Journal of
Composites Science

MDPI

Article

Surface Modification of Flax Fibers for Manufacture of Engineering Thermoplastic Biocomposites

Madina Shamsuyeva [1,*], Boon Peng Chang [2], Natalie Vellguth [3], Manjusri Misra [2,4], Amar Mohanty [2,4] and Hans-Josef Endres [1]

1 Institute of Plastics and Circular Economy IKK, Leibniz University Hannover, 30823 Garbsen, Germany; endres@ikk.uni-hannover.de
2 Bioproducts Discovery and Development Centre (BDDC), Department of Plant Agriculture, University of Guelph, Guelph, ON N1G 2W1, Canada; changb@uoguelph.ca (B.P.C.); mmisra@uoguelph.ca (M.M.); mohanty@uoguelph.ca (A.M.)
3 Fraunhofer Application Center HOFZET, Fraunhofer Institute for Wood Research WKI, 30453 Hanover, Germany; natalie.vellguth@wki.fraunhofer.de
4 School of Engineering, Thornbrough Building, University of Guelph, Guelph, ON N1G 2W1, Canada
* Correspondence: shamsuyeva@ikk.uni-hannover.de

Received: 22 April 2020; Accepted: 28 May 2020; Published: 1 June 2020

Abstract: The aim of this feasibility study is to develop application-oriented natural fiber-reinforced biocomposites with improved mechanical and durability performance. The biocomposites were manufactured via a film-stacking process of epoxy-coated flax textiles and polyamide 6 (PA6). The fabricated biocomposites were subjected to thermo-oxidative ageing for 250, 500 and 1000 h and tested with regard to tensile properties. The results show that the biocomposites with epoxy-coated flax fibers possess considerably higher tensile properties compared with the reference specimens under all tested conditions.

Keywords: biocomposites; natural fibers; surface treatment; thermo-oxidative ageing; polyamide; flax

1. Introduction

Natural fiber composites have already proven their beneficial material properties in various lightweight applications, like e.g., automotive (interior), sport and leisure or building construction [1–3]. The well-known advantages of the natural fibers such as low density, high damping and strain associated with further economic and ecological benefits like renewable origin, high availability and broad assortment of fiber types, biological degradation and recycling potential promote their commercial use in composite applications [1–4]. Although both thermoset and thermoplastic natural fiber composites find industrial applications, recycling possibilities of the thermoplastic composites represent a valuable advantage compared with the thermoset composites [3]. Among the standard thermoplastics like, for example, polyvinyl chloride, and polystyrene, polyethylene and polypropylene are used most commonly for the manufacture of the natural fiber composites [3,5]. Due to the lower processing temperature of these matrices, which is generally lower than 200 °C, the natural fibers do not undergo thermal degradation, which is associated with emission, color change and strong decrease of mechanical performance [6]. At the same time, effective use of engineering thermoplastics like, for example, polyamide would enable manufacture of natural fiber-reinforced composites with considerably higher mechanical performance, durability and thermal resistance than those with standard thermoplastics. This would open new application fields for the resulting biocomposites. The review on short cellulose fiber-reinforced polyamides for composite applications has already been published previously [7]. One of the simplest application-oriented approaches is to use polyamides

with low melting temperature like, for example, PA11 or PA12. In addition, further approaches like modification of the short cellulose fibers or adjustment of the compounding process parameters are used, in order to reduce the temperature gap between the thermal stability of cellulose-based fibers and processing temperature of the polyamides [7]. Due to this temperature gap, natural fiber textile-reinforced PA6 composites are rarely manufactured [8]. There are only few attempts reported on the improvement of thermal stability of the weaved jute [9] and flax [10] textiles. Both of the studies use epoxy resin coating of the textiles for an effective integration into polyamide. Epoxy coating is a thermoset acting as an isolating interphase between natural fibers and molten polyamide. Furthermore, PA6 and epoxy resins have good compatibility [11], i.e., epoxy resins have been used as a reactive coupler for the manufacture of PA6 blends with polycarbonate [12], polybutylene terephthalate [13,14], and poly-(phenylene ether) [15] or as crosslinking agent for the manufacture of PA6 foam [16]. Both of the aforementioned studies report that the resulting biocomposites with epoxy coated natural fibers possess increased bending, tensile and thermal properties [9,10]. However, in order to further develop this technology, the effect of temperature on the coated textiles and ageing behavior of the manufactured biocomposites have to be investigated.

The aim of this study is to investigate the effect of the epoxy-based coating of the flax textiles on the tensile properties of the textiles and the corresponding PA6 biocomposites after thermo-oxidative ageing.

2. Materials and Methods

2.1. Materials

Following materials were used for the manufacture of the epoxy-coated flax fiber-reinforced PA6 composites: twill (1/3) weaved flax fabric manufactured using a double rapier weaving machine as described in the prior publication [17]. Bisphenol A-based epoxy resin with the trade name H543 and an amine-based hardener with the trade name R131 were purchased from Hacotech and used for the surface coating of the weaved fabrics. The density of the cured epoxy resin is 0.92 ± 0.02 g/cm^3 and the T_g is 60.2 °C. PA6 in the form of 100 µm thick film was supplied by Jura-Plast.

2.2. Coating of the Weaved Textiles and Composite Manufacture

Weaved flax textiles were pre-dried at 80 °C for 24 h. Afterwards, the textiles were fixed in a frame with the dimensions of 30 × 40 cm, sprayed manually using a spray pistol with the epoxy resin (1 g/cm^2) and dried at 80 °C for 30 min in an air circulation oven. Since PA6 is hygroscopic with a water absorption of 2.8–3.2% [18], the PA6 films were dried before composite manufacture at 80 °C for at least 24 h. In order to manufacture the composites, 4 layers of the flax textiles were stacked alternatively with PA6 films. The use of the 4 textile layers enables manufacture of both types of specimens with an optimal thickness required for the testing according to the used testing standard (ISO 527). The stacked textiles and films were also stored in air-circulating oven at 80 °C prior to hot pressing, in order to prevent moisture absorption. The composites were fabricated via film stacking process using a hot press KV 322 manufactured by Rucks. The stacked sequence with dimensions of 20 × 30 cm was pressed with a force of 100 kN for 5 min at 225 ± 4 °C, cooled down to 100 °C under pressure using water cooling at a rate of 10 K/min. Finally, the pressed specimens were removed out of the hot press and cooled down to room temperature under a metal weight with a force of approximately 0.48 kN. The summary of the investigation steps as well as the nomenclature of the manufactured samples is represented in Figure 1. This figure shows that the following parameters were held constant during the study: type of the used weave art, textile spraying procedure and composite manufacturing process. Variation of these parameters influences considerably the mechanical performance of the resulting composites [8,17,19]. The fiber weight fraction of the resulting reference composite (FLA-PA6) and the composite with the coated textile (FLA-EP-PA6), were 43 wt.% and 63 wt.%, respectively. The overall weight of the reference was 160 g and of the composite with coated textile 230 g. The varied parameters

include application of the coating onto the textiles, change of the temperature during textile testing and duration of the thermo-oxidative ageing.

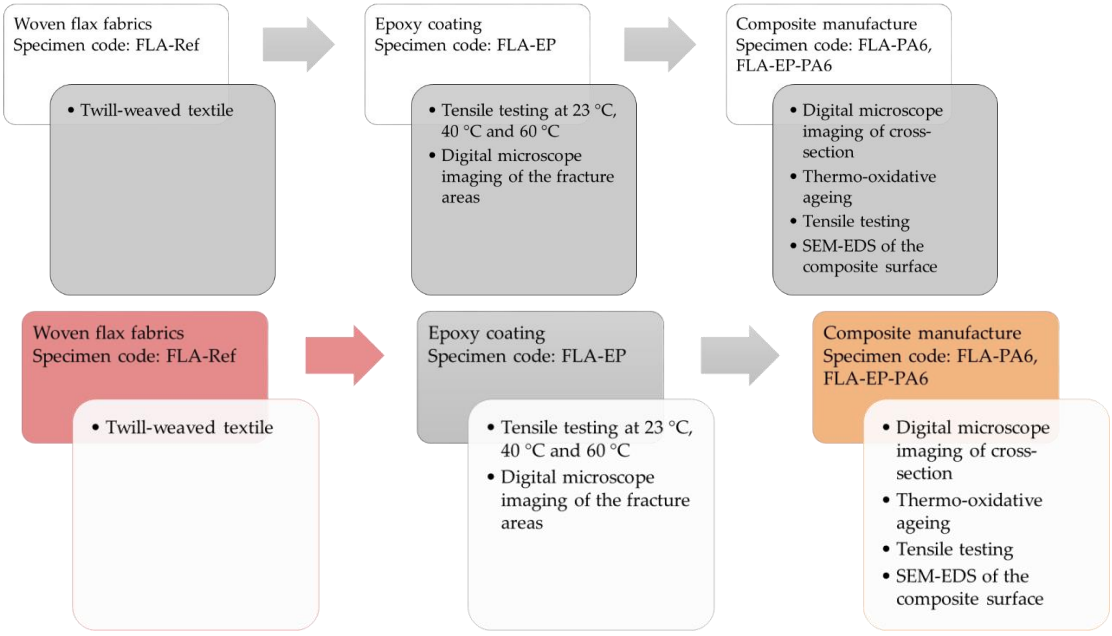

Figure 1. The main steps of the study and the nomenclature of the manufactured samples: flax reference (FLA-Ref), epoxy-coated flax, (FLA-EP), flax-reinforced polyamide 6 (FLA-PA6) and polyamide 6 reinforced with epoxy-coated flax (FLA-EP-PA6).

2.3. Accelerated Thermo-Oxidative Ageing

The accelerated thermo-oxidative ageing of the tensile specimens was performed according to ISO 188-2011 in a cabinet ageing oven EB10 at 110 °C for 250 h, 500 h and 1000 h. These specimens were evaluated in comparison with the specimens stored for the same time at standard laboratory conditions (23 °C with 40–50% humidity in a seal Ziploc bag) as according to the ASTM D618 standard. Figure 2 represents air flow schematic and photo images of the performed experiment.

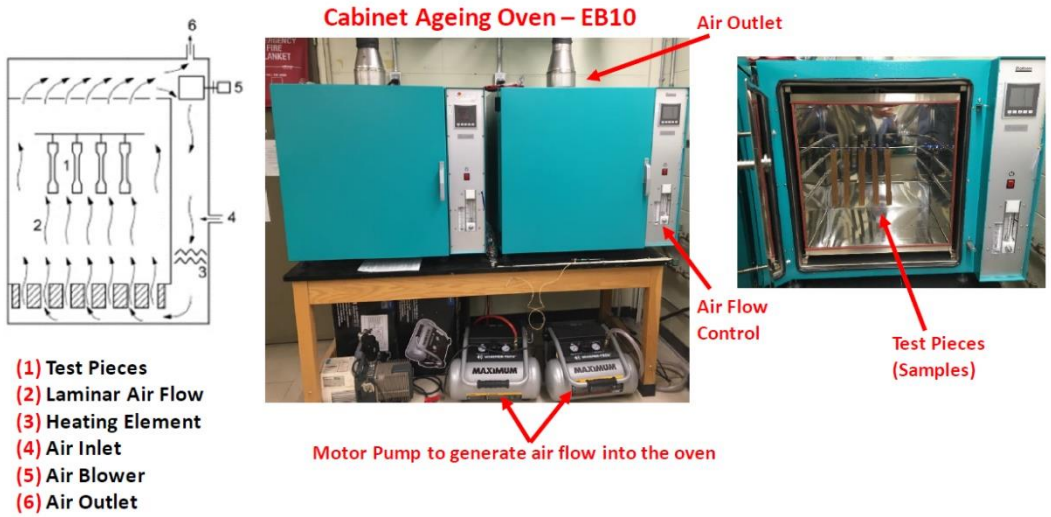

Figure 2. Schematic representation of the air flow (**left**), ageing oven (**middle**), specimens during ageing testing (**right**).

2.4. Mechanical Testing

Both coated textiles and the manufactured biocomposites were subjected to tensile testing according to ISO 527-4. The textiles were tested using Zwick/Roell Z100 TEW from ZwickRoell (Ulm, Germany) at the HOFZET and the biocomposites using Instron 3382 at the BDDC. Both tests were conducted using a 100 kN load cell with a speed of 2 mm/min. The coated textiles were tested at 23 °C, 40 °C and 60 °C without prior thermo-oxidative ageing in order to evaluate the strength of the reinforcing fibers as a function of temperature. Textile specimens and composites were conditioned prior to the testing at 23 °C and 50% relative humidity for 88 h. The average value of five tested specimens was taken for evaluation of the results. The composite specimens were manufactured using a diamond saw.

2.5. Digital Microscope Imaging

Optical imaging was performed at the Institute of Bioplastics and Biocomposites (IfBB) using a 3D digital microscope VHX 5000 Keyence (Neu-Isenburg, Germany) without further specimen preparation.

2.6. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy Analysis

The surface of both ambient and oven aged conditions of the flax-PA6 biocomposites were examined using a Phenom ProX desktop scanning electron microscope (SEM) from Phenom World (Eindhoven, The Netherlands) at an accelerating voltage of 10 kV under a high vacuum atmosphere. The samples were prior coated with a thin gold layer with a Cressington Sputter Coater 108 auto vacuum sputter chamber. Energy-dispersive X-ray spectroscopy (EDS) analysis was conducted on several zones of the flax-PA6 biocomposites to scan the oxygen content qualitatively. The oxygen concentration in atomic weight percentage for each sample under laboratory and thermo-oxidative ageing conditions was recorded. At least nine different areas of the sample surface were measured and the average and standard deviation were reported.

3. Results and Discussion

3.1. Tensile Strength of Fabrics

Tensile properties of the weaved flax fabrics tested at different temperatures are represented in Figure 3. The aim of this test is to evaluate the effect of the epoxy coating on the strength of the textiles and to predict the behavior of the coating during hot pressing. The results show that the epoxy-coated flax textiles possess considerably higher and more stable tensile properties compared with the references at all tested temperatures. The tensile strength of the reference sample, i.e., flax textile without coating is 18.7 MPa. It is important to consider, that there is a large number of factors affecting mechanical properties of weaved textiles like, for example, yarn fineness, twisting grade and counts, textile density and crimp, twill weave type, yarn finish, staple fiber strength, etc. [20] Consequently, it is not possible to compare accurately the achieved values with the literature.

The mean value of the tensile strength of the reference sample decreases with the increase of the temperature. This tendency is observed both in the case of the reference and coated textile samples. According to the literature the tensile strength of the elementary flax does not change in this temperature region [21]. Possibly, this change could be induced by the effect of temperature and drying on the textile structure, similarly, as it has already been reported for the apparent tensile strength of cotton and rayon cords [22]. To the best of authors' knowledge there is no previously published work on effect of temperature on the tensile strength of flax yarn structure. So, this latter assumption should be checked in a separate study.

Tensile strength of the epoxy coated flax textiles at room temperature is more than twice as high as of the reference sample. At the same time, the strength decreases with the increasing temperature faster than in the case of the reference, i.e., at 60 °C the difference between the uncoated and coated textile is 49%. The storage modulus of epoxy resin and flax fiber-reinforced epoxy drops considerably

in this temperature region [23]. Therefore, the faster decrease rate is also associated with the increasing flexibility of the coating. Basically, at higher temperature the reinforcing effect of the epoxy is reduced and the textile strength of the flax remains, so the values are close to those of the reference.

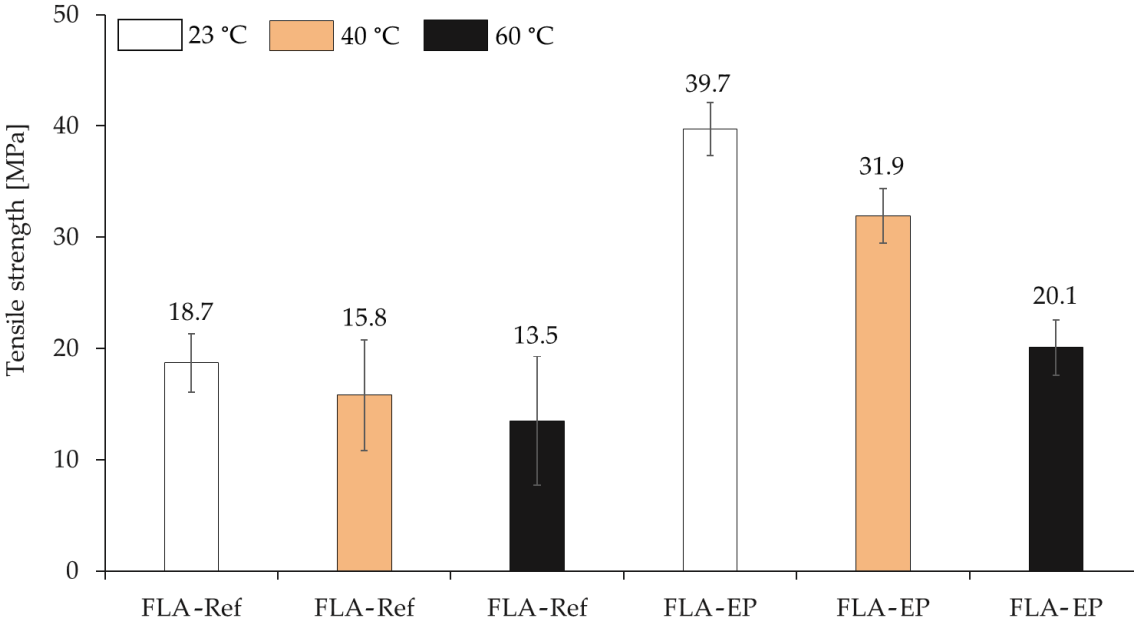

Figure 3. Tensile strength of flax textiles at 23 °C, 40 °C and 60 °C.

3.2. Digital Microscope Imaging of Flax Fabrics and Biocomposites

Mechanical properties of the coated textiles and the resulting composites are greatly influenced by the coating material and the corresponding spraying process. In order to evaluate the quality of the coating and analyse the performance of the epoxy coating during heating, the fracture area of the textiles after tensile testing was analyzed using digital microscope. The digital microscope images of the textiles at different temperatures are represented at 100× und 200× magnification in Figure 4. These images show that the reference textile has same structure at all tested temperatures. These specimens are associated with high fibrillation, a small number of dust particles and a bright color. The epoxy-coated flax textiles are, in contrast, darker due to the coating and show a splinted fracture with numerous epoxy and dust particles on the fiber surface at 23 °C. The yarns of the specimen tested at 40 °C are glossy due to the softening of the epoxy coating. In the case of the specimen tested at 60 °C the fibers of the individual yarns are glued together by the softened epoxy and single fibers possess a small number of epoxy drops at the surface. These results show, that due to the use of spray coating and short curing cycle the epoxy-coating remains mainly at the outer layers of the textiles and penetration into the yarns takes place during the second heating, i.e., hot pressing.

The spraying process is one of the most common methods used for textile finishing. Parameters like, for example, the rate of the spraying and process time influence the resulting properties and should be controlled during coating [19]. In the case of the flax fibers for composite application, spraying technology has been used for example for combined ultraviolet (UV)/water ageing [24] and as an approach for the enzymatic retting [25]. In this study, the spraying process used for the epoxy coating of the textiles did not cause any further unexpected physical changes, i.e., no change of the fiber structure could be observed using digital microscopy or scanning electron microscopy. Potentially, such physical change could affect the bonding mechanism between PA6 and coated flax fabrics like, for example, promoting or reducing mechanical interlocking and, thus, affect mechanical performance of the resulting composite.

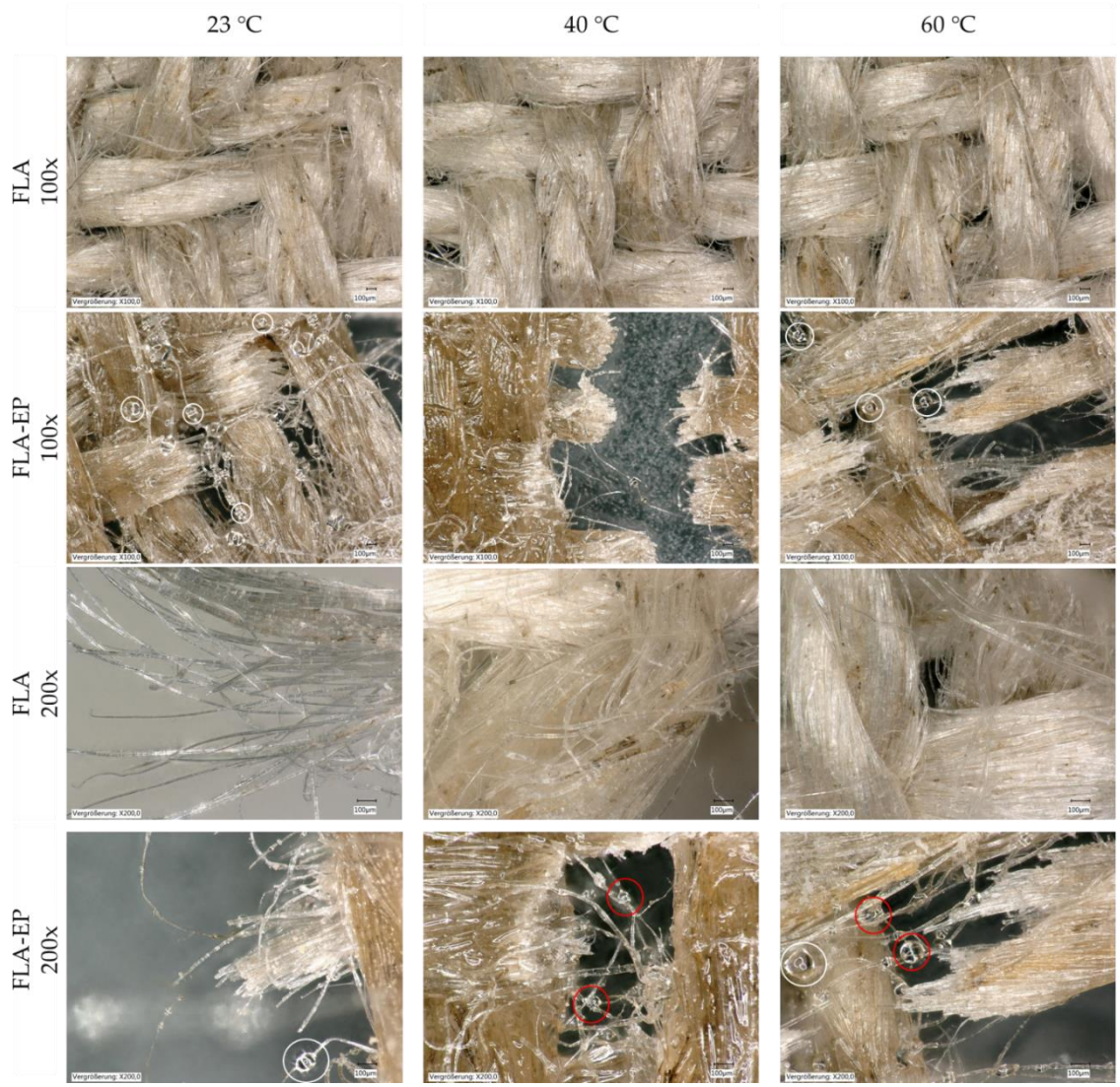

Figure 4. Digital microscope images of flax textiles after tensile testing. Epoxy drops are marked with red and air inclusions with white.

The infiltration of PA6 strongly affects the mechanical performance of the resulting composites. In order to evaluate the infiltration quality of the manufactured composites, the cross-section area of the specimens was investigated using digital microscope imaging. The digital microscope images at two magnifications are represented in Figure 5. The reference specimen has good quality without porosity showing that the pre-drying of the biocomposite constituents was effective. The images of the cross-section show that the specimen with coated textiles possesses high degree of porosity. However, visually both reference composites and those containing coated flax fabrics did not have any defects. The observed air inclusions could be induced during the spraying process. Some of these air inclusions can be observed in Figure 4 at 23 °C/100×. Since the presence of these pores leads to reduction of mechanical properties, the optimization of the spraying process should be investigated, in order to improve tensile properties. This study represents merely a one of the first feasibility studies in this field focused on the effectiveness of the epoxy coating on the durability and mechanical performance of the resulting biocomposites. Consequently, the effect of the spraying process should be investigated separately, including detailed evaluation of process parameters like, for example, the rate of the spraying, drop volume, distance to the substrate, etc. on the infiltration quality and the mechanical properties of the elementary flax fibers, yarns, textiles and the resulting biocomposites.

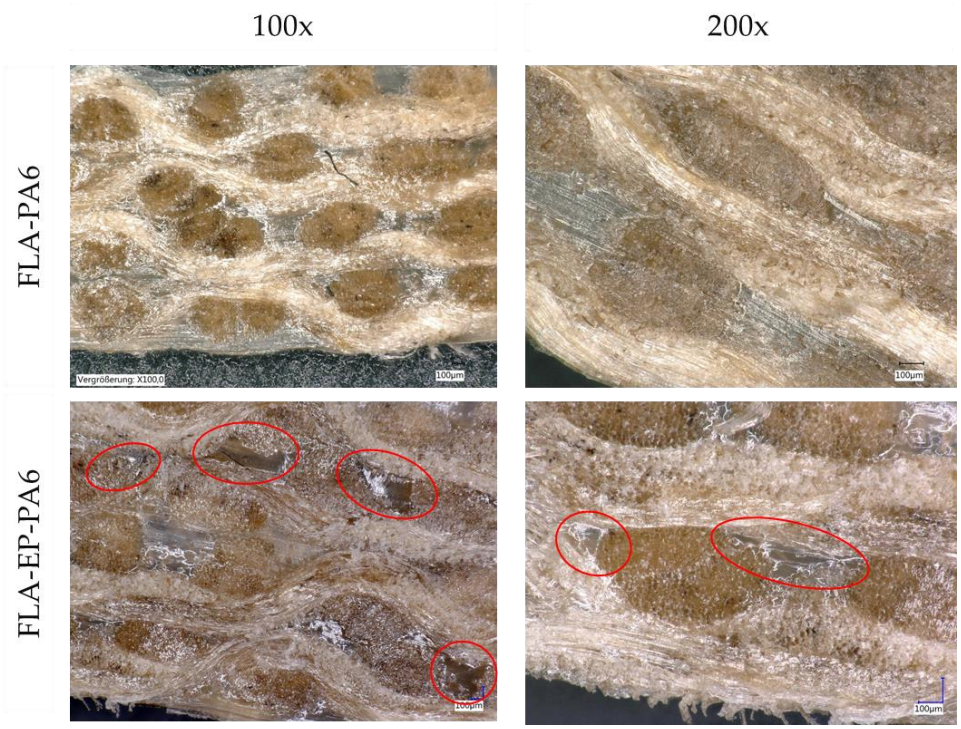

Figure 5. Digital microscope images of the cross-section of FLA-PA6 and FLA-EP-PA6 biocomposites.

3.3. Tensile Properties of Biocomposites

Tensile properties of the flax-reinforced PA6 conditioned for 250, 500 and 1000 h under ambient and thermo-oxidative conditions are presented in this part. The tensile strength of the biocomposites at ambient conditions is shown in Figure 6. The tensile strength of the reference sample at the beginning of the experiment is 69.2 MPa. This is comparable with the literature values reported for twill weaved flax-PA6 biocomposites, which range from 32.2 to 90.2 MPa [8] depending on the manufacturing parameters. The hot-pressing parameters, especially, the temperature (225 °C) and force (100 kN) used during hot pressing affect mechanical properties of the resulting composites, since the thermal degradation of some flax constituents starts already at 159–175 °C and of the hemicellulose at 200 °C. This process is accompanied by emission of volatile organic compounds and unpleasant smells as well as a decrease in mechanical performance [6]. The biocomposites with coated textiles show at the beginning of the experiment 22 % and after 1000 h 16% higher strength compared with reference. Several effects lead to this improvement simultaneously: reinforcing effect of the epoxy coating as presented above, increased fraction of the reinforcing components including flax fibers and epoxy, and, finally, chemical reaction between amine groups of PA6 and epoxide, which takes place at temperatures above 200 °C [26]. In the case of the reference composite, (FLA-PA6) the flax fiber weight fraction is 63 wt.% and in the case of the FLA-EP-PA6 43 wt.%. The latter specimen contains approx. 31 wt.% of epoxy. The weight fraction of the fibers decreased due to the coating with the epoxy resin, and thus resulted also in the increase of the overall composite weight from 160 g to 230 g, i.e., approximately 44%. Consequently, although the composites with coated textiles possess higher tensile properties, they are heavier. At the same time due to the observed porosity and the general known difficulties regarding density measurement of the natural fibers [27], it is not possible to define quantitatively density and, thus, the fiber volume fraction of the composite constituents, which would simplify accurate evaluation of the mechanical performance. Although conditioning of the specimens at ambient conditions shows a slight tendency towards improvement of the tensile strength and a pronounced increase of the modulus (Figure 7) takes place due to the physical ageing process [28,29].

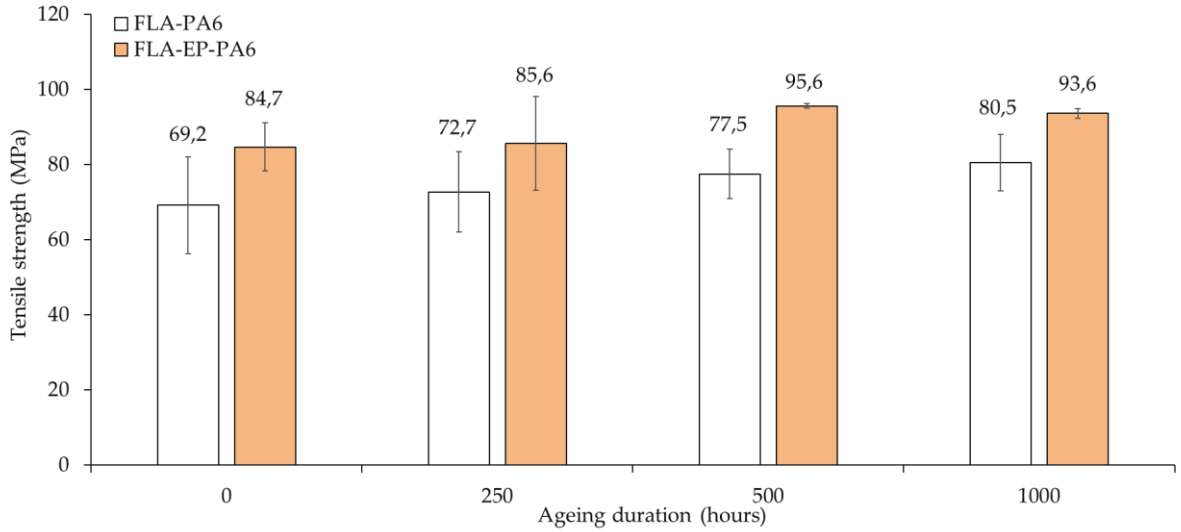

Figure 6. Tensile strength of the biocomposites at ambient conditions.

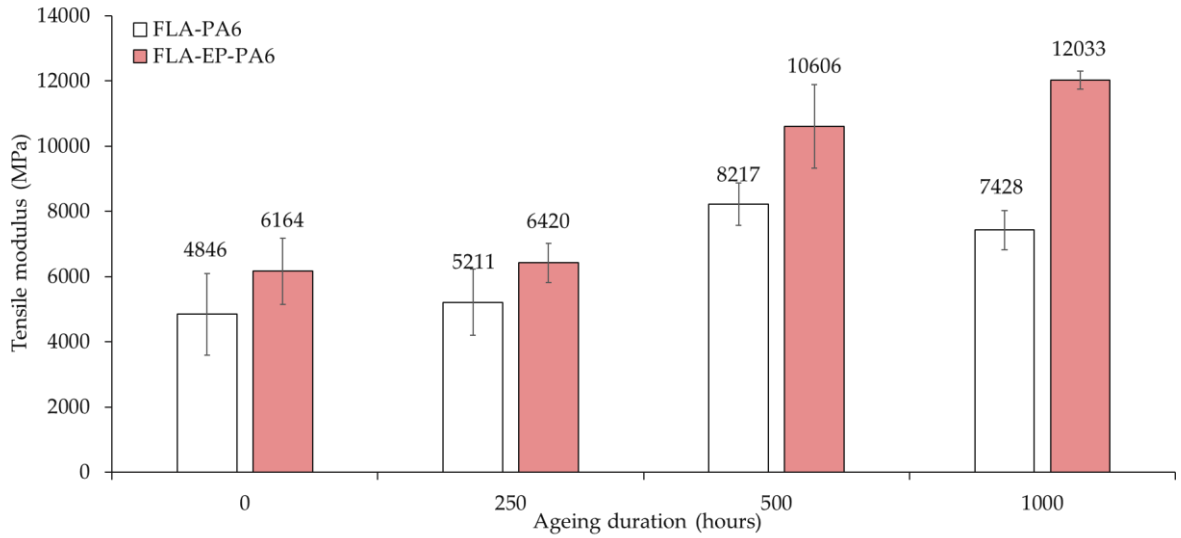

Figure 7. Tensile modulus of the biocomposites at ambient conditions.

Tensile strength of the biocomposite samples in thermo-oxidative ageing oven are represented in Figure 8. The results show that independent of the time line, the biocomposites with epoxy-coated flax textile possess higher strength than those without coating. The highest difference of 48% is observed after 250 h. At the same time the tensile strength of both biocomposites in general decreases. This decrease is induced by the simultaneous ageing effect of all composite constituents. Since the investigated composite represents a complex system consisting of natural fibers, thermoplastic and thermoset, separate study should be carried out, in order to evaluate the effect of the ageing on each of the constituents. However, even after 1000 h the composite with coated flax textiles (76.0 MPa) shows approximately 10% higher strength than the reference specimen (69.0 MPa) at the beginning of the experiment, consequently presenting the improved durability of the composites with epoxy-coated flax textiles.

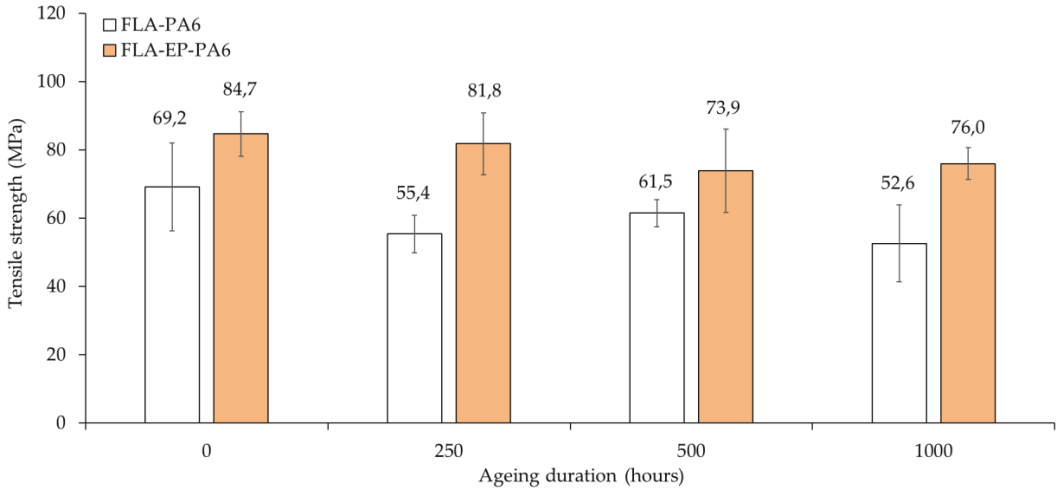

Figure 8. Tensile strength of the biocomposites under ageing conditions.

The tensile modulus of the samples after ageing is represented in Figure 9. The results show that the thermo-oxidative conditioning improves tensile modulus of the both biocomposites. Thermal and thermo-oxidative ageing of PA6 and synthetic fiber-reinforced PA6 composites has been broadly described in previous studies [8,30,31]. Chain scissoring and crosslinking of the polymer molecules during thermal ageing leads to the observed change of the mechanical properties [32]. As a result, the tensile strength of the flax biocomposites is reduced while their tensile modulus increases. This is the result of the thermal-embrittlement and oxidative-embrittlement mechanism associated with the crosslinking of the molecules [30] and thermo-chemical ageing of flax.

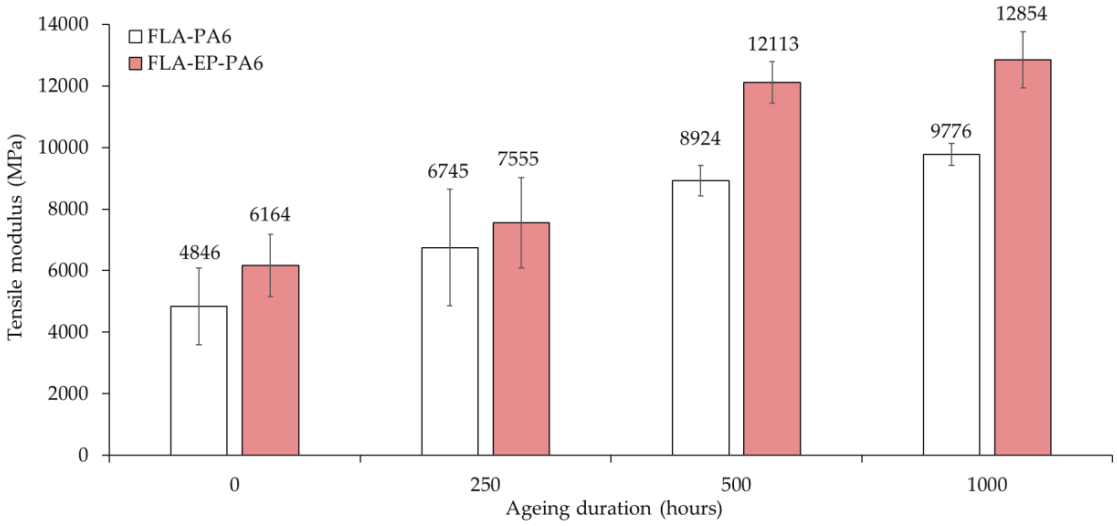

Figure 9. Tensile modulus of the biocomposites under ageing conditions.

Due to the presence of different laminate layers and flax fibers on the surfaces it is difficult to observe difference regarding fiber-matrix adhesion using scanning electron microscopy conducted on the fractured surface of the aged FLA-PA6 and FLA-EP-PA6 laminate samples. However, the degree of oxidative degradation of the samples was examined qualitatively using EDS. It has been observed that the oxygen concentration on the surface of each sample increases with the increase of ageing duration from 250 to 1000 h, Figure 10. Each of the oxygen content measurements is an average of nine areal scans of 400 to 500 µm wide of the designated spots (Figure 10 top right). The large standard deviation of the percentage oxygen content for all samples was due to the different laminate layers and flax fibers on the fracture surfaces. It was observed that the oxygen content of both biocomposites

was different even under the lab conditions. The FLA-EP-PA6 exhibited lower oxygen content on the fractured surfaces as compared to FLA-PA6. The oxygen concentration for both biocomposites increases with increasing ageing duration. Similar results were reported in the previous study [33], where the percentage oxygen content of the aged composites were higher than the lab-conditioned composite samples. The oxygen diffuses gradually from edges of the samples towards the core as the ageing time increase [29]. The FLA-EP-PA6 shows in general lower oxygen concentration than the FLA-PA6 laminates. The presence of the epoxy coating on the fiber acts as additional barrier to hinder the oxygen diffusion within the biocomposite. This result further indicates that the epoxy coated flax textiles were more effective in retarding the rate of oxidation as compared to the uncoated samples and hence improved the durability of the biocomposites.

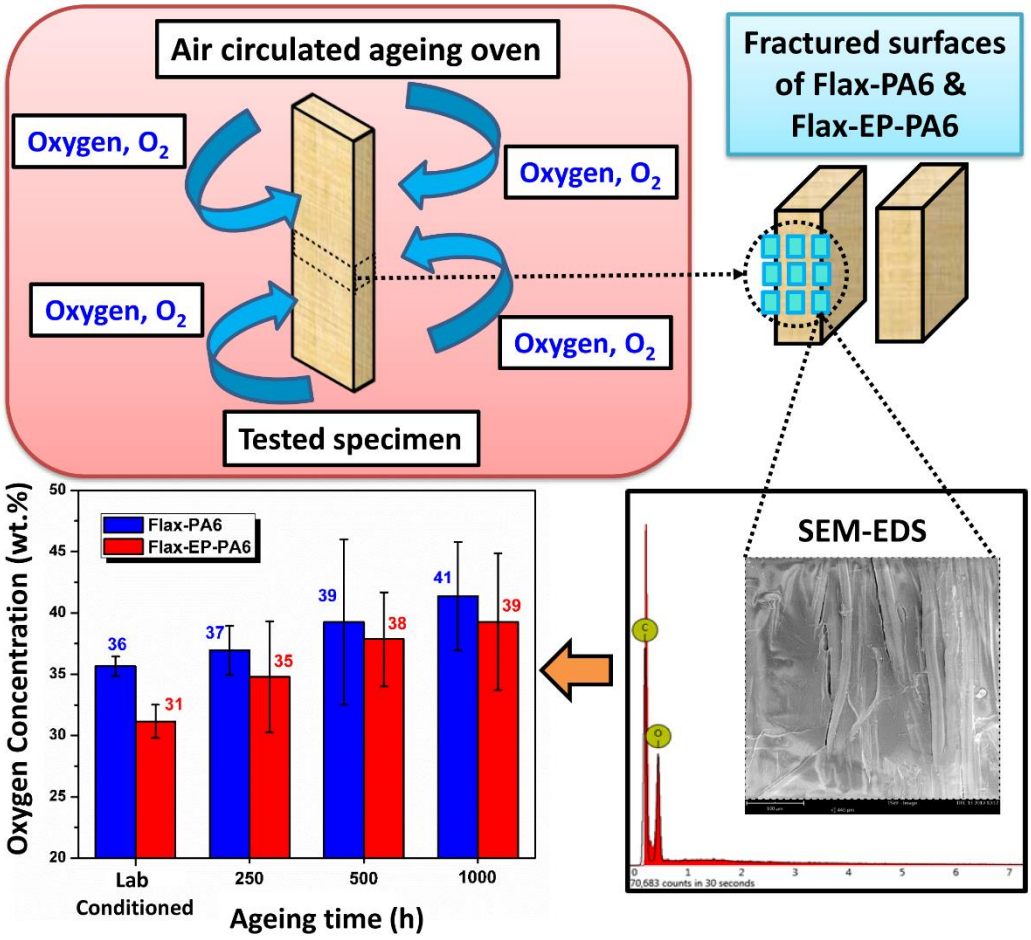

Figure 10. Schematic diagram of tested samples in ageing oven and oxygen concentration analyzed with scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) at the outer layer of the aged biocomposite specimens.

4. Conclusions

This study presents tensile properties of epoxy-coated flax textiles and PA6 reinforced with these textiles before and after thermo-oxidative ageing. The results show that the coated textiles as well as the corresponding biocomposites have considerably higher tensile properties than the reference under all tested conditions. Several factors lead to this improvement simultaneously: reinforcing effect of the epoxy resin, increase of the reinforcement fraction in the biocomposites and chemical reaction between PA6 and epoxy. Only a longer thermo-oxidative ageing leads to a slight decrease of the tensile strength and increase of modulus induced by thermal-embrittlement and oxidative-embrittlement mechanisms of the PA matrix and epoxy resin.

Basically, this study shows that the approach followed has a great potential for the manufacture of biocomposites with improved mechanical and durability performance. Furthermore, it can contribute to the manufacture of the high-performance biocomposites based on renewable resources, since all of the used composite constituents are available commercially in a biobased or a partially biobased form. Since the used thermoset coating cannot be melted, its effect on the recyclability of the composites should be investigated, e.g., its effect on the cryogenic grinding and the reinforcing effect as a filler in extrusion. To sum up, this approach would broaden the application fields of biocomposites based on renewable resources.

At the same time, there is still a great demand for further research in order to understand and further explore the individual factors leading to the improvement mechanical performance after the coating. The next studies will focus on: the optimization of the coating process, in order to reduce porosity and, thus, further improve the mechanical properties; investigation of the effect of ageing on the individual constituents of the composites, for example, using a design of experiments approach; and the effectiveness of the coating on the other woven arts like plain, satin or non-crimp textiles.

Author Contributions: Conceptualization, methodology, investigation and data curation M.S., B.P.C. and N.V.; writing—original draft preparation, M.S.; writing—review and editing, N.V., B.P.C., H.-J.E., A.M., M.M., M.S.; project administration, M.S.; resources and funding acquisition, H.-J.E., A.M., M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the German Federal Ministry of Education and Research, grant number 031B0502 and from own institutional resources.

Acknowledgments: The authors would like to thank Jana Winkelmann und Ricardo Wege for the manufacture of the weaved textiles for this study. A.K.M., M.M. and B.P.C. are thankful to the financial support from Ontario Research Fund, Research Excellence Program; Round-7 (ORF-RE07) from the Ontario Ministry of Research Innovation and Science (MRIS) (Project # 052644 and 052665); and the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)-Canada/University of Guelph-Bioeconomy for Industrial Uses Research Program Theme (Project # 030251) to carry out this research.

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

References

1. Sanjay, M.R.; Madhu, P.; Jawaid, M.; Senthamaraikannan, P.; Senthil, S.; Pradeep, S. Characterization and properties of natural fiber polymer composites: A comprehensive review. *J. Clean. Prod.* **2018**, *172*, 566–581. [CrossRef]
2. Pickering, K.L.; Efendy, M.A.; Le, T.M. A review of recent developments in natural fibre composites and their mechanical performance. *Compos. Part A-Appl. S.* **2016**, *83*, 98–112. [CrossRef]
3. Yashas Gowda, T.G.; Sanjay, M.R.; Subrahmanya Bhat, K.; Madhu, P.; Senthamaraikannan, P.; Yogesha, B. Polymer matrix-natural fiber composites: An overview. *Cogent Eng.* **2018**, *5*, 979. [CrossRef]
4. Gholampour, A.; Ozbakkaloglu, T. A review of natural fiber composites: Properties, modification and processing techniques, characterization, applications. *J. Mater. Sci.* **2020**, *55*, 829–892. [CrossRef]
5. Campilho, R.D.S.G. (Ed.) *Natural Fiber Composites*; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2016; ISBN 9781482239003.
6. Monteiro, S.N.; Calado, V.; Rodriguez, R.J.S.; Margem, F.M. Thermogravimetric Stability of Polymer Composites Reinforced with Less Common Lignocellulosic Fibers–an Overview. *J. Mater. Res. Technol.* **2012**, *1*, 117–126. [CrossRef]
7. Ogunsona, E.O.; Codou, A.; Misra, M.; Mohanty, A.K. A critical review on the fabrication processes and performance of polyamide biocomposites from a biofiller perspective. *Mater. Today Sustain.* **2019**, *5*, 100014. [CrossRef]
8. Liang, S.; Nouri, H.; Lafranche, E. Thermo-compression forming of flax fibre-reinforced polyamide 6 composites: Influence of the fibre thermal degradation on mechanical properties. *J. Mater. Sci.* **2015**, *50*, 7660–7672. [CrossRef]
9. Thitithanasarn, S.; Yamada, K.; Ishiaku, U.S.; Hamada, H. The Effect of Curative Concentration on Thermal and Mechanical Properties of Flexible Epoxy Coated Jute Fabric Reinforced Polyamide 6 Composites. *OJCM* **2012**, *02*, 133–138. [CrossRef]

10. Vellguth, N.; Rudeck, T.; Shamsuyeva, M.; Renz, F.; Endres, H.J. Thermal Stability of Natural Fibers via Thermoset Coating for Application in Engineering Thermoplastics. *KEM* **2019**, *809*, 433–438. [CrossRef]
11. Deng, S.; Ye, L. Influence of Fiber-Matrix Adhesion on Mechanical Properties of Graphite/Epoxy Composites: I. Tensile, Flexure, and Fatigue Properties. *J. Reinf. Plast. Comp.* **2016**, *18*, 1021–1040. [CrossRef]
12. Tjong, S.C.; Meng, Y.Z. Structural-mechanical relationship of epoxy compatibilized polyamide 6/polycarbonate blends. *Mater. Res. Bull.* **2004**, *39*, 1791–1801. [CrossRef]
13. Chiou, K.-C.; Chang, F.-C. Reactive compatibilization of polyamide-6 (PA 6)/polybutylene terephthalate (PBT) blends by a multifunctional epoxy resin. *J. Polym. Sci. Pol. Phys.* **2000**, *38*, 23–33. [CrossRef]
14. An, J.; Ge, J.; Liu, Y. Special effect of epoxy resin E-44 on compatibility and mechanical properties of poly(butylene terephthalate)/polyamide-6 blends. *J. Appl. Polym.* **1996**, *60*, 1803–1810. [CrossRef]
15. Chiang, C.-R.; Chang, F.-C. Polymer blends of polyamide-6 (PA6) and poly(phenylene ether) (PPE) compatibilized by a multifunctional epoxy coupler. *J. Polym. Sci. Pol. Phys.* **1998**, *36*, 1805–1819. [CrossRef]
16. Xu, Z.; Lin, X.; Luo, C.; Xiao, W. The Application of a Tri-Functional Epoxy Resin as a Crosslinking Agent in Extruded Polyamide-6 Foam. *Polym. Sci. Ser. B* **2019**, *61*, 574–581. [CrossRef]
17. Shamsuyeva, M.; Winkelmann, J.; Endres, H.-J. Manufacture of Hybrid Natural/Synthetic Fiber Woven Textiles for Use in Technical Biocomposites with Maximum Biobased Content. *J. Compos. Sci.* **2019**, *3*, 43. [CrossRef]
18. Goodship, V. *Practical Guide to Injection Moulding*; RAPRA Technology: Shrewsbury, UK, 2004; ISBN 9781859574447.
19. Almeida, L. (Ed.) *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*; Woodhead Publishing: Cambridge, UK, 2015; ISBN 978-0-85709-845-0.
20. Cherif, C. (Ed.) Textile Werkstoffe für den Leichtbau. In *Techniken, Verfahren, Materialien, Eigenschaften*; Springer: Berlin/Heidelberg, Germany, 2011; ISBN 978-3-642-17992-1.
21. Van de Velde, K.; Baetens, E. Thermal and Mechanical Properties of Flax Fibres as Potential Composite Reinforcement. *Macromol. Mater. Eng.* **2001**, *286*, 342–349. [CrossRef]
22. Busse, W.F.; Lessig, E.T.; Loughborough, D.L.; Larrick, L. Fatigue of Fabrics. *J. Appl. Phys.* **1942**, *13*, 715–724. [CrossRef]
23. Muralidhar, B.A. Study of flax hybrid preforms reinforced epoxy composites. *Mater. Des.* **2013**, *52*, 835–840. [CrossRef]
24. Yan, L.; Chouw, N.; Jayaraman, K. Effect of UV and water spraying on the mechanical properties of flax fabric reinforced polymer composites used for civil engineering applications. *Mater. Des.* **2015**, *71*, 17–25. [CrossRef]
25. Akin, D.E.; Dodd, R.B.; Perkins, W.; Henriksson, G.; Eriksson, K.-E.L. Spray Enzymatic Retting: A New Method for Processing Flax Fibers. *Text. Res. J.* **2000**, *70*, 486–494. [CrossRef]
26. Kim, S.; Kim, J.; Lim, S.H.; Jo, W.H.; Choe, C.R. Effects of mixing temperatures on the morphology and toughness of epoxy/polyamide blends. *J. Appl. Polym.* **1999**, *72*, 1055–1063. [CrossRef]
27. Le Gall, M.; Davies, P.; Martin, N.; Baley, C. Recommended flax fibre density values for composite property predictions. *Ind. Crop Prod.* **2018**, *114*, 52–58. [CrossRef]
28. Shi, X.; Fernando, B.M.D.; Croll, S.G. Concurrent physical aging and degradation of crosslinked coating systems in accelerated weathering. *J. Coat. Technol. Res.* **2008**, *5*, 299–309. [CrossRef]
29. Behazin, E.; Rodriguez-Uribe, A.; Misra, M.; Mohanty, A.K. Long-term performance of β-nucleated toughened polypropylene-biocarbon composites. *Compos. Part A-Appl. S.* **2018**, *105*, 274–280. [CrossRef]
30. Shu, Y.; Ye, L.; Yang, T. Study on the long-term thermal-oxidative aging behavior of polyamide 6. *J. Appl. Polym. Sci.* **2008**, *110*, 945–957. [CrossRef]
31. Wright, D.C. *Failure of Polymer Products Due to Thermo-Oxidation*; Rapra Technology Limited: Shrewsbury, UK, 2001; ISBN 9781859572719.
32. Jubinville, D.; Abdelwahab, M.; Mohanty, A.K.; Misra, M. Comparison in composite performance after thermooxidative aging of injection molded polyamide 6 with glass fiber, talc, and a sustainable biocarbon filler. *J. Appl. Polym.* **2020**, *137*, 48618. [CrossRef]
33. Chang, B.P.; Mohanty, A.K.; Misra, M. Sustainable biocarbon as an alternative of traditional fillers for poly(butylene terephthalate)-based composites: Thermo-oxidative aging and durability. *J. Appl. Polym. Sci.* **2019**, *136*. [CrossRef]