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Wood Flour treated with Pickering Emulsion Could Improve its Composites with High-Density Polyethylene?

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Abstract: Silica synergistically stabilized paraffin Pickering emulsion is applied to modify wood flour (WF) for preparing wood/polymer composites. The effect of Pickering emulsion on properties of the WF and its composites with high-density polyethylene (HDPE) is investigated. The impregnation of paraffin Pickering emulsion could significantly improve the WF dispersion in HDPE matrix, resulting in increased melt flow index (MFI). It increased from 1.3 g/10 min (control) to 2.1 g/10 min (Pickering treatment) due to the lubrication of paraffin and rolling friction provided by silica nanoparticles. Owing to the well distribution of WFs and silica, the mechanical properties of the composites were enhanced obviously. The optimal tensile strength and impact strength increased 23% (18.28 MPa) and 32% (14.16 kJ/m^2), respectively. It also could be attributed to the improved interfacial compatibility due to the incorporation of surfactants (Span 80 and Tween 80), which acted as a coupling agent.

Keywords: paraffin Pickering emulsion; wood flour treatment; high-density polyethylene; wood/polymer composites; properties analysis

1. Introduction

Wood flour, as the reinforcement in polymer matrix, has considerable interest in wood/polymer composites (WPCs) fabrication due to its advantages, such as biodegradability, renewability, and low cost [1-3]. As a promising alternative for nature wood, WPCs have gained increased recognition in various applications owing to their higher dimensional stability, water resistance, and fungus resistance [4,5]. However, the large amount of hydroxyl groups on the WF makes its surface incompatible with nonpolar polymers, resulting in inferior properties of the composites. In addition, the hydrophilic surface is responsible for WFs aggregation via hydrogen bonding, which causes poor fiber dispersion in the polymer matrix [6]. As a result, the incompatibility and aggregation of WFs produce negative effects on most properties of the composites, such as poor mechanical properties, higher water absorption, and shorter service life. Recently, to overcome these defects, the development of various chemical agents and additives has been applied in WF modification, such as silanes (coupling agent), isocyanates, and organo-montmorillonite [7,8]. However, it is difficult to solve some problems simultaneously and effectively due to the complex system of the composites.

To improve the compatibility between the WF and polymer, most researchers agreed that the surface property of the WF was a significant factor that could affect the fiber-polymer interaction and change the final properties of the composites [9,10]. The coupling agent is a reagent containing both polar and nonpolar groups that acts as a "bridge" to combine the WF and polymer together, resulting in a compatible interface. However, the effect of the coupling agent varies greatly when different polymers are applied [11]. Consequently, the surface modification of WFs is a useful approach to replace or consume the hydroxyl groups on WFs, resulting in better interfacial compatibility between fillers and polymers. These modification techniques include esterification, resin impregnation, WF components extraction, and heat treatment [12,13]. Except for these modifications, surface coating with hydrophobic materials is also a useful method to block inter-bonding between WFs. On the other hand, to further improve the dispersion of WFs in the polymer matrix, appropriate additives are used during WPCs preparation, such as stearic acid, sodium silicate, and mineral oil [14]. However, simultaneously with the positive influence on the WF dispersion, the incorporation of some additives like stearic acid can lead to a decrease in melt flow index (MFI) of the composites [15]. It results in decreased mobility of polymer chains at the interface and shows negative effects on flow behavior of the composites, which is disadvantageous in improving the interfacial compatibility.

Owing to the amphiphilicity, Span and Tween are normal surfactants that can improve the compatibility between hydrophobic and hydrophilic materials [16]. As another candidate, owing to the low cost and hydrophobicity, paraffin is an efficient additive used as a dispersing agent or lubricant in WPCs preparation to reduce agglomeration of fillers in the polymer matrix [17]. Additionally, nanoparticles have unique property in lubrication and tribology, such as anti-wear, reducing friction, and high load capacity [18]. Some investigations showed that the addition of nanoparticles to lubricant oil significantly improved the reducing-friction performance. Li et al. [19] used silane to modify silica nanoparticles and investigated their tribological properties. It showed that modified silica had good dispersion and stability in organic solvents with potential applications as lubrication additives. Peng et al. [20] found that oleic acid modified silica nanoparticles used as liquid paraffin additives had better tribological properties in terms of load-carrying capacity, anti-wear, and friction reduction. Therefore, it is promising to improve the WF dispersion in polymer matrix by addition of nano-silica and paraffin.

The basic idea of the present research is to combine the useful modifiers in the form of Pickering emulsion, which is rarely reported for preparing wood/polymer composites. In our previous study, paraffin Pickering emulsion was successfully prepared and used for solid wood treatment [21]. The silica and paraffin provided a synergistic positive effect on hydrophobicity, surface hardness, and mechanical properties of treated wood. Therefore, the emulsion components could also provide synergistic and positive effects on interfacial compatibility and WFs dispersion in polymer matrix. Pickering emulsion is an emulsion stabilized by solid particles, in which traditional surfactants should be substituted or partially substituted by solid particles. Such kinds of emulsions can be formed in the case of oil-in-water (O/W), water-in-oil (W/O), or multiple emulsions. Compared with emulsions stabilized by surfactants via reducing the O/W interfacial tension, solid particles stabilize the oil droplets by providing a steric barrier at the interface [22]. Silica nanoparticles are widely applied in stabilizing Pickering emulsion. The particles should be partially wetted by both the water and oil phases for an effective emulsification. Due to the hydrophilic surface of the pure silica, the partially hydrophobic silica surface should be obtained by grafting or absorption of non-polar organic groups [23]. For wood or WF modification, silica is an environmentally-friendly modifier with various positive effects [24]. Incorporating silica nanoparticles into polymer-based composites, could improve the flexural strength, impact strength, and surface hardness of WPCs [25].

Herein, hydrophilic silica nanoparticles were used as solid stabilizers for stabilizing paraffin Pickering emulsion. Span and Tween were added as emulsion stabilizers to help the adsorption of silica at oil/water interface. They were also viewed as compatibilizers to improve the compatibility between fillers and polymer matrix. WFs were impregnated by the emulsions with or without silica stabilizers. The effect of Pickering emulsion on the properties of WFs was determined by scanning electron microscope (SEM) combined with energy-dispersed X-ray analysis (SEM-EDXA), and the moisture adsorption. Additionally, the melt flow index (MFI) was measured to evaluate the WF dispersion in the polymer matrix. Furthermore, to clarify the influence of paraffin Pickering emulsion on properties the composites, the overall performances were determined by water absorption (WA), and mechanical properties. The main purpose of this study was to characterize the properties of the treated WF and its composites, and to determine whether or not the paraffin Pickering emulsion could enhance the properties of WPCs.

2. Experiments

2.1. Materials

The WFs of poplar (*Populus tomentosa Carr.*) were collected from wood sawdust with a mesh size of 10–60. They were oven-dried at 103 °C for 48 h to a consistent weight. The HDPE (0.95 $g \cdot cm^{-3}$) was provided by Sinopec Yangzi Petrochemical Co., Ltd, Nanjing, China. The liquid paraffin (purity is higher than 99%), Tween 80 (HLB = 15), and Span 80 (HLB = 4.3) were provided by Beijing Chemical Ltd., Beijing, China. Hydrophilic silica particles (Degussa AG, Frankfurt, Germany) were delivered in powder form with specific surface area 220–300 $m^2 \cdot g^{-1}$ and 20–30 nm particle size.

2.2. Pickering Emulsion Preparation and WFs Treatment

The method applied to prepare paraffin Pickering emulsion can be found in our previous study [21]. Silica dispersion with 0.5 wt % concentration (based on water mass) was prepared at pH = 3–4 condition adjusted by 0.1 $mol \cdot L^{-1}$ HCl solution. Tween 80 (1.5 wt %) and Span 80 (1.3 wt %) were added into the silica dispersion and gently stirred at a speed of 500 rpm for 1 min. Then, the oil phase (liquid paraffin; 1:5 by vol) was added into the mixture and pre-emulsified at 5000 rpm for 5 min. Afterwards, the pre-emulsion was further treated at 45 MPa for 5 min in the high-pressure homogenizer. WFs were first placed into a beaker in a treating tank and vacuum was applied at 0.01 MPa for 30 min. Then, WFs were completely submerged into Pickering emulsion and pressurized at 0.6 MPa for 40 min. Thereafter, the treated WFs were taken out and dried in an oven at 103 °C to a constant weight. Furthermore, the paraffin emulsion stabilized by only Tween 80 and Span 80 was prepared for WFs treatment. The WFs treated by different emulsion systems were labeled as Pickering emulsion treatment and Paraffin emulsion treatment, respectively.

2.3. WF/HDPE Composites Fabrication

The WF/HDPE composites contained 40 wt % of untreated or emulsion treated WFs and 60 wt % HDPE. They were blended in a high-speed mixer (SHR-10a, Huaming Machinery Co., Zhangjiagang, China) at a rotating speed of 3000 rpm for 5 min. The mixture was then dried at 103 °C for 2 h and extruded using a counter-rotating twin-screw extruder (HTY-30, Rubber Machinery Factory Co., Nanjing, China). The corresponding temperature profile along the extruder barrel was 100 °C/115 °C/120 °C/125 °C/125 °C/135 °C/150 °C/150 °C, respectively, and the screw speed was 32 rpm. The extrudate was granulated using a chipper. Thereafter, the granules were injection-molded into standard mechanical test specimens with 175 °C injection temperature and 5 MPa extrusion pressure. The density of the composites was 0.86 $g \cdot cm^{-3}$.

2.4. Analytical Methods Applied

The morphologies of untreated and treated WFs as well as the impact fracture surface of the composites were observed by SEM analysis (S-3400, Hitachi, Tokyo, Japan, 10 kV). The samples were sputter-coated with gold prior to observation. EDXA (7021-H, Horiab, Kyoto, Japan) was performed in mapping mode with an accelerating voltage of 15 kV and 10 nA. The images and distribution of Si element, which was mainly from silica for the Pickering emulsion treated WF, were captured digitally for further analysis.

Prior to the moisture adsorption test, all the WF samples were dried in an oven at 103 °C until they reached a constant weight. Untreated and emulsion treated WFs with 2 ± 0.01g were placed in a tinfoil box and then kept in desiccators with distilled water at 25 °C for 30 days. The weights of the WFs were recorded periodically, and the moisture adsorption value was calculated to evaluate the hydrophobicity of WFs. For analyzing the WF dispersion in HDPE matrix, melt flow index (MFI) was measured according to ASTM D 1238 with a loading of 2.16 kg at 190 °C. The capillary diameter was 2.08 mm. The water absorption of WF/HDPE composites were carried out according to the Chinese standard GB/T 17657-2013. Four samples with the size of $50 \times 50 \times 4$ mm^3 were completely immersed in water at 20 ± 2 °C. The water absorption was calculated based on the weight percent gains after 6, 24, and 48 h, and thereafter at 48 h intervals with removing of excess water on the surface. Thermogravimetric analysis was conducted to determine the thermal stability of the composites. The samples (*appr.* 6 mg) were placed in open Pt-crucibles (TG 300, Seiko Instruments, Chiba, Japan) and heated from 30 to 600 °C at 10 °C·min^{-1} in N_2 atmosphere.

The flexural tests were carried out according to the Chinese standard GB/T 9341-2000, which involves a three-point bending test at a speed of 1 mm.min^{-1}. The size of the samples was $80 \times 10 \times 4$ mm^3. Six samples of each group were tested in each run. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated to evaluate the flexural properties. The tensile strength (TS) tests were carried out according to the Chinese standard GB/T 1040-1992 at a speed of 2 mm.min^{-1}. The size of the samples was $150 \times 10 \times 4$ mm^3. Six specimens of each group were tested for standard deviations. The impact strength (IS) tests were carried out according to Chinese standard GB/T 16420-1996. Six replicates with the size of $80 \times 10 \times 4$ mm^3 were tested for each group.

3. Results and discussion

3.1. Microstructure of WFs

The average value of weight percentage gain of WFs after treatment was around 18%, indicating the emulsion could be successfully impregnated into WFs. Figure 1 illustrates the morphologies of untreated and treated WFs. For untreated WFs (Figure 1a), some fiber protrusions were observed. After paraffin emulsion impregnation, all specimens displayed smooth surfaces due to the coverage of paraffin (Figure 1b). After Pickering emulsion treatment (Figure 1c and d), some continuous layers of silica could be found on the surface of cell lumens (Figure 1e and f). This indicated that silica could exist like a continuous film and uniformly covered the WF surface rather than existing as separate particles. This was because the presence of liquid paraffin and surfactants adsorption on the silica surface. These two modifiers could be treated as a medium and compatibilizer, respectively, to improve the silica mobility on the WF surface. On the other hand, some silica particles could fill the pores in WFs (Figure 1d) and consume the –OH groups in WFs with hydrogen bonding, which could improve the hydrophobicity of WFs. This was also detected by others [21, 24].

The Si distribution images demonstrated whether the silica particles were deposited in the cell wall or not. Compared with untreated and paraffin emulsion treated WFs (Figure 2a and b), the presence of Si was obvious on the cross section of WFs treated by Pickering emulsion (Figure 2c and f). That is, the silica particles were not only in the cell lumens, but also penetrated into the cell wall. It is beneficial for improving properties of the WF as well as its composites. Compared with untreated WFs (Figure 2d), for paraffin emulsion treated WFs, almost no Si distribution could be found (Figure 1e and Figure 2e), indicating the successful coverage of paraffin on the internal surface of WFs.

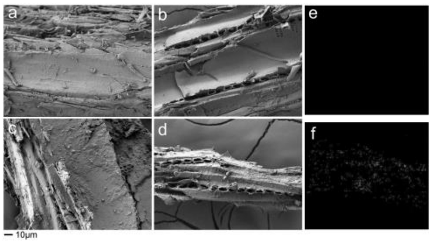

Figure 1. SEM and EDXA images of untreated and emulsion treated WFs. (**a**) without treatment; (**b**) paraffin emulsion treatment; (**c**) and (**d**) Pickering emulsion treatment; (**e**) Si distribution of (**b**); (**f**) Si distribution of (**d**).

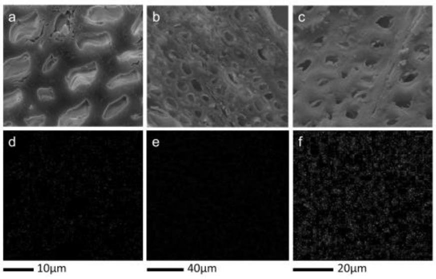

Figure 2. SEM and EDXA images of cross sections of untreated and emulsion treated WFs. (**a**) and (**d**) without treatment; (**b**) and (**e**) paraffin emulsion treatment; (**c**) and (**f**) Pickering emulsion treatment.

3.4. MFI Analysis

Generally, the higher value of MFI makes polymers flow well around the fillers and it can improve fillers distribution in the polymer matrix, as a result, promoting the interfacial interaction [26]. The MFI values of all samples are shown in Figure 3. Obviously, the MFI value decreased from 2.3 g/10 min (HDPE) to 1.3 g/10 min with the addition of untreated WFs, suggesting the untreated WFs induced inferior mobility. This was because of the rough and hydrophilic surface of WFs (Figure 1a), which might cause WF agglomeration in polymer matrix. However, with the addition of paraffin emulsion treated WFs and Pickering emulsion treated WFs, the MFI value of the mixture increased again. This phenomenon could be explained from two aspects. (1) The paraffin could be viewed as a lubricant, decreasing the friction on the interfaces between WFs and HDPE matrix. (2) The coverage and penetration of paraffin in WFs could improve the hydrophobicity of WFs. It would improve the interfacial compatibility between WFs and HDPE in some extent, resulting in the better dispersion of WFs in HDPE matrix. Both decreased the viscosity of treated WF/HDPE mixture and facilitated the fillers dispersion and mobility in the mixture.

Interestingly, the Pickering emulsion treated WF/HDPE mixture showed the optimal flow behavior. It could be ascribed to the rolling friction between WFs and HDPE matrix, due to the presence of nano-silica film on the WF surface. As seen in Figure 1c, a continuous film uniformly covered the WF surface, which was formed by silica and liquid paraffin. This surface protective film could be viewed as a physical tribo film that could change the sliding friction to mixing of sliding and rolling friction, resulting in reduced friction and improved mobility of the mixture. Similar phenomenon was found in the study where the nanoparticles were added in lubricant [27].

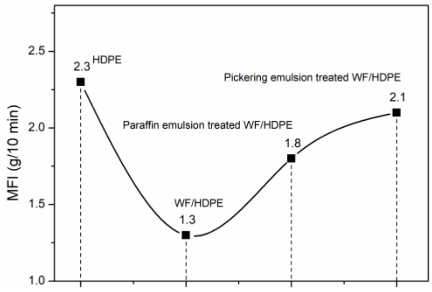

Figure 3. Melt flow index of high-density polyethene (HDPE) and WF/HDPE mixture.

3.5. WA of Composites

Natural fiber incorporation is mainly responsible for the high water absorption of the polymer-based composites. Compared with the control, the hydrophobicity was improved for the composites reinforced by emulsion treated WFs (Figure 4). The WA decreased clearly from 7.74% (control) to 5.83% (Pickering emulsion treatment). This could be due to the barrier effect of paraffin and the filling effect of silica nanoparticles, inhibiting the water absorption and penetration. Notably, in the range from 0 to 24 h, the WA values of the composites with Pickering pre-treatment were bigger than that of the composites with paraffin emulsion pre-treatment. After that, the value for the former increased slowly. This might be attributed to the exposure of some hydroxyl groups on the silica surface, providing some sites for water-uptake in the initial stage. However, after 24 h immersion, the pore-filling effect of silica dominated the water absorption, namely, it could further prevent the water penetration with the help of paraffin. It also suggested that the better mobility of the liquid paraffin and the nano-sized silica allowed them to diffuse deeply in the WFs, which led to more complete filling of cavities and blocking of hydroxyl groups.

Importantly, the well dispersion of emulsion treated WFs and better interfacial compatibility provided conditions for the improvement on hydrophobicity. It was reported that a well-dispersed mica silicate/poly(e-caprolactone) composite showed reduction in water vapor permeability compared to pure polymers [28]. These results confirmed our previous assumption that paraffin could be used as a dispersing agent to reduce WFs agglomeration and to construct the hydrophobic barrier in the WF, while the silica nanoparticles filled the pores in WFs or interfaces between WFs and polymer matrix to prevent the water penetration.

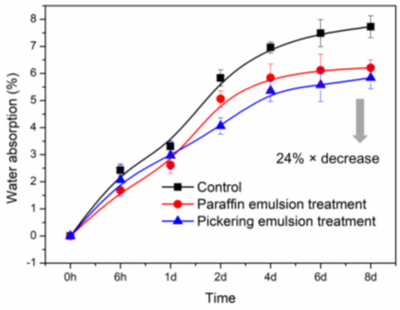

Figure 4. Water absorption of untreated (control) and emulsion treated WF/HDPE composites.

3.6. Mechanical Properties and Surface Hardness

The mechanical properties of WPCs are illustrated in Figure 5. Compared with the control, significant improvements were obtained after emulsion treatment. The tensile strength (TS) is more sensitive to matrix properties and the interface interaction, while the impact strength (IS) is a balance in properties between the matrix and fillers [29]. After Pickering emulsion treatment, the composites demonstrated a record value in TS (18.28 MPa), which increased by 23% compared with the control (14.84 MPa). However, the optimal IS value (14.16 kJ/m^2) was obtained from paraffin emulsion modification, which increased by 32% compared with the control (10.72 kJ/m^2). Impact strength depends largely on the polymer matrix ductility. It is the energy absorption capability during fracture, which represents the interfacial shear strength and bonding of composites. These results could be ascribed to two factors. (1) The liquid paraffin could help the WF to disperse well in polymer matrix. It could avoid WFs aggregation to form local stress concentration during loading, resulting in improved TS and IS. Moreover, paraffin acted as a lubricant to facilitate the polymer ductility. (2) The surfactants could improve the interfacial bonding that facilitated the transferring of impact energy to fillers and consumed the energy via shear friction at the interface. However, the silica nanoparticles have high thermodynamic surface energy and thus become easy to assemble together to reach a stable state [30]. Hence, for Pickering emulsion treatment, the local stress concentration caused by some silica aggregation could also form during loading, and a decrease was found in IS value compared with the one with paraffin emulsion treatment. A similar result was reported in the study, in which more nano-silica addition could induce decreased impact strength [19]. Additionally, the positive effects of paraffin on mechanical properties of wood should be considered, which have been claimed in the literature [31].

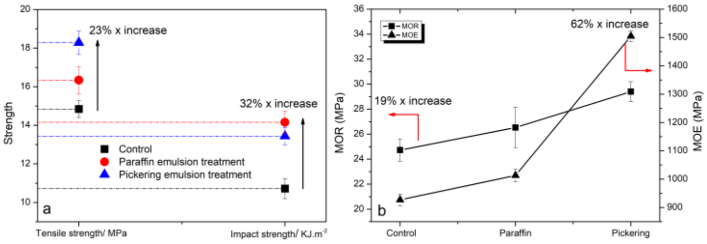

Figure 5. Mechanical properties of untreated (control) and emulsion treated WF/HDPE composites (**a**) tensile strength (TS) and impact strength (IS); (**b**) modulus of rupture (MOR) and modulus of elasticity (MOE)

The flexural properties of the polymer-based composites are affected by the properties of constituents and the interface interaction. Compared with the control, the modulus of rupture (MOR) and modulus of elasticity (MOE) for composites with Pickering emulsion pre-treatment increased by 19% (29.4 MPa) and 62% (1504 MPa), respectively. Generally, at a high level of WF dispersion, an improvement in strength of the composites could be observed. The penetration of the paraffin and silica in WFs reduced the friction between fillers and the polymer, which was determined by MFI tests, resulting in better mobility. Therefore, the increased WF dispersion contributed to the homogeneity of the composites, suggesting the smooth stress transfer during loading, providing enhanced mechanical properties. Moreover, the incorporation of the silica showed the reinforcement of flexural properties. The surfactants were interpreted as the interfacial coupling agent between the silica and HDPE matrix. It could cause effectively stress transfer from matrix to the stiff silica particles, resulting in improved flexural properties. A similar result was found in the study, in which silane modified mineral fillers were incorporated in WPCs [22,32].

4. Conclusions

The treatment of WFs with silica synergistically stabilized paraffin Pickering emulsion and its application in polymer-based composites were successfully conducted. The incorporation of paraffin acted as a lubricant and could result in greater dispersion of WFs in HDPE matrix, leading to reduced aggregation of WFs and improved interactions between fillers and polymer matrix. By changing the sliding frication to rolling frication, the silica nanoparticles played an important role in improving the mobility of WF/HDPE mixture. The adsorption of surfactants (Span 80 and Tween 80) on the silica or the WF surface could improve its dispersion in polymer matrix and interface compatibility between fillers and HDPE, which provided positive effects on the improvement of mechanical properties. The synergistically stabilized paraffin Pickering emulsion brought benefits from the hydrophobicity of paraffin, the nano-effect of silica particles, and the coupling effect of surfactants. Pre-treatment with paraffin Pickering emulsion shows the potential application in producing functional WPCs with a one-step method. Further developments should be explored, focusing on the effect of silica content on Pickering emulsion properties and its application in WPCs fabrication.

Author Contributions: J.J supervised and directed the projects. J.J. conceived and designed the experiments. J.J. performed the experiments and wrote the manuscript. C.M. and C.J provided the materials and improved the manuscript, respectively. All the authors reviewed the manuscript.

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1. Hosseinmardi, A.; Annamalai, P.K.; Wang, L.; Martin, D.; Amiralian, N. Reinforcement of natural rubber latex using lignocellulosic nanofibers isolated from spinifex grass. *Nanoscale* **2017**, *9*, 9510-9519.
2. Guo, Y.; Zhu, S.; Chen, Y.; Liu, D.; Li, D. Acoustic Emission-Based Study to Characterize the Crack Initiation Point of Wood Fiber/HDPE Composites. *Polymers*, **2019**, *11*, 701.
3. Nguyen, V.; Hao, J.; Wang, W. Ultraviolet weathering performance of high-density polyethylene/wood-flour composites with a basalt-fiber-included shell. *Polymers*, **2018**, *10*, 831.
4. Tian, S.; He, H.; Yu, P.; Zhou, L.; Luo, Y.; Jia, D. Sustainable utilization of waste printed circuit boards powders in HDPE-wood composites: Synergistic effects of multicomponents on structure and properties. *J. Clean. Prod.* **2017**, 164, 840-847.
5. Jiang, J.; Mei, C.; Pan, M.; Fei, Lu. Effects of hybridization and interface modification on mechanical properties of wood flour/polymer composites reinforced by glass fibers. *Polym. Compos.* **2019**, doi.org/10.1002/pc.25223.
6. Liu, R.; Chen, Y.; Cao, J. Effects of modifier type on properties of in situ organo-montmorillonite modified wood flour/poly (lactic acid) composites. *ACS Appl. Mater. Interfaces* **2015**, *8*, 161-168.
7. Wu, J.; Yu, D.; Chan, C.M.; Kim, J.; Mai, Y.W. Effect of fiber pretreatment condition on the interfacial strength and mechanical properties of wood fiber/PP composites. *J. Appl. Polym. Sci.* **2000**, *76*, 1000-1010.
8. Liu, R.; Luo, S.; Cao, J.; Peng, Y. Characterization of organo-montmorillonite (OMMT) modified wood flour and properties of its composites with poly (lactic acid). *Compos. Part A: Appl. Sci. Manuf.* **2013**, *51*, 33-42.
9. 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.
10. Liu, R.; Sun, W.; Cao J, Wang J. Surface properties of in situ organo-montmorillonite modified wood flour and the influence on mechanical properties of composites with polypropylene. *Appl. Surf. Sci.* **2016**, *361*, 234-241.
11. Wang, Y.; Qi, R.; Xiong, C.; Huang, M. Effects of coupling agent and interfacial modifiers on mechanical properties of poly (lactic acid) and wood flour biocomposites. *Iranian Polym. J.* **2011**, *20*, 281-294.
12. Luo, S.; Cao, J.; Peng, Y. Properties of glycerin-thermally modified wood flour/polypropylene composites. *Polym. Compos.* **2014**, *35*, 201-207.
13. Csizmadia, R.; Faludi, G.; Renner, K.; Móczó, J.; Pukánszky, B. PLA/wood biocomposites: Improving composite strength by chemical treatment of the fibers. *Compos. Part A: Appl. Sci. Manuf.* **2013**, *53*, 46-53.
14. Klyosov AA. Wood-plastic composites. John Wiley & Sons, **2007**.
15. Viksne, A.; Rence, L.; Kalnins, M.; Bledzki, A.K. The effect of paraffin on fiber dispersion and mechanical properties of polyolefin–sawdust composites. *J. Appl. Polym. Sci.* **2004**, *93*, 2385-2393.
16. Pan, Y.; Liu, Y.; Cheng, Q.; Celikbag, Y.; Via, B.K.; Wang, X.; Sun, R. Surface coating of microcrystalline cellulose with surfactants and paraffin wax. *Eur. J. Wood Wood Prod.* **2016**, *74*, 763-765.
17. Viksne, A.; Rence, L.; Berzina, R. Influence of modifiers on the physicomechanical properties of sawdust-polyethylene composites. *Mech. Compos. Mater.* **2004**, *40*, 169-178.
18. Shahnazar, S.; Bagheri, S.; Hamid, S.B.A. Enhancing lubricant properties by nanoparticle additives. *Int. J. Hydrogen Energ.* **2016**, *41*, 3153-3170.

19. Li, X.; Cao, Z.; Zhang, Z.; Dang, H. Surface-modification in situ of nano-SiO_2 and its structure and tribological properties. *Appl. Surf. Sci.* **2006**, *252*, 7856-7861.
20. Peng, D,X.; Kang, Y.; Hwang, R.M.; Shyr, S.S.; Chang, Y.P. Tribological properties of diamond and SiO_2 nanoparticles added in paraffin. *Tribol. Int.* **2009**, *42*, 911-917.
21. Jiang, J.; Cao, J.; Wang, W.; Shen, H. Preparation of a synergistically stabilized oil-in-water paraffin Pickering emulsion for potential application in wood treatment. Holzforschung **2018**, *72*, 489-497.
22. Aveyard, R.; Binks, B.P.; Clint, J.H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.*, **2003**, *100*, 503-546.
23. Binks, B.P. Particles as surfactants-similarities and differences. *Curr. Opin. Colloid Interf. Sci.* **2002**, *7*, 21-41.
24. Jiang, J.; Cao, J.; Wang, W. Characteristics of wood-silica composites influenced by the pH value of silica sols. *Holzforschung* **2018**, *72*, 311-319.
25. Zhou, H.; Hao, X.; Wang, H.; Wang, X.; Liu, T.; Xie, Y.; Wang, Q. The reinforcement efficacy of nano-and microscale silica for extruded wood flour/HDPE composites: the effects of dispersion patterns and interfacial modification. *J. Mater. Sci.* **2018**, *53*, 1899-1910.
26. Balasuriya, P.W.; Ye, L.; Mai, Y.W. Mechanical properties of wood flake–polyethylene composites. Part I: effects of processing methods and matrix melt flow behaviour. *Compos. Part A: Appl. Sci. Manuf.* **2001**, *32*, 619-629.
27. Liu, W.; Chen, S. An investigation of the tribological behaviour of surface-modified ZnS nanoparticles in liquid paraffin. *Wear* **2000**, *238*, 120-124.
28. Messersmith, P.B.; Giannelis, E.P. Synthesis and barrier properties of poly (ε-caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. Polym. Chem.* **1995**, *33*, 1047-1057.
29. Phillips, D.C.; Harris, B. The Strength, Toughness and Fatigue Properties of Polymer Composites, M.O.R. Richardson (Ed.), Polymer Engineering Composites, Applied science publishers, London **1977**, 197-235.
30. Jiang, J.; Wang, W.; Shen, H.; Wang, J.; Cao, J. Characterization of silica particles modified with γ-methacryloxypropyltrimethoxysilane. *Appl. Surf. Sci.* **2017**, *397*, 104-111.
31. Esteves, B.; Nunes, L.; Domingos, I.; Pereira, H. Improvement of termite resistance, dimensional stability and mechanical properties of pine wood by paraffin impregnation. *Eur. J. Wood Wood Prod.* **2014**, 72, 609-615.
32. Koohestani, B.; Ganetri, I.; Yilmaz, E. Effects of silane modified minerals on mechanical, microstructural, thermal, and rheological properties of wood plastic composites. *Compos. Part B-eng.* **2017**, *111*, 103-111.