

Fabrication and characterisation of ultrafine leather powder: a functional reinforcement containing SiO₂ particles

Chongyi Li, Feng Xue, Enyong Ding

College of Material Science and Engineering, South China University of Technology, Wushan Road, Guangzhou 510641, People's Republic of China
E-mail: eyding@scut.edu.cn

Published in Micro & Nano Letters; Received on 14th December 2013; Revised on 4th March 2014; Accepted on 27th March 2014

The water-based dispersion of ultrafine leather fibres was firstly prepared in the authors' laboratory by high-pressure homogenisation. The hybridisation method of ultrafine leather fibres and SiO₂ particles was used to eliminate the serious agglomeration of ultrafine leather fibres, and finally the dry hybrid leather powder (HLP) was obtained successfully. The morphology of the HLP was investigated using scanning electron microscopy (SEM). The micrograph of SEM revealed that the leather fibres were coated with a layer of scattered SiO₂ particles and still maintained their intrinsic fibrous structures. Surface element analysis (energy dispersive X-ray spectrometry) confirmed that the SiO₂ particles were anchored on the surface of the leather fibres. Furthermore, the formation of bonding effect between the leather fibres and the SiO₂ particles was also demonstrated by X-ray photoelectron spectrometry measurement. The obtained leather fibres were observed to be approximately less than 30 µm in length and 70 nm in width. X-ray diffraction analysis and thermogravimetric analysis were also used to investigate the characterisation of ultrafine leather powders, and one of the results showed that the HLP had greater thermal stability than leather shavings.

1. Introduction: In recent years, the development of composites reinforced by natural fibre has attracted significant attention because of growing environmental concerns [1–3]. Moreover, more important is that these natural fibres can also vest polymers with some new special functions. Leather fibres have generated a great deal of interest as a source of functional reinforcement owing to their abundant surface reactive functional groups. These microfibrils have large aspect ratio and can also produce products with more new properties not present in the original resin such as a heat-insulating property, good air permeability and sound absorption in comparison with other natural fibres. Statistical data of the leather industry shows that only 20% of the raw materials by weight are converted into final leather products, whereas large amounts of chromed leather shavings are abandoned, which inevitably impose enormous ecological pressure on the environment. Extensive researches have been made for the use of chromed leather shavings in composites. Both natural and synthetic polymers have been used as matrixes including natural rubber [4], butadiene–acrylonitrile rubber [5, 6], styrene butadiene rubber [7], nitrile rubber [8], poly(vinyl butyral) [9], nylons [10] and so on, and most of the composites have shown a significant improvement in properties.

The main ingredient of chromed leather shavings is collagen, which has a typical triple helical structure stabilised by trivalent chromium. In nature, collagen molecular chains are biosynthesised and self-assembled into microfibrils. Theoretically, ultrafine leather powders can serve as a kind of excellent functional reinforcement in polymer composites, but in fact it is very hard to accomplish this goal because of the great difficulty in fine-pulverisation of leather shavings. Because of strong bonding effects such as hydrogen bonds and ionic bonds, these assembled leather fibres obtain a feature of being twisted together stably, which makes it difficult for them to be crushed into ultrafine powders. Especially for the current use of leather particles as reinforcements in composites, their particle sizes are usually several hundreds of microns in length [11, 12]. Therefore the fabrication of ultrafine leather powders will be a real big challenge.

It is found that the high-pressure homogenisation process is an effective and attractive technique for the disaggregation and

dispersion of materials in water [13], which could compel a fluid to flow through a very narrow orifice under high-pressure, accompanied by strong shear stress, impingement and so forth. Recently, high-pressure homogenisation has been widely used in many fields [14–16]. However, no research on the application of high-pressure homogenisation in the pulverisation of leather shavings has been reported in the open literature.

The work reported in this Letter is the first attempt to prepare ultrafine leather powders by high-pressure homogenisation, a totally new environmentally-friendly method, which has never been reported by any scientific research groups before. To the best of our knowledge, although leather shavings are significantly less dense than water, they will be submerged ultimately because of their water-absorbing capacity and swelling. These tangled leather microfibrils can be disconnected and smashed into ultrafine leather fibres (ULFs) by intense shearing under high pressure, and the whole system is made into a smooth paste; this phenomenon is very similar to that of prepared nanocrystalline cellulose [17, 18]. Many surface reactive functional groups of ULFs are exposed compulsively, which shows strong water absorption so that the maximum solid content of the ULF/water paste is amid 2–3%. How to dry this paste is an urgent project. The smashed ULFs will aggregate irreversibly again after being dried directly because of various strong bonding effects. Therefore the surfaces of ULFs must be modified by weakening or eliminating bonding effects to restrain their aggregation. So far, no study on the fabrication of ultrafine leather powders by the hybridisation method has been reported. In this work, dry ultrafine leather powders are firstly obtained by using SiO₂ particles as the blocking agent of the various strong bonds between the ULFs; the process schematic representation is presented in Fig. 1. The characteristics of the obtained product have been measured by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS) and energy dispersive X-ray spectrometry (EDS).

2. Material and methods

2.1. Materials: Chromed leather shavings from cattle skin were donated by a tannery in the province of Zhejiang; tetraethyl

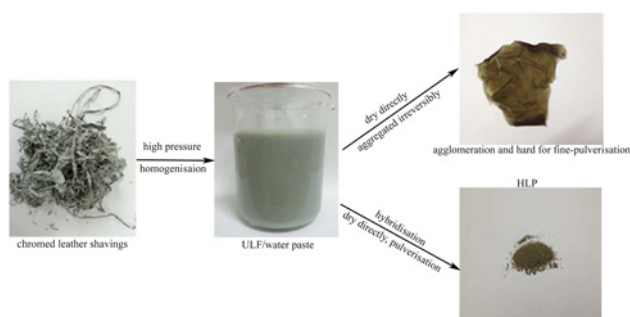


Figure 1 Schematic representation of HLP preparation

orthosilicate (TEOS, 98%) as a silica source was purchased from the Aldrich-Sigma Company, and the other solvents and reagents were purchased from the Guangzhou Chemical Reagents Company. All chemicals were used as received without further purification.

2.2. Method: Chromed leather shavings were swelled and smashed to form the ULF/water paste with a solid content of 2.13% after high-pressure homogenisation at a pressure of 70 MPa for 1.5 h at ambient temperature. We then prepared ultrafine leather powder through optimising the reaction condition. In a typical reaction, 20 g of the ULF/water paste and 0.3 ml of acetic acid were added into 80 ml of water, and the mixture was stirred at 40°C for 10 min. Then, 0.2 ml of TEOS ethanol solution (33.7 mmol/l) was added dropwise into the mixture under stirring. After reacting at 90°C for 4 h, the obtained product was centrifuged, and then washed three times with water and absolute ethanol in sequence. The final product, denoted as hybrid leather powder (HLP), was vacuum-dried, grinded and sieved through a 200 mesh size.

2.3. X-ray diffraction: The samples were characterised by XRD performed on a MSALXD2 with Cu K α radiation (40 kV, 20 mA and $\lambda = 1.54051 \text{ \AA}$) at a scanning rate of 5°/min for 2θ ranging from 5° to 75°.

2.4. Morphological analysis: The morphology of samples was observed by using field emission SEM (NovaNanoSEM 430) operated at an accelerating voltage of 10 kV. The TEM model FEI Tecnai 12 was used to observe the dispersion of nanoSiO₂ particles and the size of the leather fibres.

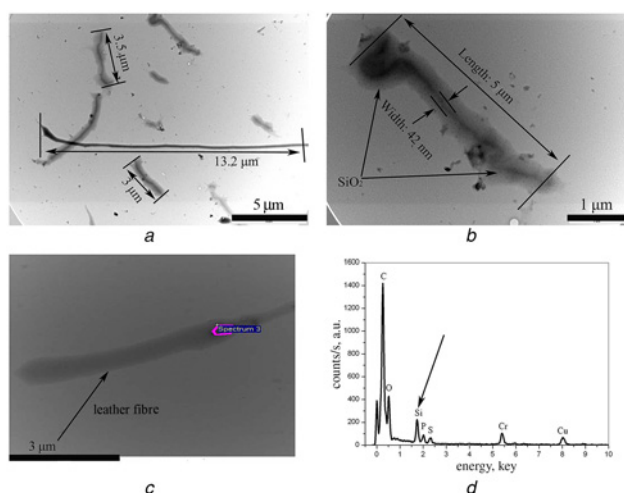


Figure 2 Typical TEM of HLP and EDS analysis for HLP
a, b Typical TEM of HLP
c, d EDS analysis for HLP

2.5. Surface element analysis: The samples were analysed by EDS (EDS, JEOL-2010), using an accelerating voltage of 200 kV.

2.6. Thermogravimetric analysis (TGA): The thermal stability of samples was characterised by NETZSCH TG209F1, and the specimens were scanned from 25 to 750°C at a rate of 20°C/min under air atmosphere.

2.7. X-ray photoelectron spectrometry: The surface elements of the HLP were identified by XPS with Al K α (Kratos Axis Ultra DLD, $h\nu = 148\,606 \text{ eV}$).

3. Results and discussion: The dispersion of the ULFs and nanoSiO₂ particles were observed using regular TEM. The typical TEM images are presented in Fig. 2. Figs. 2a and b show that the individual leather fibres were separated with a large aspect ratio, and the sizes of the leather fibres were estimated to be less than 70 nm in width and 30 μm in length. Numerous nanoSiO₂ particles were scattered around the leather fibres because the leather fibres could induce in situ synthesis of the nanoSiO₂ particles owing to their abundant surface reactive functional groups. The EDS analysis of leather fibres (Figs. 2c and d) showed that they were coated with a layer of SiO₂ particles anchored on the surface, because the plentiful surface active hydroxyl groups of the fibres could interact with the nanoSiO₂ particles to generate a new bonding effect (Si–O–C).

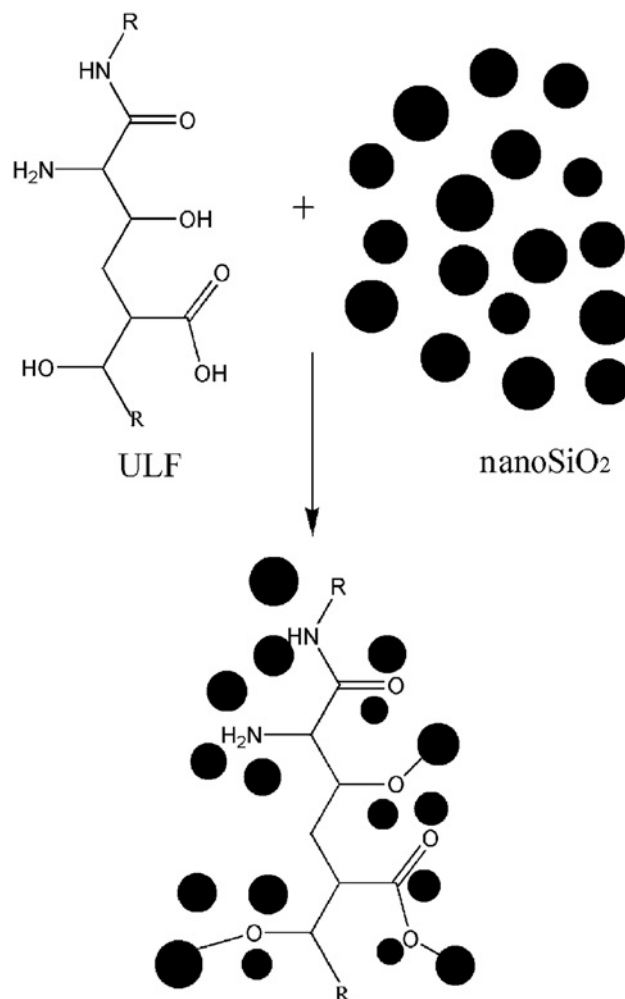


Figure 3 Schematic representation of interaction between leather fibres and nanoSiO₂

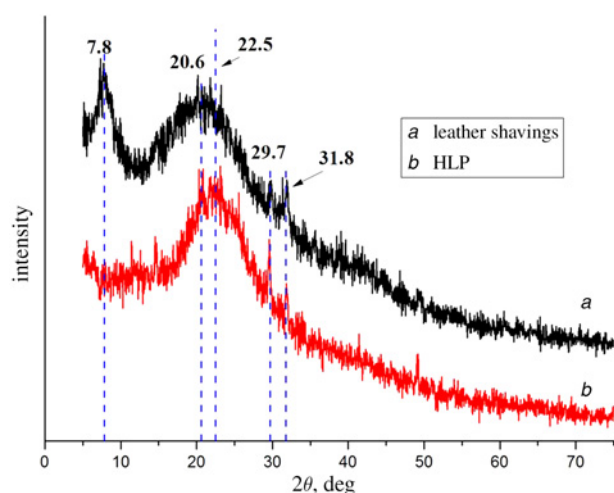


Figure 4 X-ray diffractograms from leather shavings and HLP

Furthermore, the nanoSiO₂ particles could also be absorbed on the surface of the leather fibres by the strong electrostatic attraction and hydrogen bonds between them. The corresponding schematic representation of the interaction between the leather fibres and the nanoSiO₂ particles is shown in Fig. 3.

The XRD patterns of leather shavings and HLP are presented in Fig. 4. It is evident that the aggregation structure of the leather shavings was significantly different from that of the HLP. The first intense peak at 7.8° for the HLP disappeared completely, compared with leather shavings, which indicated that the extension of the interplanar spacing gave rise to the collapse of the crystalline structure, because the in situ generated SiO₂ particles could play a blocking role between leather fibres in the ordered region. Besides, the weakening of the broad peak at 20.6° implied that multi-structures in the amorphous region were also loosened because of the permeation of the SiO₂ particles. The broad XRD reflection peak for the HLP at 22.5° could be assigned to the amorphous structures of SiO₂. More importantly, the XRD data suggested that both samples still maintained the triple helical structure, which was indicated by the presence of characteristic peaks located at 29.7° and 31.8°, and this was the key for the HLP to function as a functional reinforcement.

The morphology of the leather shavings and HLP were investigated using SEM. As shown in Fig. 5, the SEM micrographs showed significant changes in the morphology between the leather shavings and HLP. Fig. 5a reveals that plentiful collagen fibres with a smooth surface were aggregated tightly and constituted various irregular shaped fibrils, which implied the difficulty of

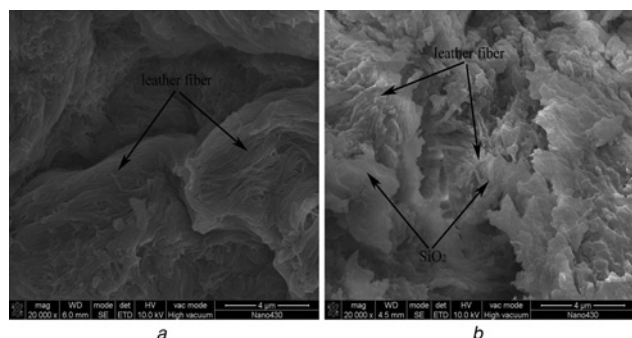


Figure 5 Typical SEM of leather shavings and of HLP
a Leather shavings
b HLP

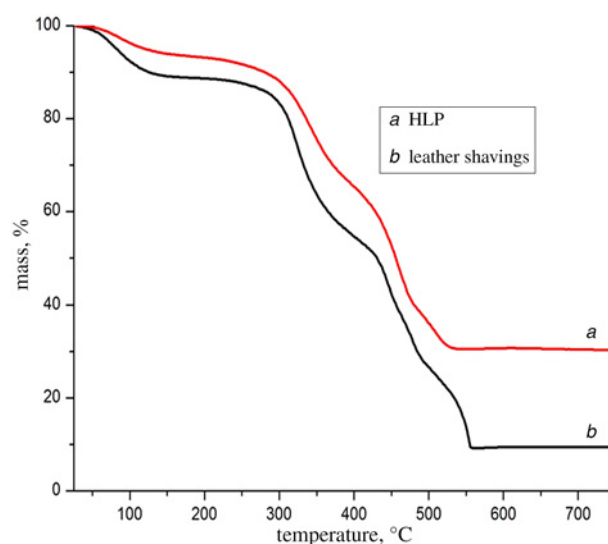


Figure 6 Typical TGA for leather shavings and HLP

leather fine-pulverisation and the powerful trend that ULFs obtained by high-pressure homogenisation would aggregate irreversibly again after being dried directly because of the various strong bonding effects. By contrast, Fig. 5b shows that all the fibres were coated with a compact layer of SiO₂ particles and the SiO₂-coated fibres could not support their hard aggregation,

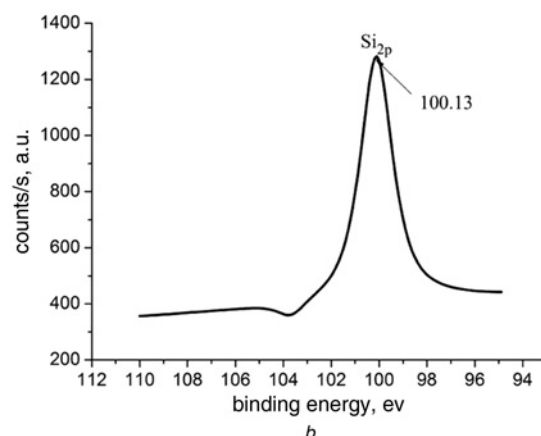
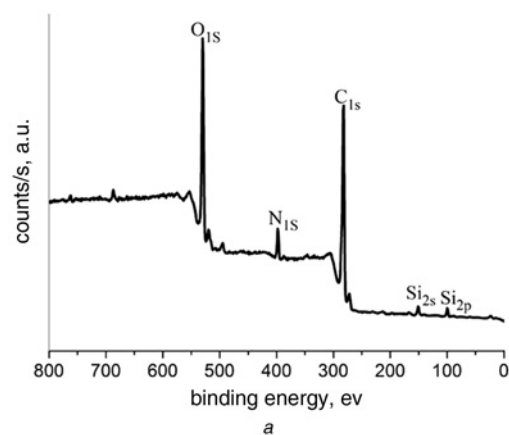


Figure 7 XPS spectra survey of HLP and high-resolution spectra of Si_{2p}
a XPS spectra survey of HLP
b High-resolution spectra of Si_{2p}

because massive surface polar groups were shielded completely by this isolating layer composed of SiO₂ particles.

The TGA for leather shavings and HLP are shown in Fig. 6. In the case of leather shavings, the absorbed and bound water was lost with a weight loss of about 11.25% at the first degradation stage, and the residual ash was about 9.38%. In addition, the maximum degradation temperatures were 323.8 and 444.6°C, which indicated the elimination of small molecular substances and the breakage of the backbone, respectively. For the HLP, the water content was reduced to 6.40% compared with the leather shavings because abundant polar groups were shielded by SiO₂, and the residual ash increased to 30.30%, indicating the loading ratio of the HLP reached nearly 20%. Moreover, the maximum degradation temperature shifted to 342.3 and 448.8°C, respectively. This increase could be associated to the formation of a new bonding interaction (Si–O–C) between leather fibres and SiO₂ particles. Based on these results, we can conclude that the thermal stability of HLP improved markedly.

The surface information is quite significant for analysing the hybrid materials. To further demonstrate the presence of Si species, XPS was employed to investigate the surface elemental composition of the HLP. Fig. 7 shows the survey of the XPS spectra of the HLP as well as the high-resolution spectra of Si_{2p}. As shown in Fig. 7a, the characteristic peaks of C, N, O and Si were found clearly in the HLP. In addition, the chemical state of the silicon could be acquired based on the resulting Si_{2p} spectra. Fig. 7b shows a peak around the binding energy 100.13 eV instead of 103 eV, which is in agreement with the formation of a covalent band between leather fibre and SiO₂ (Si–O–C).

4. Conclusions: This Letter opens a brand-new greener way for the fabrication of ultrafine leather powder as a kind of new functional reinforcement. Ultrafine leather powders were successfully prepared by hybridisation of SiO₂ particles and ULFs smashed through high-pressure homogenisation. The sizes of the produced ULFs were found to be less than 30 µm in length and 70 nm in width. Morphological analysis and structural analysis of the generated HLP showed that the leather fibres still maintained an intrinsic fibrous structure and were coated with a layer of SiO₂ particles, which is confirmed by XRD analysis and the EDS test, respectively. Improvement in thermal stability of the HLP was also observed, which was induced by the formation of new bonding interaction (Si–O–C) between SiO₂ particles and the leather fibres. The formation of the new bonding interaction was powerfully proved by the XPS measurement. Therefore, the present studies have shown the potential for HLPs to be used as a kind of functional reinforcement in the development of polymer composites.

5. Acknowledgments: The authors are grateful for financial support from the National Natural Science Foundation of China (no. 21075043) and the Fundamental Research Fund for the Central Universities (no. 2011ZM0008).

6 References

- [1] Dehghani A., Madadi Ardekani S., Al-Maadeed M.A., Hassan A., Wahit M.U.: 'Mechanical and thermal properties of date palm leaf fiber reinforced recycled poly (ethylene terephthalate) composites', *Mater. Des.*, 2013, **52**, pp. 841–848
- [2] Shubhra Q.T.H., Alam A.K.M.M., Beg M.D.H.: 'Mechanical and degradation characteristics of natural silk fiber reinforced gelatin composites', *Mater. Lett.*, 2011, **65**, (2), pp. 333–336
- [3] Ficai A., Andronescu E., Trandafir V., Ghitulica C., Voicu G.: 'Collagen/hydroxyapatite composite obtained by electric field orientation', *Mater. Lett.*, 2010, **64**, (4), pp. 541–544
- [4] Ravichandran K., Natchimuthu N.: 'Vulcanization characteristics and mechanical properties of natural rubber-scrap rubber compositions filled with leather particles', *Polym. Int.*, 2005, **54**, (3), pp. 553–559
- [5] El-Sabbagh S.H., Mohamed O.A.: 'Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber', *J. Appl. Polym. Sci.*, 2011, **121**, (2), pp. 979–988
- [6] Przepiorkowska A., Chronska K., Zaborski M.: 'Chrome-tanned leather shavings as a filler of butadiene-acrylonitrile rubber', *J. Hazard Mater.*, 2007, **141**, (1), pp. 252–257
- [7] Ferreira M.J., Almeida M.F., Freitas F.: 'Formulation and characterization of leather and rubber wastes composites', *Polym. Eng. Sci.*, 2011, **51**, (7), pp. 1418–1427
- [8] Chronska-Olszewska K., Przepiorkowska A.: 'A mixture of buffing dust and chrome shavings as a filler for nitrile rubbers', *J. Appl. Polym. Sci.*, 2011, **122**, (5), pp. 2899–2906
- [9] Ambrósio J.D., Lucas A.A., Otaguro H., Costa L.C.: 'Preparation and characterization of poly (vinyl butyral)-leather fiber composites', *Polym. Compos.*, 2011, **32**, (5), pp. 776–785
- [10] Mohamed O.A., El Sayed N.H., Abdelhakim A.A.: 'Preparation and characterization of polyamide-leather wastes polymer composites', *J. Appl. Polym. Sci.*, 2010, **118**, (1), pp. 446–451
- [11] Ramaraj B.: 'Mechanical and thermal properties of ABS and leather waste composites', *J. Appl. Polym. Sci.*, 2006, **101**, (5), pp. 3062–3066
- [12] Rajaram J., Rajnikanth B., Gnanamani A.: 'Preparation, characterization and application of leather particulate-polymer composites (LPPCS)', *J. Polym. Environ.*, 2009, **17**, (3), pp. 181–186
- [13] Xu J., Zhang J., Wang Q., Wang A.: 'Disaggregation of palygorskite crystal bundles via high-pressure homogenization', *Appl. Clay Sci.*, 2011, **54**, (1), pp. 118–123
- [14] Augusto P.E.D., Ibarz A., Cristianini M.: 'Effect of high pressure homogenization (HPH) on the rheological properties of tomato juice: creep and recovery behaviours', *Food Res. Int.*, 2013, **54**, (1), pp. 169–176
- [15] Huang D., Wang W., Xu J., Wang A.: 'Mechanical and water resistance properties of chitosan/poly (vinyl alcohol) films reinforced with attapulgite dispersed by high-pressure homogenization', *Chem. Eng. J.*, 2012, **210**, pp. 166–172
- [16] Meng S., Ma Y., Sun D.-W., Wang L., Liu T.: 'Properties of starch-palmitic acid complexes prepared by high pressure homogenization', *J. Cereal Sci.*, 2014, **59**, (1), pp. 25–32
- [17] Valentini L., Cardinali M., Fortunati E., Torre L., Kenny J.M.: 'A novel method to prepare conductive nanocrystalline cellulose/graphene oxide composite films', *Mater. Lett.*, 2013, **105**, pp. 4–7
- [18] Mohamad Haafiz M.K., Hassan A., Zakaria Z., Inuwa I.M., Islam M. S.: 'Physicochemical characterization of cellulose nanowhiskers extracted from oil palm biomass microcrystalline cellulose', *Mater. Lett.*, 2013, **113**, pp. 87–89