single-wall carbon nanotubes or a large diameter (10–100 nm) multi-wall carbon nanotubes (SWCNT and MWCNT, respectively). In addition to this functionalization of CNT can also be carried out in order to significantly improve the flame retardant performance. This can be performed in three different ways. Surface modification by coupling agents allows for enhancement of dispersion state of CNT. For example, addition of 9 wt% content of CNT functionalized with vinyltrichlorosilane into epoxy composite allowed for increase of limiting oxygen index (LOI) from 22 to 27% and improvement of UL-94 rating from V-1 to V-0. This also resulted in increase of char yield at 750 °C by 46.94%. Char yield can be also enhanced through covalent linkage of organic flame retardants to CNT following surface treatment. Functionalization of CNT can facilitate their dispersion within the polymer matrix and enhance interfacial adhesion between the CNT and the polymer. Formation of genuine composites can be confirmed by an increase in the Young's modulus and flame resistance of compositions containing pristine CNT. Finally, hybridization of CNT by inorganic particles can allow for superior flame retardant properties. In addition to that other key parameters, such as thermal stability and dielectric properties, can be also enhanced. Generally speaking, flame retardants in terms of CNTs are classified as phase change. Char layer formed on the entire sample surface acts as insulation layer that reduces the amount of volatiles escaping to the flame. The formation of continuous layer is obtained by formation of three-dimensional network structure when the content of CNT reaches a threshold value. Good quality char plays major role in reduction of peak heat release rate (pHRR). During the scope of presented research few-layered MoS₂ nanosheets functionalized with MₓOᵧ nanoparticles served as catalysts for growth of CNT in the CVD process were prepared. The obtained nanomaterials were used as flame retarding agents in PLA composites. Detailed description of synthesis, as well as full characteristics and analysis of properties of obtained PLA-based composites were provided. Additionally, a thorough analysis of thermal stability, fire performance and thermal conductivity of these materials was also performed and discussed in details.

Methods

**Materials.** Bulk MoS₂ (powder), N-Methyl-2-pyrrolidone (NMP) (anhydrous, 99.5%), cobalt(II) acetate tetrahydrate (99%), iron(II) acetate (95%) and nickel(II) acetate tetrahydrate (98%) were purchased from Merck. PLA was obtained from Goodfellow. Hydrogen peroxide (30%) and ethanol (96%) were purchased from Chempur. Gaseous nitrogen and ethylene were purchased from Messer and Air Liquid, respectively.

**Preparation of few-layered MoS₂.** 1 g of bulk MoS₂ powder was transferred into a 250 mL flat-bottomed flask, plugged to reflux and consciously stirred at 360 rpm for 24 h. Final dispersion was centrifuged four times at 10 000 rpm for 20 minutes and washed with ethanol.

**Preparation of MoS₂/MₓOᵧ/CNT.** In order to obtain MoS₂/MₓOᵧ/CNT modified nanomaterials following procedure was applied. First, 150 mg of few-layered MoS₂ and 150 mg of respective source of metal oxide (cobalt(II) acetate tetrahydrate, iron(II) acetate or nickel(II) acetate tetrahydrate) were dispersed in ethanol and sonicated in an ultrasonic washer for 2 h. Next, dispersions were stirred for 48 h, after which they were dried under high vacuum at 440 °C for 3 h. This resulted respectively in MoS₂/CoₓOᵧ, MoS₂/FeₓOᵧ and MoS₂/NiₓOᵧ modified nanomaterials. Next CVD was performed in tube furnace under constant 100 mL min⁻¹ flow of nitrogen at 850 °C with a 15 minute long, 60 mL min⁻¹ flow of ethylene as a source of carbon.

**Extrusion of MoS₂/MₓOᵧ/CNT modified PLA composites.** PLA was utilized as a polymer matrix. Four composites were prepared, containing addition of few-layered MoS₂, MoS₂/CoₓOᵧ/CNT, MoS₂/FeₓOᵧ/CNT or MoS₂/NiₓOᵧ/CNT, respectively. For each composite three samples containing different amounts of nanomaterials additives were prepared — 0.5 wt%, 1 wt% and 2 wt%, respectively. Following 12 h of drying the nanomaterial ware blended with PLA using twin-screw extruder (Zamak Mercator EHP 2 × 12). For reference a sample of pristine PLA was also extruded.

**Characterization.** Morphology of nanomaterials obtained during each stage was analyzed using transmission electron microscopy (TEM) (Tecnai F20, FEI) with 200 kV accelerating voltage. Raman analysis was performed in microscope mode (InVia, Renishaw) with a 785 nm laser in ambient air. Number of layers in few-layered MoS₂ samples was determined using atomic force microscopy (AFM) (MultiMode 8, Bruker).

For the obtained composites and pristine PLA following analyses were performed. Thermogravimetric analysis (TGA) was performed using thermal analyzer (SDT Q600, TA Instruments) under airflow of 100 mL min⁻¹. In each case individual sample (ca. 5 mg in an alumina crucible) was heated from room temperature to 800 °C at a linear heating rate of 10 °C min⁻¹. In addition to this, gaseous products from the heating process were analyzed in situ with a mass spectrometer (ThermoStar, Pfeiffer Vacuum) coupled with the TGA, under 100 mL min⁻¹ argon flow. Microscale combustion calorimetry (MCC) was employed for measurement of flame retardancy using FAA
Micro Calorimeter, from FTT. This allowed for determination of pHHR, heat release capacity (HRC) and total heat release (THR) from 2 mg specimens. Thermal conductivity of the obtained samples was measured using laser flash apparatus (XFA 300, Linseis). Prior to this measurement the samples were spray coated with thin layer of graphite in order to facilitate the absorption of laser at the surface.

Results and Discussion
Successful preparation of few-layered MoS$_2$ samples was confirmed using TEM and AFM (Fig. 1). Number of MoS$_2$ layers was determined through analysis of high profile with AFM (Fig. 1C). The flakes were typically 5 nm in height, which corresponded to approximately 7 layers of MoS$_2$ (assuming average thickness of single layer ca. 0.7 nm$^{36}$ (Dependence between lateral size and aspect ratio in Supplementary information)). This was verified later with Raman spectroscopy as the intensity of $E_{2g}$ and $A_{1g}$ peaks changes between bulk MoS$_2$ and few-layered MoS$_2$. With the increased number of layers the frequency of $E_{2g}$ (~382 cm$^{-1}$ for bulk MoS$_2$) decreases while that of the $A_{1g}$ (~407 cm$^{-1}$ for bulk MoS$_2$) increases. This effect is caused by the interlayer van der Waals force in MoS$_2$ suppressing the atom vibration, which results in higher force constants$^{36,37}$.

Dispersion of metal oxide nanoparticles on the surface of MoS$_2$ was determined from collected high-resolution TEM images presented in Fig. 2. Metal oxide nanoparticles appeared to be well dispersed on the surface and deposited homogeneously. The nanoparticles size was measured and ranged between 5 and 25 nm for all metal oxide nanoparticles. Presence of CNT on samples from the CVD process was confirmed with TEM (Fig. 3). As observed, internal diameter of nanotubes matched the diameter of specific metal oxide nanoparticles. Hallow core and an open end were visible and the surface appeared to be smooth.

Thermal stability. TGA measurements were performed in order to study the influence of MoS$_2$ as well as MoS$_2$/M$_{O_y}$/CNT nanomaterial on the thermal stability of PLA. Figure 4 presents the TGA curves for PLA/MoS$_2$ and MoS$_2$/M$_{O_y}$/CNT composites in comparison to pristine PLA. Based on accumulated data $T_{10\text{wt%}}$, $T_{50\text{wt%}}$ and $T_{\text{max}}$ values (which represent temperatures at which 10%, 50% and maximum weight loss occur) were registered and displayed in Table 1. It can be observed that in case of PLA modified only by the addition of few-layered MoS$_2$ (Fig. 4A) at loading of 0.5 wt% thermal decomposition proceeded at a slightly higher rate in comparison to pristine PLA, suggesting accelerated decomposition of polymer matrix as a result of flame retardant (FR) condensed phase action, which affected flow of the polymer$^{38}$. As recorded in this case $T_{10\text{wt%}}$ value was lowered and was equal to 306 °C- it was 18 °C below that of a pristine PLA. In addition to this, further reduction in $T_{50\text{wt%}}$ and $T_{\text{max}}$ values in comparison to pristine PLA was also observed for this sample. In case of samples
containing 1 wt% and 2 wt% of loading of few-layered MoS₂ only T_{max} was strongly affected which suggested that in both cases decomposition of polymer matrix proceeded at a normal rate in initial stages and stopped at a lower temperature. Therefore, it appears that addition of few-layered MoS₂ nanoparticles has resulted in disruption of heat and gas diffusion. This effect was dependant on the FR load, as well as quality of dispersion in the polymer matrix. Combined with barrier effect, which limited access to fuel, it has caused the combustion process to finish at lower temperature. For samples containing addition of MoS₂/Co₂O₃/CNT (Fig. 4B) a significant decrease in every recorded value was observed. T_{10wt%} values were lowered by up to 40 °C for sample containing 0.5 wt% load of FR. T_{50wt%} values were as much as 20 °C below that of pristine PLA for samples containing 0.5 wt% and 1 wt% FR load. Highest reduction in T_{max} value was observed for sample containing 2 wt% load of FR and was 65 °C below that of pristine PLA. It appears that accelerated decomposition of the PLA matrix was caused by condensed action of the MoS₂/Co₂O₃/CNT. This resulted in pronounced flow of the polymer and its withdrawal from the sphere of influence. Change in melt-flow properties was confirmed during the preparation of samples for thermal conductivity testing. Composite samples needed to be preheated to glass transition temperature (about 150 °C) to form tablets using a table press. In case of PLA containing addition of MoS₂/Co₂O₃/CNT the glass transition temperature appeared to be significantly lower (equal to about 110 °C) in comparison to another samples. In literature it was reported that poly(lactic acid) and poly(methyl methacrylate) (PMMA) blends containing addition of isopropylated triaryl phosphate ester flame retardant displayed accelerated breakdown of polymer during the TGA testing, combined with accelerated melt dripping during the UL-94 rating testing, favouring the melt-flow

Figure 2. TEM images of MoS₂/Co₂O₃ (A–C), MoS₂/Fe₂O₃ (D–F) and MoS₂/Ni₂O₃ (G–I) nanoparticles.
As a result of this, PLA/PMMA/FR blends have achieved V-0 classification in the UL-94 test. In case of MoS$_2$/Fe$_2$O$_3$/CNT (Fig. 4C) only a significant reduction in $T_{\text{max}}$ value was observed, which was highest (14 °C) for sample containing 2 wt% of nanomaterial, while the largest amount of charred residue was observed with sample containing 1 wt%. Recorded $T_{10\text{wt} %}$ and $T_{50\text{wt} %}$ values remained within the range of temperatures observed for pristine PLA. The composite samples containing addition of MoS$_2$/Ni$_2$O$_3$/CNT (Fig. 4D) placed between those derived from Co$_2$O$_3$ and Fe$_2$O$_3$ nanoparticles – at lower FR loads polymer decomposition was accelerated but the stability of matrix increased with wt% of FR. In summary, obtained results suggest improved fire resistant performance due to disruption of heat and gas transfer within the composites, as well as barrier effect introduced through the addition of MoS$_2$ and CNT.

CO content analysis performed with use of mass spectrometry during the TGA pyrolysis cycle in argon atmosphere revealed promising results. In each case the amount of CO released was lower in comparison to that observed for pristine PLA (Fig. 5). For PLA modified only with addition of few-layered MoS$_2$ (Fig. 5A) the reduction in CO release ranged from 38 up to 70%, with the highest value recorded for sample containing 1 wt% of nanomaterials which also corresponded to the largest recorded charred residue value. Previously we observed that introduction of few-layered MoS$_2$ into the poly(vinyl alcohol) (PVA) composite resulted in significant decrease (up to 94%) in permeability of hydrogen gas in comparison to pristine PVA. This effect was attributed to the incorporation of impermeable MoS$_2$ nanosheets with high aspect ratio. As a result a high number

Figure 3. TEM images of MoS$_2$/Co$_2$O$_3$/CNT (A–C), MoS$_2$/Fe$_2$O$_3$/CNT (D–F) and MoS$_2$/Ni$_2$O$_3$/CNT (G–I) nanoparticles.
of tortuous pathways was created which restricted the diffusion of penetrants, such as H₂ or CO₃⁹,⁴⁰. Reduction of CO emission during pyrolysis was further enhanced in case of MoS₂/MₓOᵧ/CNT composites. Highest reduction of CO emission in respect to pristine PLA was observed for all samples containing MoS₂/Fe₂O₃/CNT (Fig. 5C), and it was always above 90%. This was attributed to a well developed and thermally stable char barrier, which protected the molten zone from the burning zone, as reported by Attia et al.⁴¹ in case of polystyrene composites containing addition of MWCNT.

Flammability studies. Fire performance testing was conducted using MCC, which allowed for laboratory evaluation of fire resistant properties of composites. Examples of heat release rate curves of prepared composites were presented in Fig. 6. Average values for key parameters - pHRR, HRC and THR were calculated from three measurements for each sample and presented in Table 2. All of these values were lowered for samples containing the addition of FR in comparison to pristine PLA. The samples containing an addition of MoS₂ (Fig. 6A) showed

| FR load [wt%] | T₉₅% [°C] | T₅₅% [°C] | Tmax [°C] |
|---------------|----------|----------|----------|
| PLA           | —        | 324      | 354      | 485      |
| 0.5           | 306      | 346      | 445      |
| PLA MoS₂      | 1        | 320      | 351      | 459      |
| 2             | 322      | 353      | 465      |
| 0.5           | 284      | 334      | 496      |
| PLA MoS₂/Co₂O₃/CNT | 1 | 286      | 334      | 488      |
| 2             | 295      | 339      | 420      |
| 0.5           | 326      | 354      | 491      |
| PLA MoS₂/Fe₂O₃/CNT | 1 | 326      | 356      | 483      |
| 2             | 323      | 354      | 469      |
| 0.5           | 291      | 337      | 493      |
| PLA MoS₂/Ni₂O₃/CNT | 1 | 301      | 342      | 480      |
| 2             | 314      | 351      | 468      |

Table 1. Summary of TGA results for PLA and PLA composites.
satisfying FR performance with significant decrease of pHRR and THR values in comparison to pristine PLA. Therefore, it was evident that the addition of MoS2 into the PLA matrix introduced the barrier effect which effectively impeded oxygen filtration, heat and mass transmission and the release of combustible gases produced during the combustion process, as previously reported for PVA, polystyrene (PS) and PMMA\textsuperscript{11,42,43}. Formation of this barrier prevented underlying material from further combustion. For composite samples containing addition of MoS2/MxOy/CNT FR best results were observed for 2 wt% load. This effect could be attributed to strong barrier effect due to formation of an enhanced char layer thanks to the presence of CNT\textsuperscript{21,44}. In case of samples containing addition of MoS2/Co2O3/CNT (Fig. 6B) and MoS2/Ni2O3/CNT (Fig. 6D) there was a visible shoulder within the temperature range of 250–350 °C. This suggested occurrence of an overlapping stage, preceding main combustion of PLA. This may be attributed to the release of FR additive via vaporisation or cleavage. In addition, a secondary peak was also observed for those samples within the temperature range of 425–515 °C which could be attributed to the increase in volume of sample due to intumescence. The intensity of this peak decreased with increase in FR loading, which suggests that rigidity of the barrier was directly tied to the FR contents and it is optimal at 2 wt%. While both of the effects could be also observed for samples containing addition of MoS2 as well as MoS2/Fe2O3/CNT (Fig. 6C), the size of the before mentioned shoulder as well as intensity of the secondary peak were much lower.

**Thermal conductivity.** In order to verify thermal conductivity of obtained composites samples with a diameter of 12.7 mm were prepared using tablet press. For each composite a batch of 3 tablets were prepared. Thickness of each tablet was measured and recorded. In order to facilitate laser adsorption at the surface all tablets were covered with a thin layer of graphite prior to measurement. Tests were carried out at room temperature, which was measured at 25.4 °C. Obtained data (average out of 3 tablets for each composite) was presented in Table 3. In case of samples prepared with addition of only few-layered MoS2 highest level of thermal conductivity – 0.502 Wm\(^{-1}\)K\(^{-1}\) was observed for sample containing addition of 2 wt% of FR and it was 54% higher than that of a pristine PLA sample. Similar effects were reported in literature for epoxy samples containing addition of nanomaterial such as graphene oxide or graphene nanosheets\textsuperscript{45}. For samples containing CNT based structures thermal conductivity increased with increase in loading, resulting in up to 0.538 Wm\(^{-1}\)K\(^{-1}\) or a 65% increase over pristine PLA in case of a sample containing 2 wt% of MoS2/Fe2O3/CNT. It is however worth noting that even in case of 0.5 wt% of MoS2/Fe2O3/CNT a 50.9% increase in thermal conductivity was observed. Kashiwagi et al. also observed similar increase in thermal conductivity in case of polypropylene composites containing addition of carbon nanotubes which suggests that further enhancement of thermal conductivity of CNT based composites could be attributed to their presence\textsuperscript{46}.

![Figure 5. CO emission of PLA composites in comparison to pristine PLA.](image-url)
In this work, in order to improve fire performance of PLA, few-layered MoS$_2$ and MoS$_2$/M$_x$O$_y$/CNT nanomat-
erials were prepared and introduced into the PLA composites through twin-screw extrusion blending process. TGA analysis revealed 40 °C and 65 °C decrease of $T_{\text{max}}$ value for samples containing 0.5 wt% of few-layered MoS$_2$ and 2 wt% of MoS$_2$/Co$_2$O$_3$/CNT, respectively. Thanks to the addition of few-layered MoS$_2$ a formation of charred residue layer was observed which allowed for up to nearly 70% decrease in CO emission during burning in case of a sample containing 1 wt% of MoS$_2$. Over 90% of reduction in CO emission was achieved through introduction of MoS$_2$/Fe$_2$O$_3$/CNT into the PLA matrix. MCC analysis showed best performance of few-layered MoS$_2$ and MoS$_2$/Fe$_2$O$_3$/CNT composites, while MoS$_2$/Co$_2$O$_3$/CNT and MoS$_2$/Ni$_2$O$_3$/CNT composites displayed strong effects of secondary stage preceding the main combustion of PLA as well as instability of barrier at 0.5 wt% and 1 wt% of FR. Thermal conductivity of all of the composites was increased in comparison to pristine PLA, up to 65% in

**Conclusions**

In this work, in order to improve fire performance of PLA, few-layered MoS$_2$ and MoS$_2$/M$_x$O$_y$/CNT nanomate-
rials were prepared and introduced into the PLA composites through twin-screw extrusion blending process. TGA analysis revealed 40 °C and 65 °C decrease of $T_{\text{max}}$ value for samples containing 0.5 wt% of few-layered MoS$_2$ and 2 wt% of MoS$_2$/Co$_2$O$_3$/CNT, respectively. Thanks to the addition of few-layered MoS$_2$, a formation of charred residue layer was observed which allowed for up to nearly 70% decrease in CO emission during burning in case of a sample containing 1 wt% of MoS$_2$. Over 90% of reduction in CO emission was achieved through introduction of MoS$_2$/Fe$_2$O$_3$/CNT into the PLA matrix. MCC analysis showed best performance of few-layered MoS$_2$ and MoS$_2$/Fe$_2$O$_3$/CNT composites, while MoS$_2$/Co$_2$O$_3$/CNT and MoS$_2$/Ni$_2$O$_3$/CNT composites displayed strong effects of secondary stage preceding the main combustion of PLA as well as instability of barrier at 0.5 wt% and 1 wt% of FR. Thermal conductivity of all of the composites was increased in comparison to pristine PLA, up to 65% in
case of a composite containing addition of 2 wt% of MoS$_2$/Fe$_2$O$_3$/CNT due to the presence of CNT. In conclusion, introduction of few-layered MoS$_2$ and CNT functionalized MoS$_2$ nanomaterials shows good potential for reduction of fire hazard of the PLA, which could prove beneficial for academic research and practical applications.

Data availability
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Received: 8 January 2019; Accepted: 27 December 2019; Published online: 20 January 2020

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| FR load [wt%] | Thermal conductivity [W m$^{-1}$K$^{-1}$] | Increase from pristine PLA [%] |
|---------------|---------------------------------|-----------------------------|
| PLA           | —                               | —                           |
| 0.5           | 0.326                           | 12.0                        |
| PLA MoS$_2$   | 1                               | 0.421                       | 29.1 |
| 2             | 0.502                           | 54.0                        |
| 0.5           | 0.341                           | 4.6                         |
| PLA MoS$_2$/Co$_2$O$_3$/CNT | 1 | 0.392 | 20.2 |
| 2             | 0.465                           | 42.6                        |
| 0.5           | 0.466                           | 42.9                        |
| PLA MoS$_2$/Fe$_2$O$_3$/CNT | 1 | 0.487 | 49.4 |
| 2             | 0.538                           | 65.0                        |
| 0.5           | 0.492                           | 50.9                        |
| PLA MoS$_2$/Ni$_2$O$_3$/CNT | 1 | 0.500 | 53.4 |
| 2             | 0.519                           | 56.4                        |

Table 3. Thermal conductivity of PLA and PLA composites.
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Acknowledgements
The authors are grateful for the financial support of the National Science Centre Poland OPUS 10 UMO-2015/19/B/ST8/00648. Research project funded by National Science Centre Poland OPUS 10 UMO-2015/19/B/ST8/00648.

Author contributions
P.H. prepared all of the samples, gathered, analyzed and interpreted the data and was a major contributor in writing the manuscript. E.M. helped with interpretation of data and writing of the manuscript. K.W. prepared TEM images, TGA, XRD and Raman spectroscopy data. All authors read and approved the final manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-020-57708-1.

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