Effects of calcium carbonate on preparation and mechanical properties of wood/plastic composite

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Abstract: In order to reduce the cost and improve the performance of wood/plastic composite (WPC), the effects of additive amount of calcium carbonate on preparation and mechanical properties of high density polyethylene (HDPE) based WPC were studied. The results showed that the calcium carbonate can improve preparation and mechanical properties effectively. The 20% calcium carbonate additive could effectively improve the melt fluidity of the composites and reduce the energy consumption in the processing. The calcium carbonate had a favorable toughening effect on polymer and was effectively filled in WPC. For the best tensile, flexural and impact properties of WPC, the appropriate additive amounts of calcium carbonate were 25%, 10% and 30%, respectively. The additive amount for preparation of WPC should be based on the processing requirements and the demands for different working conditions.

Keywords: wood/plastic composite, calcium carbonate, preparation, mechanical property, fluidity, SEM

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1 Introduction

The wood/plastic composite (WPC) is a new kind of environment-friendly composites with high performance and added value. It is made from wood flour (WF) and thermoplastic mixed with certain proportion of coupling agent, lubricant, stabilizer, etc. under injection molding, extrusion and other forming process. WPC shares the wood texture of original solid wood products as well as excellent mechanical properties, workability[1], corrosion resistance, water tolerance, fireproofing, etc. Its earliest popularization and applications can be dated to 1980s in America. Presently, it has been widely used in decoration, automobile interior, public infrastructure, furniture material, warehouse logistics, consumptive durable products, electronic products and so on[2-4]. As the wood flour is a major component of WPC, the governments have been strongly encouraging and promoting the development and applications of wood/plastic products in recent years in order to facilitate recycling of waste plastics and reduce the consumption of forest resources[5]. Under the background of scale commercialized application of wood/plastic products, it has become a research hotspot to improve the quality and cut down the production cost of the wood/plastic products. The principal research approaches include increasing the additive amount of wood flour, reducing the additive amount of plastics, adding padding, and improving production process. The mineral substances such as calcium carbonate, talcum powder and diatomaceous earth are very common padding in plastics industry,

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among which the calcium carbonate superfine powder (0.1-10 μm) is most widely used[6,7] due to features such as extensive sources, low cost and non-toxic. It could also improve the mechanical properties of plastic products and enhance the flame retardation of the material. Zhang et al. and Fu et al.[8,9] discovered that calcium carbonate could improve elasticity modulus, flexural strength, and tensile strength of polypropylene/calcium carbonate composites, reduce the impact strength and elongation. When the mass fraction of calcium carbonate was 20%, the comprehensive mechanical property of the composite was good. Generally these mineral substances could also be used as padding of WPC in order to improve the stability and toughness and reduce cost of production of the composite. Other scholars have concluded from experiment that calcium carbonate could enhance elasticity modulus of WPC[10]. Zhao et al. and da Cunha Lapa et al.[11,12] found that the particles of calcium carbonate closely contacted with wood flour and high polymer so that it impeded thermal decomposition of wood flour and polymer. It means that adding calcium carbonate in the WPC can significantly defer the time to ignition, decrease the heat of combustion and improve flame retardation of WPC. In this study, the effects of the additive amount of calcium carbonate on preparations and mechanical properties of WPC were investigated when it was used as padding of HDPE-based WPC.

2 Materials and methods

2.1 Experimental materials

Before experiment, the wood flour prepared by fast grown poplar was oven dried at 105°C until the moisture content decreased to 3%. Wood flour particles with size 60-100 meshes were used in this study. The High density polyethylene coded 9001 (HDPE) was manufactured by USI Corporation, Taiwan province, China. The coupling agent, i.e. maleic anhydride-grafted polyethylene (MAPE 1002) was prepared by Suzhou Yasai Plastics & Chemical Co., Ltd, Jiangsu province, China. The polyethylene wax (Tissuemat E LP0020P) was prepared by Longgang Dingguo Plastics Firm, Guangdong Province, China, and the calcium carbonate (1250 meshes) was prepared by Gao'an Jiabai Calcium Industry Co., Ltd, Jiangxi province, China.

Figure 1 Wood flour of 60-100 meshes

Figure 2 Maleic anhydride-grafted polyethylene

2.2 Instrument and equipment

The instrument and equipment used in the experiment included a high-speed mixer (JHN-15, Zhengzhou Jintai Metal Materials Co., Ltd. Zhengzhou, China), twin screw extruder (BP-8177, Dongguan Baopin International Precision Instrument Co., Ltd. Guangdong Province, China), universal mechanical testing machine (5969, INSTRON, America), torque rheometer (RM200C, Harbin Harpo Electric Technology Co., Ltd. Harbin, China), scanning electron microscope (SEM) (FEI Sirion200, America).

Figure 3 Twin screw extruder

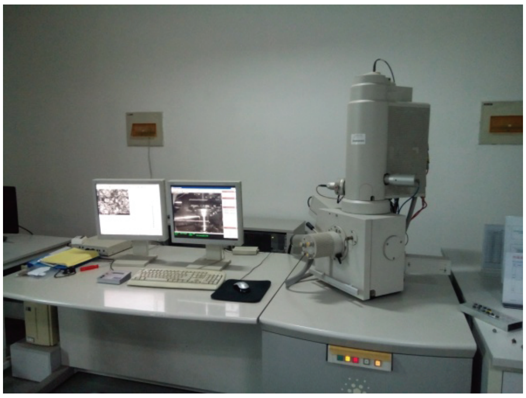


Figure 4 Scanning electron microscope

2.3 Preparations of samples

The WF, HDPE, Tissuemat E, MAPE and calcium carbonate were weighed according to formulations given in Table 1. And then the weighted materials were mixed with high speed mixer for 8 min.

The WPC samples were prepared by a twin screw extruder, with a barrel temperature of 120°C, 135°C, 150°C, 165°C and 175°C, respectively, and a rotating speed of 40 r/min.

Table 1 Compositions of WPC %wt

No.	WF	HDPE	Tissuemat E	MAPE	Calcium carbonate
1	50	50	4	8	0
2	50	50	4	8	5
3	50	50	4	8	10
4	50	50	4	8	15
5	50	50	4	8	20
6	50	50	4	8	25
7	50	50	4	8	30

2.4 Melt fluidity testing

The RM200C torque rheometer was used in the melt fluidity of composite testing. When the temperature in the charging barrel reached the set value (175°C), the weighed mixture according to formulations given in Table 1 was put in and kept for 10 min. The rotor speed was set at 40 r/min. This experiment should be repeated at least three times, the data averaged.

2.5 Mechanical testing

The rectangular bars of 160 mm×20 mm×4 mm for tensile properties tests and 80 mm×10 mm×4 mm for flexural properties tests and impact strength tests were prepared before the mechanical testing.

The tensile properties were measured according to ASTMD638-10 with INSTRON 5969 at a crosshead speed rate of 5 mm/min. Each set of tensile properties data reported was an average of at least five measurements.

The flexural properties were measured according to ASTMD790-10 with INSTRON 5969 at a crosshead speed rate of 5 mm/min. Each set of flexural properties data reported was an average of at least five measurements.

The impact strength was tested using a JB-300B electronic impact testing machine (Jinan Hengsi Shengda Instrument Co., Ltd., Shandong, China) according to GB/T 1043.1-2008, and the final measurement result was the average of the 10 repeating testing values at least.

2.6 SEM

The topography of the scratched surfaces of WPC was studied by scanning electron microscope. The surfaces were coated by 20 nm layer of gold to prevent charge build up. The FEI Sirion200 SEM operated at an accelerating voltage of 10 kV was used in this study.

3 Results and discussion

3.1 Melt fluidity

In the course of WPC preparation and processing, the melt fluidity would affect the processing technique and extrusion velocity as well as the product performances. An overly low fluidity may cause a difficulty in the mold filling or product extrusion[13], and thus increase production energy consumption. On the other hand, an overly high fluidity may cause insufficient extrusion pressure and the poor mechanical properties of the WPC. With torque rheometer, the fluidity could be preferably simulated, so could be the energy consumption of plasticization and stability of materials within screws during actual processing.

After the mixture from mixer was heated and melted, the wood flour and calcium carbonate were added into melted materials with mixing, the hot melt gradually became uniform. The viscosities of hot melt generated resistance on screws, and then torque rheometer could be used to measure the resistance by balancing the torque. The equilibrium torque could reflect the fluidity performance of heated and melted materials in the actual processing, i.e., apparent viscosities of hot melt. In Figure 5, the equilibrium torque decreases rapidly after adding calcium carbonate. The minimum equilibrium torque was about 15.1 N·m at the 10% calcium carbonate. There was no significant difference of the equilibrium torque with the increasing content of calcium carbonate from 5% to 20%. When the content of calcium carbonate exceeded 20% in mass, the equilibrium torque increased significantly. The plastizing energy consumption was the lowest when the content of calcium carbonate was 20%, about 39.01 N·m, which was about 5.5% less than that without calcium carbonate adding. Comparing two curves in Figures 5 and 6, the general change tendencies of energy consumption of plasticization and equilibrium torque tend to be consistent. Both values of them decreased with increasing calcium carbonate at first, and then increased when the content of calcium carbonate was over 20%. The same tendency indicates that the melt fluidity is a key factor to affect productive energy consumption in actual processing. While the amount of calcium carbonate was about 5% to 20%, it could enable the melt to mix more homogeneous and thus improved melt fluidity and reduced energy consumption of plasticization. Once the amount of calcium carbonate exceeded 20%, the value of the plastizing energy consumption and equilibrium torque would increase rapidly.

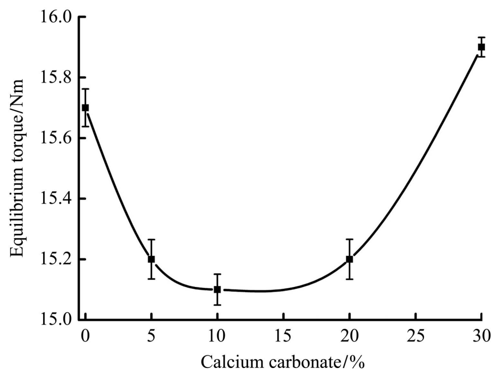


Figure 5 Effects of calcium carbonate on equilibrium torque of melt

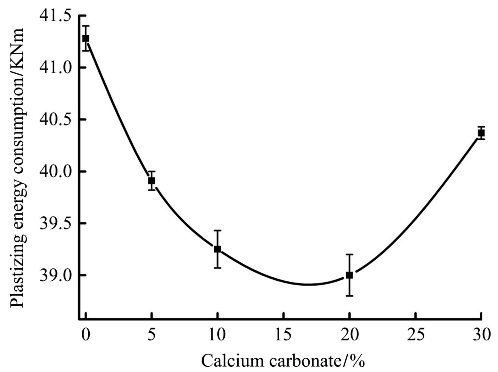


Figure 6 Effects of calcium carbonate on plastizing energy consumption of melt

3.2 Mechanical properties

The mechanical property of WPC is the most concerned for the practical application. The good mechanical properties of WPC could increase the fatigue life, widening the field of use, and improve the safety factor.

As shown in Figures 7 and 8, when the additive amount of calcium carbonate increased from 0 to 15%, both tensile strength and elongation at break of WPC were improved to some extent. The elongation at break increased from 3.94% to 6.26%. The hydroxyl radical from cellulose could easily form intramolecular and intermolecular hydrogen bonding when the amount of wood flour exceeded 40%. It could result agglomeration and generating the tiny gaps between wood fibers in WPC[14]. With increased additive amount of fine calcium carbonate (0-15%), the inner structure of WPC became more homogeneous (see SEM photos). As the diameter of calcium carbonate particles are much smaller than that of wood flour, therefore, the tiny gaps between wood fibers in WPC would be filled by calcium carbonate particles so that the internal structure becomes more compact and the density is greater (Table 2). Like calcium carbonate toughened HDPE[12], there is certain critical value for calcium carbonate toughened WPC. Only when the additive amount of calcium carbonate is larger than the critical value, it will appear obvious toughening effect. When the additive amount exceeded 25%, the change of tensile strength of composite was plateaued. The tensile test showed that the calcium carbonate could improve the tensile property of the composite and the appropriate the additive amount was 25%.

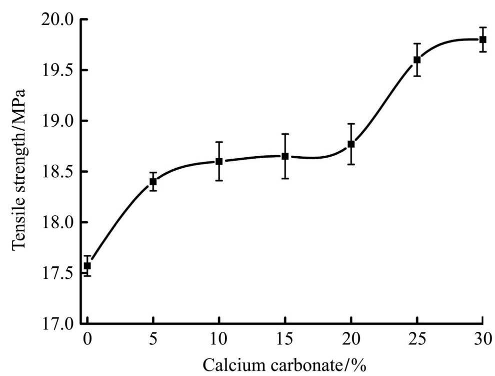


Figure 7 Effects of calcium carbonate on tensile strength of WPC

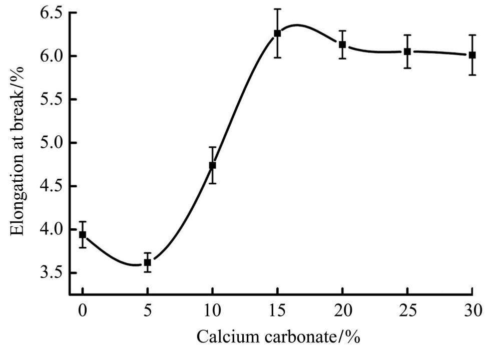


Figure 8 Effects of calcium carbonate on elongation at break of WPC

Table 2 WPC density under different additive amount of calcium carbonate

Calcium carbonate/wt%	0	5	10	20	30
Density/10^3 kg·m^{-3}	1.25	1.26	1.28	1.33	1.38

The flexural strength of WPC was about 38.2 MPa without the addition of calcium carbonate. The Figure 9 shows that the value of the flexural strength became higher with the less content of calcium carbonate (0-10%) and reached the maximum 39.36 MPa when the content was about 10%. After that, the flexural strength decreases rapidly from 39.36 to 37.78 MPa until the additive content of calcium carbonate reached 15%. Applying more calcium carbonate to 30% made the value of the flexural strength increased again. The addition of calcium carbonate could enhance filling effect within WPC, and after adding MAPE, the calcium carbonate and wood flour could be better in crosslink with polyethylene so as to further increase flexural strength. With increasing additive amount of calcium carbonate, the crosslink effect among calcium carbonate particles, plastics, and wood fiber was weakened, and more calcium carbonate particles were merely mechanically extruded and mixed together, which resulted in decreased intermolecular forces within internal structures of composite and consequently lowered the flexural strength. When the additive amount of calcium carbonate exceeded 20%, the extrusion velocity was slowed down and the density of prepared sample evidently increased. The calcium carbonate particles filler had promoting effects on crystallization of polymer[15,16], i.e. they generate heterogeneous nucleation and made the sphaerocrystal fine in the course of crystallization. As consequently, the better crystallization properties enhanced the flexural strength of WPC. Figure 10 shows that when adding amount of calcium carbonate less than 10%, the flexural modulus of sample was slightly reinforced; when the additive amount of calcium carbonate exceeded 10%, the flexural modulus of WPC significantly dropped. The flexural modulus increased when the amount of calcium carbonate was less than 10% because of the toughening effect of the calcium carbonate on polymer[17,18]. However, with increasing amount of calcium carbonate, such effect would change to be less apparent. Instead, excessive additive amount of calcium carbonate (more than 10%) could result in weakened intermolecular forces, insufficient stability of internal structures and decreased the flexural modulus.

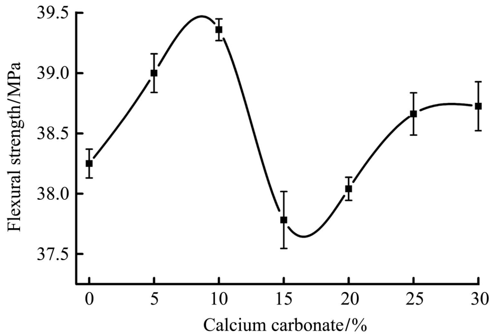


Figure 9 Effects of calcium carbonate on flexural strength of WPC

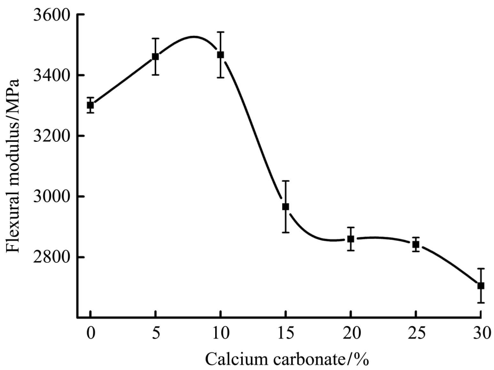


Figure 10 Effects of calcium carbonate on flexural modulus of WPC

Figure 11 shows the effects of calcium carbonate on impact strength of WPC. As wood flour particles were unevenly scattered in WPC, the scattered wood flour particles were unable to effectively terminate the flaws or generate crazes to absorb the impact energy when the WPC was suffering from impact forces[19,20]. As can be seen from SEM photos of WPC impact fracture (Figure 12), there was no visual evident filling effect from calcium carbonate and the calcium carbonate fails to effectively fill in tiny gaps among wood flour particles while the additive amount of calcium carbonate adding was less than 10%. There were more stress concentration points (Figure 12b) generated to wreck continuity within composite, so that the composite generated big flaw easily and broke after bearing impact forces. This is in agreement with previous literatures[21,22]. If adding calcium carbonate until 30%, it can be found from SEM photos that the calcium carbonate can favorably fill in WPC and make internal structures to be denser. When the additive amount of calcium carbonate reached 30%, the impact fractures became smoother with dense and continuous internal structure of sample that being in good integrity, which indicated the calcium carbonate has satisfactory filling effect[23]. The WPC had a best impact property with 30% calcium carbonate additive. The situation of over 30% additive amount was not studied because the preparation property is poor in such conditions. A good integrity can enable the sample to disperse impact energy under condition of impact and enhance impact strength of sample.

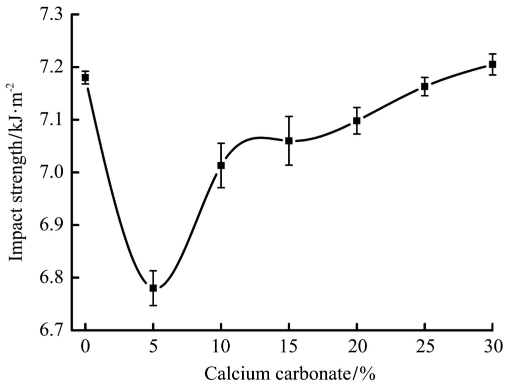
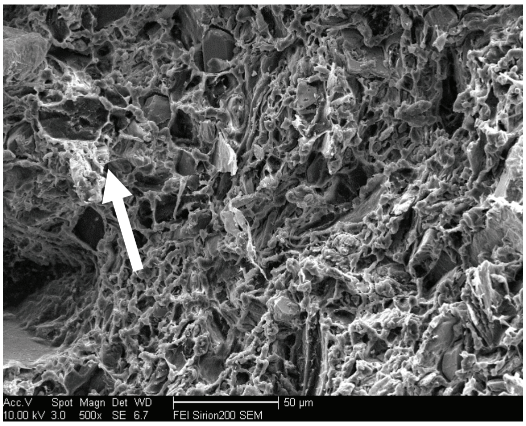
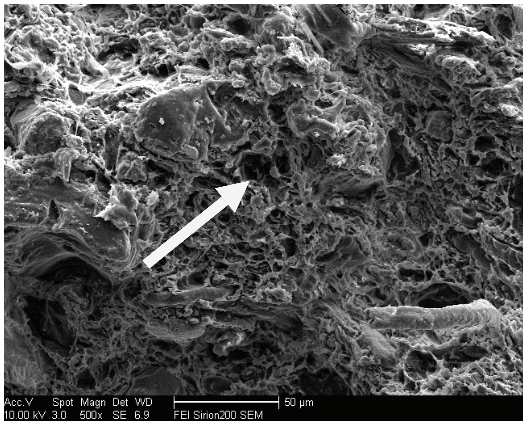


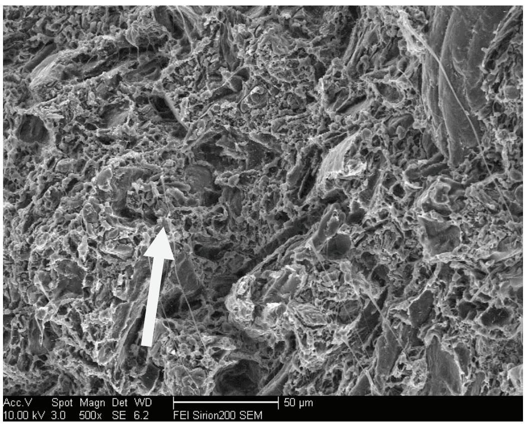
Figure 11 Effects of calcium carbonate on impact strength of WPC



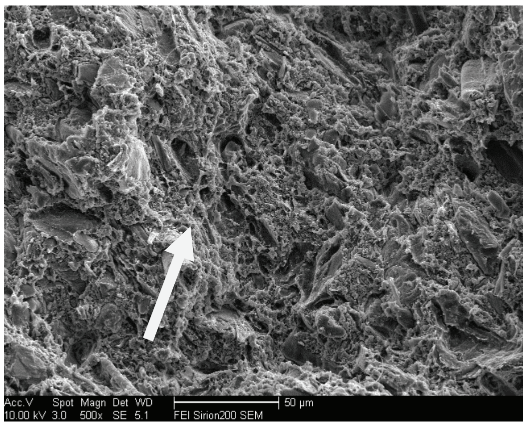
a. Without calcium carbonate (×500)



b. Added 5% calcium carbonate (×500)



c. Added 10% calcium carbonate (×500)



d. Added 30% calcium carbonate (×500)

Figure 12 SEM photos of WPC impact fracture under different additive amount of calcium carbonate

4 Conclusions

In this study, the HDPE based WPC were prepared by extruding technological process and the effects of calcium carbonate on preparation and mechanical properties of WPC were discussed. The results showed that the additive amount should be based on the processing requirements and the demands for different working conditions. The appropriate amount of calcium carbonate is 20% for the preparation properties of composites; the appropriate amount of calcium carbonate is 25% for the tensile properties; the appropriate amount of calcium carbonate is 10% for the flexural properties; the appropriate amount of calcium carbonate is 30% for the impact properties. The calcium carbonate as WPC padding can reduce the cost of raw material, reduce production energy consumption, and improve preparation and mechanical properties effectively.

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