Mechanical and Thermal Properties of Electrospun PMIA Nanofibers Reinforced PLA Composites

Bin HE [*], **Chao LIU**, **Zexing WANG**

Institute of Textile and Fashion, Hunan Institute of Engineering, Xiangtan, Hunan, 411104, China

The well-aligned electrospun Poly (mphenylene isophthalamide) (PMIA) nanofibers reinforced Polylactic acid (PLA) composites is fabricated via hot-pressing. Scanning electron microscopy (SEM), differential scanning calorimeter/thermal gravimetric analyser (DSC-TGA) and Dynamic Mechnical Analysis (DMA) are used to characterize morphologies of the broken sections and properties of composites. The results show that the tensile breaking strength and initial modulus have been enhanced much compared to that of pure PLA. The remarkable improvement emerges at the load 38 wt.% of nanofibers with the tensile strength and initial modulus increase by ca. 235 % and ca. 149 %, respectively. The hot-press process did not damage the nanofibers figuration and there are appear cracks link together with nanofibers by increasing the nanofiber contents. The initial degradation temperature of nanofibers reinforced composites are lower than that of pure PLA, but the final residual rate of composites increases with the increase of nanofibers mass fraction. Both the storage modulus and loss modulus of the composites increased with the addition of PMIA nanofibers. The addition of 38 wt.% of nanofibers yields an increase of the storage modulus ca. 11 % and the loss modulus ca. 13 % at 40 °C.

Keywords: electrospinning, nanofibers, composites, mechanical properties, thermal properties.

1. INTRODUCTION

The fiber-reinforced composites are very appropriate for high-performance components due to their excellent structural properties such as high strength-to-weight and stiffness-to-weight ratios, and the ability in providing both mechanical as well as functional performances [1, 2]. At present, there have been increasing needs for light-weight materials in emerging mechanical and thermal properties, which can be used in aeronautics, vehicles, civil engineering and various structural applications [1, 3]. In the development of light-weight materials, polymeric composites have received considerable attention [4, 5].

Nanofibers have a large specific surface area, high aspect ratio and other attractive multifunctional properties compared to conventional microfibers, they can provide more interaction between reinforcing fibers and polymer matrix and enables the applied load to be transferred on fibers-matrix interface, and lead to an improvement on the properties of the composites [6, 7]. Electrospinning technique is a flexible and effective way to produce nanofibers with high speed, simple device and low cost [8 – 10].

In recent years, the use of electrospun nanofibers as reinforcements in polymeric composites has drawn people's attention [11 – 16]. Among them, Kim et al. [11] have estimated the reinforcing effects of electrospun polybenzimidazole (PBI) nanofibers in both epoxy and rubber matrices. They found that the PBI nanofibers toughened the brittle epoxy resin with higher fracture toughness and elastic moduli of 15 wt.% nanofibers reinforced epoxy composites as compared to those of

composite counterparts of 17 wt.% PBI fibrids. Uyar et al. [12] used electrospun polyvinylalcohol (PVA) to reinforce the Polymethylmethacrylate (PMMA) composites resins, and theirs results indicated that the mechanical properties of PMMA composites were improved, and the improvement was higher when aligned PVA nanofibers were used. The maximum values were 5.1 MPa (flexural strength), 0.8 GPa (elastic modulus), and 170 kJ·m^{-3} (toughness) in three-point bending test. Tang et al. [13] used the electrospun cellulose to reinforce PVA composites, they found that the nanofibers had improved the composites of tensile strength and Young's modulus by 50 % and 600 %, respectively, with an optimal fiber content of 40 wt.%. Chen et al. [14] have used the well-aligned electrospun polyimide (PI) nanofibers containing carbon nanotubes (CNTs) as reinforcement to heighten the tensile strength and toughness of PI films. Compared with pure PI film prepared by solution casting, the tensile breaking strength and elongation at break in the PI film reinforced with CNTs/PI nanofibers were strikingly increased by 138 % and 104 %, respectively.

Poly (mphenylene isophthalamide)(PMIA) has especially prominent thermo-stability, high flame retardant and mechanical properties, etc [17]. Our group successfully prepared PMIA nanofibers with excellent morphology and mechanical properties via electrospinning [18], and following the previous work, well-aligned electrospun PMIA nanofibers were fabricated [19]. Polylactic acid (PLA) is a thermoplastic, bio-degradable and renewable polymer, which is industrially obtained respectively, through the polymerization of lactic acid or by the ringopening polymerization of lactide. The PLA is regarded as one of popular biopolymers which has gained enormous attention as an alternative to petrochemical-based synthetic polymers in packaging and textile sectors

---

[*] Corresponding author. Tel.: +8618973289695.
E-mail address: *hb126_b@163.com* (B. He)

and engineering at present. The production of PLA composites is realized using the following techniques mainly: (a) melt-compounding, (b) solvent-based, (c) pultrusion, (d) co-extrusion (fibers, films, sheets), (e) hot pressing (film stacking). Among them, techniques of (c), (d) and (e) are usually used to produce fiber reinforced PLA composites [20 – 22]. Okubo et al [23] have studied the process and properties of PLA nanocomposites, the microfibrillated cellulose (MFC) reinforced PLA composites were processed and they found that the addition of 1 and 2 wt.% of MFC had a positive impact on the modulus as well as on composites' fracture energy with the maximum improvement of modulus by 31 % and the fracture energy by almost 200 %, but the strength did not show any improvements. Haafiz et al [24] have prepared PLA composites filled with microcrystalline cellulose (MCC) through solution casting. They reported that the T_{50} decomposition temperature of the composites improved with addition of MCC which showed increase in thermal stability of the composites. The Young's modulus increased by about 30 %, while the tensile strength and elongation at break for composites decreased with addition of MCC. Niu et al [25] have used rosin modified cellulose nanofiber (R-CNF) to reinforce PLA matrix which was the coated with chitosan (CHT) to prepare a two-layer composite film. The Young's modulus of the composite film reached 962 MPa with 8 % R-CNF, which was 1.498 times higher than that of neat PLA/CHT film.

In this paper, well-aligned electrospun PMIA nanofibers were fabricated, which have been used to reinforce the PLA matrix by layer-by-layer by using the hot-pressing. The effects of the PMIA nanofibers reinforced PLA composites on the tensile mechanical properties and morphologies of the broken sections and the thermal properties and the dynamic thermal mechanical properties were investigated in detail.

2. EXEERIMENTAL DETAILS

2.1. Materials

Commercial PMIA fibers (tensile breaking strength was ca. 4.5 cN·dtex^{-1}, and density 1.37 – 1.38 g·cm^{-3}) were supplied by Yantai Spandex Co. Ltd. (China). PLA (PLLA, $\overline{Mw} \approx 170000$) was provided by W. Wplastic Ningbo Co. Ltd. (China). Dimethylacetamide (DMAc) was purchased from J&K Scientific Co. Ltd. Anhydrous lithium chloride (LiCl) was purchased from Shanghai Jufeng Chemical Scientific Co. Ltd. (China). Dichloromethane was provided by Sinopharm Chemical Reagent Co., Ltd. (China). All the chemicals were of analytical reagent grade.

2.2. Preparation of electrospun nanofibers

Firstly, the spinning solution was prepared with the PMIA and LiCl in the solution were 12 wt.% and 6 wt.%, respectively. Then the well-aligned electrospun PMIA namofibers were fabricated via electrospinning on the Nanofiber Electrospinning Unit (KATO TECH Co. Ltd., Japan). Spinning parameters were as follows: inner diameter of spinneret 0.45 mm, voltage 23 kV, collecting spinning distance 11 cm, solution flow rate 0.26 ml·h^{-1}, spinneret scan speed 14 cm·min^{-1}, collector rotating speed

6 m·min^{-1}. The detailed steps were described in our previous work [19].

2.3. Preparation of hot-pressed nanofibers reinforced composites

Firstly, the PLA was added into dichloromethane and stirred untill it was dissolved completely with the mass fractions of PLA is about 3 ~ 4 %, and followed 2 layers of the well-aligned PMIA nanofibers (50 mm × 40 mm) were laminated into the solution layer-by-layer. Then the solvent evaporated at room temperature and gained the prepregs. Then the prepregs were hot-pressed at the parameters of pressure as 1000 Pa, temperature as 180 °C, time as 30 min, and trimmed their sides carefully after cooling under the room temperature, as shown in Fig. 1. The composites obtained finally with the mass fractions of nanofibers in composites were controlled range from 0 % to 50 %.
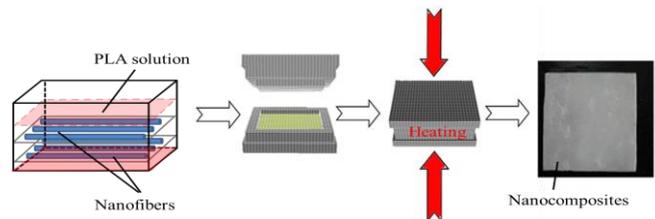

Fig. 1. The schematic diagram of composites forming

2.4. Measurements

The mechanical properties of the composites were tested by Instron 5967 mechanical testing machine with gauge length 20 mm, crosshead speed 20 mm·min^{-1}. The tensile test progressed along the axial (parallel to the aligned fibers) directions, and the sample was cut into dumbbells showed in Fig. 2. The tensile strength at breakage was calculated by the mean of 5 samples. All of the samples were conditioned in a laboratory environment (20 ± 1 °C and 65 ± 3 %) for 24 h before testing.
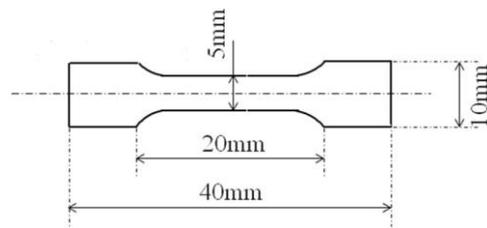

Fig. 2. The sample diagram of tensile test

The morphologies of the electrospun PMIA nanofibers and the morphologies of the broken sections of the composites after the tensile test were observed by scanning electron microscopy (SEM) (Hitachi S-4800, Japan). The mean diameter of fibers was measured by image analyzing system (Image-Pro Plus 5.0), and 100 measurements were taken, then the average value was calculated.

Thermal properties of the composites were evaluated by using an SDT Q600 simultaneous differential scanning calorimeter/thermal gravimetric analyser (DSC-TGA) instrument (TA Instruments, USA). The sample was ramped at 10 °C·min^{-1} from room temperature to 600 °C under a nitrogen atmosphere.

The Dynamic Mechnical Analysis (DMA) of the composites was measured by using the DMA Q800 instrument (TA Instruments, USA). The sample was ramped at 3 °C·min^{-1} from 30 °C to 240 °C with the test frequency of 1 Hz in stretch film test patter. The sample size is 36 mm × 6 mm.

3. RESULTS AND DISCUSSION

3.1. Nanofibers morphology

Fig. 3 and Fig. 4 show SEM image and the diameter distribution of the PMIA nanofibers. It is clearly that the nanofibers were uniform and well-aligned along the fiber axis. The average diameter of nanofibers is about 298.52 ± 53.58 nm.
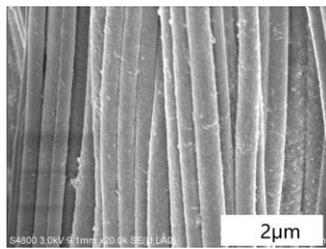

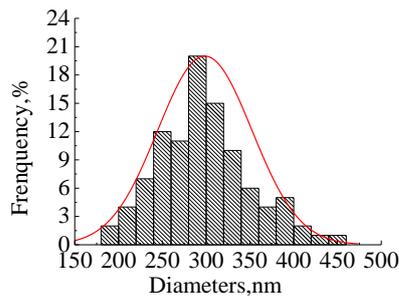**Fig. 3.** SEM image of the PMIA nanofibers

Fig. 4. Diameter distribution of the PMIA nanofibers

3.2. Mechanical properties

Fig. 5 and Table 1 show the mechanical properties of composites at different eletrospun PIA nanofiber contents. The thickness of the composites with different nanofiber contents of 0, 10, 23, 30, 38 and 49 wt.% were 0.293 ± 0.016, 0.206 ± 0.013, 0.235 ± 0.015, 0.268 ± 0.014, 0.296 ± 0.013 and 0.315 ± 0.016 mm, respectively. The results indicated that the tensile breaking strength and initial modulus had been enhanced much compared to that of pure PLA. The remarkable improvement emerges at the load 38 wt.% of nanofibers with the tensile breaking strength and initial modulus increased by ca. 235 % and ca. 149 %, respectively. There is a higher rate of increase of the tensile strength and the initial modulus of PMIA/PLA

composites comparing with some other reports [23 – 25] about PLA composites. The mechanical properties of fiber-reinforced composites. The mechanical properties of fiber-reinforced composites largely depend on stress transfer of fiber and matrix; the fibers undertake the main load during the tensile process. So the mechanical properties of composites increased with the increase of fiber content in a certain extent. However, when the fiber contents exceed a certain amount, the adhesion between the fiber and the matrix becomes worse due to the decrease of the mass fraction of the matrix, and even can arise the matrix poor area, which can lead to the emergence of matrix discontinuity. The stress transfer between the matrix and the fiber is disjointed, and the mechanical properties of the composites decrease. That is may be the reason to explain the tensile breaking strength and initial modulus of the composites decreased at the load 49 wt.% of nanofibers.
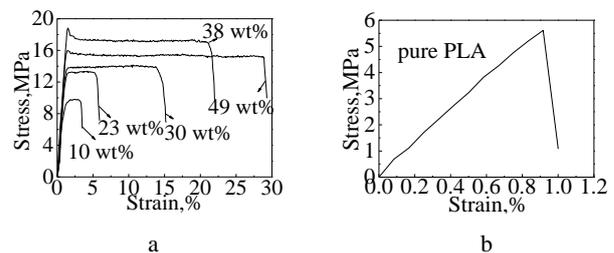

Fig. 5. Mechanical properties of composites: a – mass fractions of nanofibers range from 10 % to 50 %; b – pure PLA (0 wt.%)

3.3. Morphologies of the broken sections

Fig. 6 shows SEM images of the broken sections of the composites after the tensile test, the inserted image is the magnified parts. The nanofibers revealed excellent morphologies, which demonstrated that the hot-press process did not damage the nanofibers figuration. There is only a single neat fracture when tensile fracture occurs at the load 0, 10, 23 wt.% of nanofibers, and there are appears cracks link together with nanofibers by increasing the nanofiber contents of 33, 38, 49 wt.%. For the reason is that the bonding interface between nanofibers and matrix is increased by increasing the nanofiber contents, the nanofibers are not pulled or broken during the tensile process, which hinders the fracture formation from the crack, that is beneficial to the enhancement of tensile mechanical properties. For the load 49 wt.% of nanofibers, the number of slipped nanofibers increased because of the emergence of matrix poor area, and the matrix appears the fault phenomenon after the stretching, which further explains the reason for the decline on mechanical properties at the load 49 wt.% of nanofibers.

Table 1. Mechanical properties of the composites

Nanofiber contents, wt.%	0	10	23	30	38	49
Tensile breaking strength, MPa	5.61 ± 0.52	9.82 ± 1.15	13.32 ± 1.41	14.09 ± 1.69	18.77 ± 1.73	15.91 ± 1.97
Initial modulus, MPa	610.03 ± 63.75	720.60 ± 86.52	1306.77 ± 137.57	1426.27 ± 156.83	1517.25 ± 148.99	1372.03 ± 178376
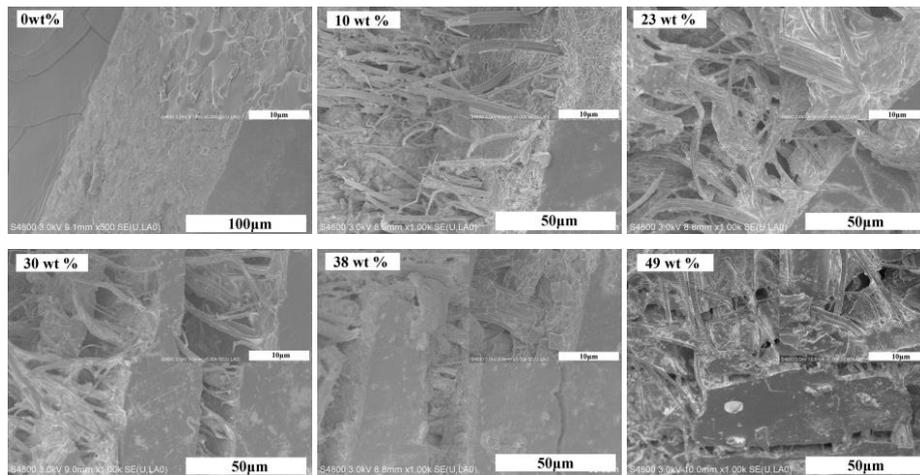
**Fig. 6.** SEM images of the broken sections of the composites after the tensile test

3.4. Thermal analysis

Fig. 7 shows DSC-TGA curves of the composites at different nanofiber contents. On DSC curve of pure PLA (0 wt.%), it can be seen that there are three endothermic peaks near 90 °C and 150 °C and 340 °C, which are caused by the volatilization of adsorbed water in PLA and by the melting of PLA and by the decomposition of PLA, respectively. There is significant mass loss take place from 250 °C to 400 °C correspond to the TGA curve. For the nanofibers reinforced composites, there are two peaks endothermic peaks near 90 °C and 150 °C as the same of pure PLA. The strong endothermic peak near 280 ~ 300 °C caused by PLA decomposition in addition to the release of crystal waters in PMIA nanofibers. The decomposition temperature of the composites is lower than that of pure PLA for the reason is that the LiCl attached to the PMIA nanofibers has high water absorbing ability, and water molecules can promote the fracture of PLA ester bond, which brings the accelerated thermal degradation of PLA. The initial degradation temperature of nanofibers reinforced composites are also lower than that of pure PLA showed on TGA curves. The endothermic peak near 370 °C may be caused by thermal decomposition of PMIA. The TGA curves show that the final residual rate of composites increases with the increase of nanofibers mass fraction. This is because that the PLA has been degraded at the temperature lower than 400 °C and only the thermal degradation of PMIA occurs at a temperature range of 400 ~ 600 °C.

3.5. Dynamical mechanical analysis (DMA)

The dynamic thermal mechanical properties of composites are depicted in Fig. 8. The results indicated that both the storage modulus and the loss modulus of the composites increased with the addition of PMIA nanofibers. The addition of 38 wt.% of nanofibers yielded an increase of the storage modulus ca. 11 % and the loss modulus ca. 13 % at 40 °C. This behavior can be explained in terms of interfacial interactions between the PMIA nanofibers and PLA matrix [26].
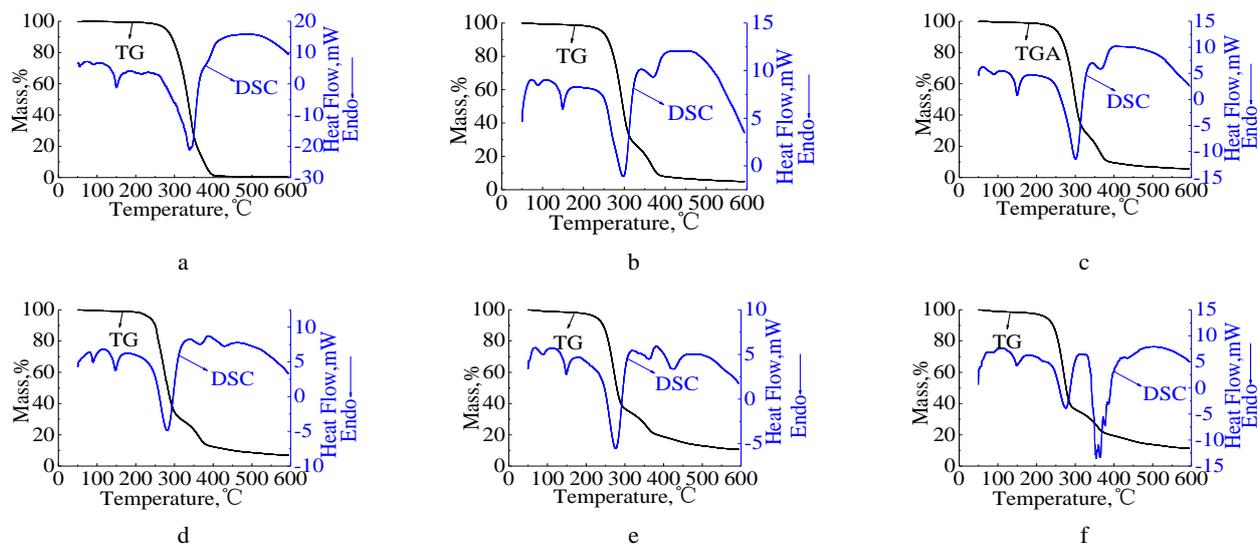
Fig. 7. TGA-DSC curves of the composites at different nanofiber contents: a – pure PLA; b – 10 wt.%; c – 23 wt.%; d – 30 wt.%; e – 38 wt.%; f – 49 wt.%

Both the storage modulus and loss modulus of pure PLA are reduced to zero due to the PLA macromolecule chain are in a state of completely free movement when over 150 °C, while there are the existence of storage modulus and loss modulus in composites because of the PMIA nanofibers are withstand stress in the same condition.
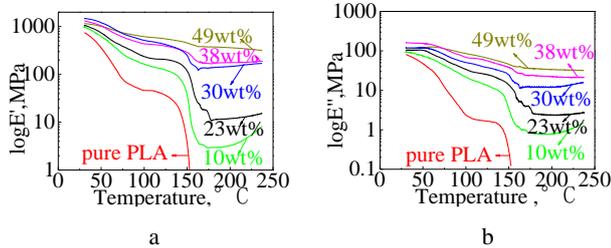
Fig. 8. The dynamic thermal mechanical properties of composites
a – storage modulus (E'); b – loss modulus (E")

4. CONCLUSIONS

Well-aligned PMIA nanofibers with the average diameter about 298.52 ± 53.58 nm were fabricated via electrospinning, which had been used to reinforce the PLA matrix by layer-by-layer via hot-pressing. The results showed that the tensile breaking strength and initial modulus had been enhanced much compared to that of pure PLA. The remarkable improvement occurs at the load 38 wt.% of nanofibers with the tensile strength and initial modulus increased by ca. 235 % and ca. 149 %, respectively. The broken sections of the composites after the tensile test showed that the hot-press process did not damage the nanofibers figuration. There is only a single neat fracture when tensile fracture emerges at the load 0, 10, 23 wt.% of nanofibers, and there are appear cracks link together with nanofibers by increasing the nanofiber contents of 30, 38, 49 wt.%. The initial degradation temperature of nanofibers reinforced composites are lower than that of pure PLA, but the final residual rate of composites increases with the increase of nanofibers mass fraction. Both the storage modulus and loss modulus of the composites increased with the addition of PMIA nanofibers. The addition of 38 wt.% of nanofibers yielded an increase of the storage modulus ca. 11 % and the loss modulus ca. 13 % at 40 °C.

REFERENCES

1. **Mohammadzadehmoghadam, S., Dong, Y., Davies, I.J.** Recent Progress in Electrospun Nanofibers: Reinforcement Effect and Mechanical Performance *Journal of Polymer Science Part B Polymer Physics* 53 (17) 2015: pp. 1171 – 1212.
https://doi.org/10.1002/polb.23762

2. **Asmatulu, E., Twomey, J., Overcash, M.** Recycling of Fiber-Reinforced Composites and Direct Structural Composite Recycling Concept *Journal of Composite Materials* 48 (5) 2014: pp. 593 – 608.
https://doi.org/10.1177/0021998313476325

3. **Song, W.L., Veca, L.M., Anderson, A., Cao, M.S., Cao, L., Sun, Y.P.** Light-weight Nanocomposite Materials with Enhanced Thermal Transport Properties *Nanotechnology Reviews* 1 (4) 2012: pp. 363 – 375.
https://doi.org/10.1515/ntrev-2012-0023

4. **Paul, D.R., Robeson, L.M.** Polymer Nanotechnology: Nanocomposites *Polymer* 49 (15) 2008: pp. 3187 – 3204.
https://doi.org/10.1016/j.polymer.2008.04.017

5. **Kim, H., Abdala, A.A., Macosko, C.W.** Graphene/Polymer NNanocomposites *Macromolecules* 43 (16) 2010: pp. 6515 – 6530.
https://doi.org/10.1021/ma100572e

6. **Schaefer, D.W., Justice, R.S.** How Nano are Nanocomposites? *Macromolecules* 40 (24) 2007: pp. 8501 – 8517.
https://doi.org/10.1021/ma070356w

7. **Lin, S., Cai, Q., Ji, J., Sui, G., Yu, Y., Yang, X., Ma, Q., Wei, Y., Deng, X.** Electrospun Nanofiber Reinforced and Toughened Composites Through in Situ Nano-interface Formation *Composites Science and Technology* 68 (15 – 16) 2008: pp. 3322 – 3329.
https://doi.org/10.1016/j.compscitech.2008.08.033

8. **Huang, Z.M., Zhang, Y.Z., Kotaki, M., Ramakrishna, S.** A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites *Composites Science and Technology* 63 (15) 2003: pp. 2223 – 2253.
https://doi.org/10.1016/S0266-3538(03)00178-7

9. **Angammana, C.J, Jayaram, S.H.** Fundamentals of Electrospinning and Processing Technologies *Particulate Science and Technology* 34 (1) 2016: pp. 72 – 82.
https://doi.org/10.1080/02726351.2015.1043678

10. **Mirjalili, M., Zohoori, S.** Review for Application of Electrospinning and Electrospun Nanofibers Technology in Textile Industry *Journal of Nanostructure in Chemistry* 6 (3) 2016: pp. 1 – 7.
https://doi.org/10.1007/s40097-016-0189-y

11. **Kim, J.S., Reneker, D.H.** Mechanical Properties of Composites using Ultrafine Electrospun Fibers *Polymer Composites* 20 (1) 2010: pp. 124 – 131.
https://doi.org/10.1002/pc.10340

12. **Uyar, T., Çökeliler, D., Doğan, M., Koçum, I.C., Karatay, O., Denkbaş, E.B.** Electrospun Nanofiber Reinforcement of Dental Composites with Electromagnetic Alignment Approach *Materials Science and Engineering C* 62 2016: pp. 762.
https://doi.org/10.1016/j.msec.2016.02.001

13. **Tang, C., Liu, H.** Cellulose Nanofiber Reinforced Poly(vinyl alcohol) Composite Film with High Visible Light Transmittance *Composites Part A: Applied Science & Manufacturing* 39 (10) 2008: pp. 1638 – 1643.
https://doi.org/10.1016/j.compositesa.2008.07.005

14. **Chen, D., Wang, R., Tjiu, W.W., Liu, T.** High Performance Polyimide Composite Films Prepared by Homogeneity Reinforcement of Electrospun Nanofibers *Composites Science and Technology* 71 (13) 2011: pp. 1556 – 1562.
https://doi.org/10.1016/j.compscitech.2011.06.013

15. **Chen, J., Li, X., Cui, W., Zou, J., Zou, B.** Fibrous Composites with Anisotropic Distribution of Mechanical Properties after Layer-by-Layer Deposition of Aligned

Electrospun fibers *Advanced Engineering Materials* 12 (9) 2010: pp. 529 – 538.
https://doi.org/10.1002/adem.200980079

16. **Li, B., Pan, S., Yuan, H., Zhang, Y.** Optical and Mechanical Anisotropies of Aligned Electrospun Nanofibers Reinforced Transparent PMMA Nanocomposites *Composites Part A* 90 2016: pp. 380 – 389.
https://doi.org/10.1016/j.compositesa.2016.07.024

17. **Machalaba, N.N., Perepelkin, K.E.** Heterocyclic Aramide fibers – Production Principles, Properties and Application *Journal of Industrial Textiles* 3 2002: pp. 189 – 204.
https://doi.org/10.1101/152808302026484

18. **He, B., Li, J., Pan, Z.** Morphology and Mechanical Properties of MWNT/PMIA Nanofibers by Electrospinning *Textile Research Journal* 82 (13) 2012: pp. 1390 – 1395.
https://doi.org/ 10.1177/0040517512441990

19. **He, B., Tian, L., Li, J., Pan, Z.** Effect of Hot-Stretching on Morphology and Mechanical Properties of Electrospun PMIA Nanofibers *Fibers and Polymers* 14 (3) 2013: pp. 405 – 408.
https://doi.org/10.1007/s12221-013-0405-z

20. **Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lip, D., Ruffieux, K., Wintermantel, E.** Thermal and Mechanical Properties of Plasticized Poly(L-lactic acid) *Journal of Applied Polymer Science* 90 (7) 2003: pp. 1731 – 1738.
https://doi.org/10.1002/app.12549

21. **Auras, R., Harte, B., Selke, S.** An Overview of Polylactides as Packaging Materials *Macromolecular Bioscience* 4 (9) 2004: pp. 835 – 864.
https://doi.org/10.1002/mabi.200400043

22. **Murariu, M., Dubois, P.** PLA composites: From Production to Properties *Advanced Drug Delivery Reviews* 107 2016: pp. 17 – 46.
https://doi.org/10.1016/j.addr.2016.04.003

23. **Okubo, K., Fujii, T., Thostenson, T.** Multi-scale Hybrid Biocomposite: Processing and Mechanical Characterization of Bamboo Fiber Reinforced PLA with Microfibrillated Cellulose *Composites Part A* 40 (4) 2009: pp. 469 – 475.
https://doi.org/10.1016/j.compositesa.2009.01.012

24. **Haafiz, M.K., Hassan, A., Zakaria, Z., Inuwa, I.M.** Properties of Polylactic Acid Composites Reinforced with Oil Palm Biomass Microcrystalline Cellulose *Carbohydrate Polymers* 98 (1) 2013: pp. 139 – 145.
https://doi.org/10.1016/j.carbpol.2013.05.069

25. **Niu, X., Liu, Y., Song, Y., Han, J., Pan, H.** Rosin Modified Cellulose Nanofiber as a Reinforcing and Co-Antimicrobial Agents in Polylactic Acid /Chitosan Composite Film For Food Packaging *Carbohydrate Polymers* 183 2018: pp. 102 – 109.
https://doi.org/10.1016/j.carbpol.2017.11.079

26. **Gabr, M.H., Phong, N.T., Okubo, K., Uzawa, K., Kimpara, I., Fujii, T.** Thermal and Mechanical Properties of Electrospun Nano-cellulose Reinforced Epoxy Nanocomposites *Polymer Testing* 37 (8) 2014: pp. 51 – 58.
https://doi.org/10.1016/j.polymertesting.2014.04.010