Direct measurement of temperature diffusivity of nanocellulose composite films

Hiroki Fujisawa¹, Meguya Ryu¹, Stefan Lundgaard², Denver P. Linklater³, Elena P. Ivanova³, Yoshiaki Nishijima⁴,⁵, Saulius Juodkazis²,⁵,⁶, Junko Morikawa¹,∗

¹ CREST - JST and School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8550, Japan
² Optical Sciences Centre and ARC Training Centre in Surface Engineering for Advanced Materials (SEAM), School of Science, Swinburne University of Technology, Hawthorn, VIC 3122, Australia
³ School of Science, RMIT University, Melbourne, VIC 3000, Australia
⁴ Department of Physics, Electrical and Computer Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
⁵ Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
⁶ World Research Hub Initiative (WRHI), School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8550, Japan

* Correspondence: M. R., S. J. and J. M.

Abstract: The thermal properties of novel nanomaterials play a significant role in determining the performance of the material in technological applications. Herein, direct measurement of the temperature diffusivity of cellulose nanocomposite films was carried out by the micro-contact method. Polymer films containing up to 2%wt. of nanocellulose were synthesised by a simple chemical process. Films of a high optical transmittance $T \approx 80\%$ (for a 200-$\mu$m-thick film), which were up to 44% crystalline, were characterised. Two different modalities of temperature diffusivity based on: 1) a resistance change and 2) micro-thermocouple detected modulation of a heat wave, were used for the polymer films with cross-sections of $\sim 100\ \mu$m thickness. Twice different in-plane $\alpha_\parallel$ and out-of-plane $\alpha_\perp$ temperature diffusivities were directly determined with high fidelity: $\alpha_\parallel = 2.12 \times 10^{-7}\ \text{m}^2/\text{s}$ and $\alpha_\perp = 1.13 \times 10^{-7}\ \text{m}^2/\text{s}$. An amorphous polyethylene terephthalate (PET) fiber was measured for comparison $\alpha_\parallel = 1.15 \times 10^{-7}\ \text{m}^2/\text{s}$. This work provides an example of a direct contact measurement of thermal properties of nanocellulose composite films. The thermal diffusivity, which is usually high in strongly interconnected networks and crystals, was investigated for the first time in this composite.

Keywords: thermal properties, temperature diffusivity, nano cellulose

1. Introduction

Polymers are among the most widely used materials across the globe for the production and packaging of goods; there are very few industries that do not utilise polymers for their commercial outputs. Therefore, their production by simpler and more environmentally friendly methods is crucial. Cellulose is the most abundant material in nature that can be used for polymer fabrication. Nanocellulose (NC), or cellulose nanofibers (CNFs), were introduced as a building block for the production of more complex polymer composites with custom-designed electrical, optical, mechanical or electrical properties [1,2]. High temperature diffusivity $\alpha = \kappa/(\rho c_p)$, defined by the thermal conductivity $\kappa\ [\text{W/(m-K)}]$, mass density $\rho\ [\text{kg/m}^3]$ and specific heat capacity $c_p\ [\text{J/(kg-K)}]$, is a necessary trait for optimised polymeric materials and their composites. Since graphene has a very high in-plane 3000 $\text{W/(m-K)}$ conductivity, it is a potential filler in polymeric and epoxy hosts for increased thermal and electrical conductivity; the out-of-plane conductivity of graphene-stack is only 5 $\text{W/(m-K)}$ [3]. In composites using graphene as the filler, it was previously shown that the thermal
conductivity is increasing linearly with its weight percentage (up to 30wt% before saturation) and in the case of NC-paper with 10 wt% of graphene, reached high 25 W/(m·K) values [4].

The thermal conductivity of these nanomaterials and their composites is usually measured by a non-contact flash method to determine temperature diffusivity $\alpha$. During this measurement, one side of the sample is excited by an optical flash (such as a laser) onto an opaque absorbing (blackened) plane while the temperature rise and its diffusion transport is detected by a pyrometer (non-contact) on the opposite side. The pyrometer detects the thermal radiation (irradiance) $J$ of the black body emission according to the Stefan–Boltzmann (S-B) law $J = \epsilon \sigma T^4$, where $\epsilon$ is the emissivity of the object, $\sigma$ is the S–B constant and $T$ is the absolute temperature. Moreover, the specific heat capacity $c_P$ is usually measured by differential scanning calorimetry (DSC) for the known mass density of the sample according to $\kappa = a\rho c_P$. However, for determination of nanoscale thermal properties ($\alpha$, $\kappa$) of materials, there exists limitations to the flash method due to the need for a blackened absorptive transducer, well known emissivity $\epsilon$, and a need of calibration.

Determination of temperature diffusivity $\alpha$ by a direct measurement is preferable for the determination of heat transport and focusing by nano-/micro-structured materials exploiting long-range (hundreds-of-nm) ballistic phonon heat transport, which can be considerably more efficient on the nanoscale and can be directionally controlled [5]. Contact methods of measuring the thermal properties of materials experience reduced sensitivity due to the large thermal capacitance of the micro-volume of the thermocouple brought into direct contact with the sample. In this study, we used miniaturised thermocouples and thermistors for direct measurements of $\alpha$. Such measurements are in high demand to evaluate the variable thermal properties of nanomaterials and their composites, e.g., the typical thermal conductivity of protein-based polymers is 0.1 W/(m.K) [6] whereas $\alpha$ values exceeding that of metallic Cu (~400 W/(m.K)) have been reported for drag-line silk (416 W/(m.K)) [7]. Exact determination of temperature diffusivity $\alpha$ is particularly important in micro-robotic applications [8] to control the volume-phase transitions, activated by light, harnessed for directional motion inside liquid. The link between optical, mechanical and thermal anisotropy in composite materials due to their microscopic (nanoscale) structure would benefit from direct measurement capabilities.

Here, we characterise the temperature diffusivity $\alpha$ of NC polymer films by the thermal wave method [9] with heater and detector directly deposited onto the sample. The measurement is compared with other widely-used industrial polymer fibers (polyethylene terephthalate - PET). Measurements of the in-plane and out-of-plane temperature diffusivity were made to reveal the anisotropy of thermal properties.

2. Method: thermal wave

Temperature diffusivity $\alpha$ [m$^2$/s] was measured by the thermal wave method [10,11] which determines the phase delay of a heat wave traversing the thickness $d$ of the sample when the heat source is modulated at the frequency $f$:

$$\Delta \Theta = -\sqrt{\frac{f}{2\alpha}} d - \frac{\pi}{4}. \quad (1)$$

The amplitude of detected signal is defined by the thermal effusivity of the sample and substrate, $e$ and $e_s$, respectively:

$$Amp = A \epsilon \sqrt{f(e + e_s)^2 e^{-kd}}, \quad (2)$$

where $k = \sqrt{f/2\alpha}$ and $A$ is the empirical constant defined by experimental conditions. The temperature diffusivity $\alpha$ can be obtained from the $Amp$ measurements; however, experimental detection of phase delay (Eqn. 1) is simpler and potentially more reliable due to absence of additional error sources. The phase-based thermal wave method as outlined by Eqn. 1 was used in this study.
Figure 1. Two modalities of thermal wave measurements using detection by a resistance (a) and thermocouple (b) directly applied to the sample (polymer); heater is deposited directly on the opposite side of the sample. Temperature diffusivity in direction normal to the polymer sheet (out of plane) and along the plane (in plane) can be measured. Micro-tome slice is used to prepare samples for the in-plane heat transport measurements. Heat source is modulated at frequency $f_1 = 4 - 36$ Hz and detected by lock-in technique.

The thickness of sample $d$ should be larger than the diffusion length $L_D = \sqrt{\alpha f}$, i.e., a thermally thick sample condition. Temperature modulation $\Delta T(f)$ can be applied electrically using a resistor (Fig. 1) or optically by light absorbed on the surface of the sample and detected by either: 1) electrical resistivity change of a resistor (the bolometer principle) or 2) by a thermo-couple. Both modalities of the measurement were used.

3. Experimental

Nanocellulose (NC) fibers have a typical diameter 2-5 nm and length between 44 and 108 nm when dispersed in water. NCs were incorporated into polymer films at 2 wt% concentration. The polymeric host for NC fibers was gelatinised starch and polyhydroxyurethane mixture [12]. This green nanohybrid composite has a high 8.5 MPa tensile strength and reaches $\sim30\%$ elongation at breaking point due to the hydrogen-bonding enhanced network, has a high melting temperature of $\sim200^\circ C$ and is $38\%$ crystalline [12]. The nanocomposite polymer film with NC loading was made by a simple physical blending method. Briefly, starch, glycerol, and water were added to a beaker and mixed to form a starch suspension with a final solid concentration of 5 wt% (w/w). After vigorously stirring at $\sim95^\circ C$ for 1 h, NC powder (at a loading of 2 wt%), was incorporated into the well-dispersed starch medium and stirring was continued for another 15 min. The mixture was sequentially homogenised with a T25 Ultra-Turrax (IKA-Labortechnik, Staufen, Germany) at 10k rpm for 2 min and sonicated with a Sonopuls ultrasonic homogenizer (Bandelin, Berlin, Germany) for 2 min to ensure an adequate dispersion of NC within the matrix. Afterwards, the homogenised dispersion was cast in plastic Petri dishes and the solvent was evaporated under ambient environment conditions.

Gold (Au) is heavily used in industry for the fabrication of electrodes, thermo-couples, and resistive heaters. The resistivity of Au is $\rho = 2.44 \times 10^{-8} \, \Omega\cdot m$ and a typical heater of length $l = 1 \, mm$, width $w = 0.25 \, mm$ and thickness $t = 10 \, nm$ has resistance $R = \rho L / (wt) = 9.8 \, \Omega$ (Fig. 1).

The direct measurement of thermal diffusivity by the thermal wave method (Eqn. 1) has become an industrial standard (ISO22007) using ai-Phase apparatus. It can be used for measurement of anisotropy in temperature diffusivity due to molecular alignment within the polymeric film. This method was recently used to demonstrate two orders of magnitude difference in $\alpha$ of polymeric spherulites of poly-l-lactic acid (PLLA) [13].

The calibration procedures for the measurement of thermal diffusivity $\alpha$, thermal effusivity $e$, thermal conductivity $\kappa$ and heat capacity per unit volume $c_{\rho \rho}$ have been established for the resistive
heater in a previous study [9]. We used the same heater and bolometer within their linear response range to the applied voltage (heater) and change of current/voltage (bolometer).

For the thermocouple sensor that detects temperature changes on the rear surface of the sample by a change in the electromotive force at the hot junction, the linearity of response has been established [10, 14]. The sensor is wired via a cold junction with a copper lead, and it is assumed that the temperature change at the cold junction is negligible for the frequency of the measurement (a room temperature thermostat). Thus, the generated electromotive force is due to the temperature change at the hot junction and the detected electric signal is directly related to the temperature response from the sample. This type of sensor is capable of sensitive detection of minute temperature changes from micro-sized regions [14]. All the measurements were carried out within the linear response range.

The PET fibers were embedded in epoxy resin and cured at 70°C. The embedded sample was cut with a hand saw perpendicular to the fiber axis and the surfaces were polished using a doctor-lap with #600 and #2000-grit polishing paper. Further polishing was carried out with an alumina micro-particle slurry. On the front surface, an electrode with low electrical resistance was fabricated by sputtering gold. The heater, with size 500 × 2000 µm² and resistance of approximately 50 Ω, was fabricated by gold sputtering. On the rear surface, a thermocouple sensor of approximately 16 × 16 µm² was fabricated by sputtering gold and nickel using a metal shadow mask made by fine laser machining.

4. Results

4.1. Nanocellulose polymer

The experimentally measured phase delay of the temperature wave detected through the thickness $d$ of the NC composite film is shown in figure 3. The heater is a 10-nm-thick Au film with 0.5 mm width sputtered between Au contacts (40-nm-thick) on one side of the sample, while the detector is placed on the opposite side; Cr adhesion layer was not been used. For measurement of the temperature diffusivity through the sample (out off plane; Fig. 1(a)), the detector was a 0.25 mm wide area of 10-nm-thick gold. For the in-plane (Fig. 1(b)) measurement, an Au-Ni thermocouple was made on the polymer which was embedded into resin and sliced with micro-tome (ISOMET, Manassas, USA; top inset in Fig. 3). Au and Ni thermocouples were made with 50 × 100 µm² stripes centered on the NC polymer.

Direct measurement of the temperature conductivity of the NC composite films was carried out with a very good signal-to-noise ratio and at a range of frequencies and linear fit (Fig. 3). The in-plane temperature diffusivity was ~ 53% larger as compared with the out-of-plane diffusivity. A temperature diffusivity of $a \approx 10^{-7}$ m²/s is typical for most polymers including biopolymers such as chitin, e.g., cicada wings have an in-plane diffusivity of $a_{||} = 3.6 \times 10^{-7}$ m²/s [15] and an out-of-plane diffusivity of $a_{\perp} = 0.7 \times 10^{-7}$ m²/s. For comparison, the temperature diffusivity of air at normal conditions is $a = 2.17 \times 10^{-5}$ m²/s, diamond $(7 \pm 4) \times 10^{-4}$ m²/s and copper (Cu) $1 \times 10^{-4}$ m²/s. The extremities in
the temperature diffusivity of these different materials are separated only by three orders of magnitude, which is small compared with other properties such as electrical conductivity.

The NC composite films were inspected under cross-polarised light microscopy for the presence of optical/structural anisotropy. However, no birefringence was observed at visible spectral range. This is consistent with the high transparency of 0.2-mm-thick polymer films (Fig. 2). The refractive index of a material is proportional to the mass density, hence, birefringence is expected to also reflect the anisotropy in the mass density and could be linked to the packing density of a composite which has anisotropic constituents such as fibers. For example, the birefringence of silk fiber (one of the most birefringent biopolymers) is $\Delta n = 1.7 \times 10^{-2}$ [16] and that of NC $\Delta n = 7.4 \times 10^{-2}$ [17] at visible spectral range.

NC fibers were shown to increase the temperature diffusivity by approximately two times, even at very small (2%wt) loading of NC. Next, we demonstrate another application of the same measurement technique using PET fibers which are increasingly used in air/water filter applications and full characterisation of their thermal and mechanical properties are of paramount importance.

4.2. Polyethylene terephthalate (PET) fiber

Figure 4 shows the fabrication sequence and results of the temperature diffusivity measurement of PET fibers embedded in epoxy resin. A temperature diffusivity of $\alpha_\parallel = 1.15 \times 10^{-7}$ m$^2$/s was recorded. The micro-thermocouple was centered on the fiber core. The fiber was amorphous as revealed by X-ray diffraction.

5. Discussion

The differences between the in-plane and out-of-plane temperature diffusivity are related to the structure of the polymer and molecular alignment of the building blocks. Polymeric fibers fabricated by electro-spinning and extrusion can exhibit increased thermal conductivity along the stretch direction. Thermal conductivity in a ‘stretched’ polymer is higher since $k \propto \sqrt{E}$, where $E$ is the Young’s modulus. For example, in silk which has a $\sim 85\%$ crystalline fraction [18], the beta-sheets are ordered directionally along the fiber, as directly measured by IR microscopy [19,20]. The largest temperature diffusivity for silk is expected along the fiber. Fibroin extracted from silk (depolymerised) and remade into amorphous silk film showed temperature diffusivity $1.6 \times 10^{-7}$ m$^2$/s [21], very similar to the amorphous PET
Figure 4. (a) Sample preparation and fabrication of heater and thermocouple on its ends. Sample: PET fiber made at a spinning speed of 1 km/min, thickness of cut \(d = 128 \, \mu m\), orientation function 0.029 (from past experiments). (b) Frequency dependence of phase delay of the temperature wave along PET fiber. (c) Optical image of the sample made by process shown in (a). (d) The wide-angle X-ray diffraction (WAXD) of the PET fiber revealing its amorphous nature.

Fiber measured in this study. Crystals aligned along the fiber direction underpin the mechanical and thermal properties of bio-polymeric fibers and their optical properties can be determined with ~ 20 nm resolution using scanning near-field optical microscopy (SNOM) [22] or atomic force microscopy (AFM) tip detection under thermal expansion of the surface illuminated at IR absorption bands [23]. It is noteworthy to add that the conductivity of air could influence the in-plane temperature diffusivity, especially on nano-micro rough surfaces such as cicada wings or when the interface contact is by mechanical attachment [15].

The temperature diffusivity of an epoxy resin with a greater (58%wt.) loading of NC was high at \(5.9 \times 10^{-7} \, m^2/s\) [17] compared with our NC nanocomposite polymer sample at only 2%wt. of NC (Fig. 3). The anisotropy between in-plane (high) and out-of-plane (low) thermal diffusivity of the epoxy nanocomposite film was approximately \(\frac{\alpha_\parallel}{\alpha_\perp} = 0.59/0.13 \approx 4.5\) [17]. Here, the nanocomposite film had a mass density \(\rho = 1.39 \, g/cm^3\), specific heat capacity at constant pressure \(c_p = 1.31 \, J/(g.K)\) and thermal conductivity \(\kappa_\parallel = 1.1 \, W/(m.K)\). Since NC fibers have a very low coefficient of thermal expansion (CTE) of 0.1 ppm/K in the axial direction [17], composites with NC are promising for sealant applications at varying temperatures. NC increases the storage modulus of elasticity by 25% as compared with pure epoxy [17].

Another field of research where the direct measurement of thermal conductivity is important is the manufacture of thermoelectric materials where the dimensionless parameter \(ZT = S^2\sigma T/\kappa\) is used to determine the ability of charge flow while resisting the heat flow. Here, \(\sigma\) is the electrical conductivity and the thermopower or Seebeck coefficient \(S = -\Delta V/\Delta T\). A temperature gradient \(\Delta T\) applied to an electrically conductive material causes charge carriers to diffuse. The difference of charge concentration at the hot and cold ends defines a potential difference \(\Delta V\). The design of nanocomposites with high-\(ZT\) values are an active field of thermoplasmonics research where control of anisotropy is playing a large role [24]. Temperature diffusivity and thermal conductivity are key parameters which define the performance of perfect absorbers [25] which are defined by the ratio of optical energy absorbed during an optical cycle to that dissipated.

6. Conclusions

The temperature diffusivity of NC composite films for the in-plane \(\alpha_\parallel = 2.12 \times 10^{-7} \, m^2/s\) and out-off-plane \(\alpha_\perp = 1.13 \times 10^{-7} \, m^2/s\) were directly measured by the contact mode method.
Measurements were carried out using samples with < 200 µm cross sections. The same direct method using a thermocouple was applied for the measurement of temperature diffusivity of PET fibers, along the fiber $a_\parallel = 1.15 \times 10^{-7} \text{m}^2/\text{s}$.

**Author Contributions:** Author contributions: conceptualization, J.M., M.R., S.J.; methodology, M.R. and J.M.; validation, H.F.; formal analysis, H.F. and J.M.; investigation, D.P.L., E.P.I., S.L.; resources, J.M. and E.P.I.; data curation, S.J. and Y.N.; writing—original draft preparation, H.F. and S.J.; writing—review and editing, all the authors; visualization, H.F.; supervision, J.M. and M.R.; project administration, J.M.; funding acquisition, J.M.

**Funding:** This work was supported by JST CREST Grant Number JPMJCR19I3, Japan, the ARC Discovery DP190103284, Linkage LP190100508 grants.

**Acknowledgments:** Support of operational costs of Nanotechnology facility by Swinburne Univ. Technol. is acknowledged. We are grateful to Mehran Ghasemlou and Prof. Benu Adhikari for nano-cellulose polymer samples.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Miyashiro, D.; Hamano, R.; Umemura, K. A Review of Applications Using Mixed Materials of Cellulose, Nanocellulose and Carbon Nanotubes. *Nanomaterials* 2020, 10, 186.
2. Kose, O.; Tran, A.; Lewis, L.; Hamad, W.; MacLachlan, M. Unwinding a spiral of cellulose nanocrystals for stimuli-responsive stretchable optics. *Nature Comm.* 2019, 10, 510.
3. Potenza, M.; Cataldo, A.; Bovesecchi, G.; Corasaniti, S.; Coppa, P.; Bellucci, S. Graphene nanoplatelets: Thermal diffusivity and thermal conductivity by the flash method. *AIP Advances* 2017, 7, 075214.
4. Ren, L.; Wang, M.; Lu, S.; Pan, L.; Xiong, Z.; Zhang, Z.; Peng, Q.; Li, Y.; Yu, J. Tailoring Thermal Transport Properties of Graphene Paper by Structural Engineering. *Sci. Reports* 2019, 9, 4549.
5. Anufriev, R.; Ramiere, A.; Maire, J.; Nomura, M. Heat guiding and focusing using ballistic phonon transport in phononic nanostructures. *Nature Comm.* 2017, 8, 15505.
6. Xue, Y.; Lofland, S.; Hu, X. Thermal Conductivity of Protein-Based Materials: A Review. *Polymers* 2019, 11, 456.
7. Huang, X.; Liu, G.; Wang, X. New Secrets of Spider Silk: Exceptionally High Thermal Conductivity and Its Abnormal Change under Stretching. *Adv. Mat.* 2012, 241, 1482–1486.
8. Mourran.; Zhang, H.; Vinokur, R.; Møller, M. Soft Microrobots Employing Nonequilibrium Actuation via Plasmonic Heating. *Adv. Mater.* 2017, 29, 1604825.
9. Ryu, M.; Morikawa, J. Simultaneous measurements of anisotropic thermal diffusivity and thermal effusivity of liquid crystals using temperature wave analysis method. *Ipn. J. Appl. Phys.* 2016, 55, 111701.
10. Morikawa, J.; Orie, A.; Hashimoto, T.; Juodkazis, S. Thermal and optical properties of the femtosecond-laser-structured and stress-induced birefringent regions of sapphire. *Opt. Express* 2010, 18, 8300–8310.
11. Morikawa, J.; Orie, A.; Hashimoto, T.; Juodkazis, S. Thermal diffusivity in femtosecond-laser-structured micro-volumes of polymers. *Appl. Phys. A.* 2010, 98, 551–556.
12. Ghasemlou, M.; Daver, F.; Ivanova, E.P.; Adhikari, B. Use of Synergistic Interactions to Fabricate Transparent and Mechanically Robust Nanohybrid Materials Based on Starch, Non-Isocyanate Polyurethanes and Cellulose Nanocrystals 2020. p. (submitted).
13. Orie, A.; Morikawa, J.; Hashimoto, T. Micro-scale thermal diffusivity measurements of banded spherulites of poly-(l-lactic acid) using a thermo-electric micro sensor. *Thermochimica Acta* 532 2012, 532, 148–151.
14. Balcys, A.; Ryu, M.; Juodkazis, S.; Morikawa, J. Micro-thermocouple on nanomembrane: thermometer for nanoscale measurements. *Sci. Rep.* 2018, 8, 6324.
15. Morikawa, J.; Ryu, M.; Seniutinas, G.; Balcys, A.; Maximova, K.; Wang, X.W.; Zamengo, M.; Ivanova, E.; Juodkazis, S. Thermal and optical properties of cicada wing. *Langmuir* 2016, 32, 4698 – 4703.
16. Honda, R.; Ryu, M.; Li, J.L.; Mizeikis, V.; Juodkazis, S.; Morikawa, J. Simple multi-wavelength imaging of birefringence: case study of silk. *Sci. Rep.* 2018, 8, 17652.
17. Shimazaki, Y.; Miyazaki, Y.; Takezawa, Y.; Nogi, M.; Abe, K.; Ifuku, S.; Yano, H. Excellent Thermal Conductivity of Transparent Cellulose Nanofiber/Epoxy Resin Nanocomposites. *Biomacromolecules* 2007, 8, 2976–2978.
18. Ryu, M.; Honda, R.; Cernescu, A.; Vailionis, A.; Balcytis, A.; Vongsvivut, J.; Li, J.L.; Linklater, D.P.; Ivanova, E.P.; Mizeikis, V.; Tobin, M.J.; Morikawa, J.; Juodkazis, S. Nanoscale optical and structural characterisation of silk. *Beilstein J. Nanotechnol.* **2019**, *10*, 922–929.

19. Honda, R.; Ryu, M.; Moritake, M.; Balcytis, A.; Mizeikis, V.; Vongsvivut, J.; Tobin, M.J.; Appadoo, D.; Li, J.L.; Ng, S.H.; Juodkazis, S.; Morikawa, J. Infrared Polariscopy Imaging of Linear Polymeric Patterns with a Focal Plane Array. *Nanomaterials* **2019**, *9*, 732.

20. Ryu, M.; Balcytis, A.; Wang, X.; Vongsvivut, J.; Hikima, Y.; Li, J.; Tobin, M.J.; Juodkazis, S.; Morikawa, J. Orientational Mapping Augmented Sub-Wavelength Hyper-Spectral Imaging of Silk. *Sci. Reports* **2017**, *7*, 7419.

21. Morikawa, J.; Ryu, M.; Maximova, K.; Balcytis, A.; Seniutinas, G.; Fan, L.; Mizeikis, V.; Li, J.; Wang, X.; Zamengo, M.; Wang, X.; Juodkazis, S. Silk fibroin as a water-soluble bio-resist and its thermal properties. *RSC Adv.* **2016**, *6*, 11863–11869.

22. Ryu, M.; Honda, R.; Reich, A.; Cernescu, A.; Li, J.L.; Hu, J.; Juodkazis, S.; Morikawa, J. Near-Field IR Orientational Spectroscopy of Silk. *Appl. Sci.* **2019**, *9*, 3991.

23. Ryu, M.; Kobayashi, H.; Balcytis, A.; Wang, X.; Vongsvivut, J.; Li, J.; Urayama, N.; Mizeikis, V.; Tobin, M.; Juodkazis, S. Nanoscale chemical mapping of laser-solubilized silk. *Mater. Res. Express* **2017**, *4*, 115028.

24. Patel, S.; Chabinyc, M. Anisotropies and the thermoelectric properties of semiconducting polymers. *Appl. Polym. Sci.* **2017**, *134*, 44403.

25. Lundgaard, S.; Ng, S.; Nishijima, Y.; Mazilu, M.; Juodkazis, S. Black metals: Optical absorbers. *Micromachines* **2020**, *11*, 256.