

Preparation of PBS and CaCO₃ Composite Degradable Materials based on Melt Blending

Ligui Xiong¹, Zhigang Tu^{2,*}, Shangxian Zhang³, Xiaoyuan Liu⁴ and Xingni Peng⁵

^{1,2,3,5} Guangdong Polytechnic Institute, Zhongshan, China

⁴ Guangzhou Vocational College of Technology & Business, Guangzhou, China

*Corresponding author e-mail: 1049661754@qq.com

Abstract. Poly (butylene succinate)(PBS)/ Calcium carbonate (CaCO₃) composite were prepared by melt blending, and studied the effect of different coupling agents, PBS and CaCO₃ mass ratio and coupling agent for composite. The results showed that aluminum acid coupling agent for the properties of composite materials improved the most obviously effect; with CaCO₃ content increased, the degradation properties and tensile strength of composite materials rose, the impact strength and elongation at break decreased. With aluminum acid content increased, the tensile properties and impact strength increased and then stabilization but no influence on degradation. When the PBS and CaCO₃ mass ratio was 7:3, the coupling agent in an amount of 1.5%, the performance of PBS/ CaCO₃ composite was better, meeting the basic requirements. Compared with pure PBS, it reduced the cost of nearly 30%, and application further.

1. Introduction

Polybutylene succinate (PBS) is a typical fully biodegradable polymer material that is easily decomposed and metabolized by various microorganisms or enzymes in animals and plants, and eventually decomposed into carbon dioxide and water. Compared with degradable plastics such as polylactic acid (PLA), polyhydroxybutyrate (PHB), polycaprolactone (PCL), and polyhydroxyalkanoate (PHA), PBS has low cost, excellent mechanical properties, and convenient processing. It can adapt to the advantages of conventional molding processing equipment and good heat resistance.[1-4] It can replace polyethylene and polypropylene. At the same time, it has a wide range of raw materials, which can be obtained from petroleum resources or fermented by biological resources. And industry attention, PBS is the leader in biodegradable plastic materials, but compared to traditional plastics, its price is too high, it is difficult to promote its application, so reducing its cost becomes the key to the future development of PBS plastics. Calcium carbonate is a low-cost mineral material derived from nature and has been widely used in the modification of various polymer materials. It is feasible to reduce the cost of PBS by using calcium carbonate filling.[5-6]

In this paper, PBS/CaCO₃ composites were prepared by blending PBS with calcium carbonate as filler. The coupling agent type, the amount of coupling agent and the mass ratio of PBS/CaCO₃ were studied. The effects of elongation, impact properties and degradation properties.

2. Experimental Part

2.1. Main Ingredient

Light calcium carbonate: 2000 mesh, Zhongshan Yongfeng Chemical Co., Ltd.;

PBS: Blow molding grade, Shandong Huiying New Material Technology Co., Ltd.;



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Aluminate coupling agent: DL-411, Foshan Shengyi Plastic Chemical Co., Ltd.;
 Silane coupling agent: KH550, Foshan Shengyi Plastic Chemical Co., Ltd.;
 Titanate coupling agent: CS-104, Nanjing Chuangshi Chemical Additive Co., Ltd.

2.2. Main Instruments and Equipment

Twin-screw extruder: TES-65, Jiangsu Nanjing Noda Extrusion Equipment Co., Ltd.;
 Mixer: x(S) N-35, Jiangsu Nanjing Kaichi Machinery Co., Ltd.;
 Injection molding machine: JN55E, Guangdong Dongguan Zhenxiong Machinery Co., Ltd.;
 PC type intelligent electronic tensile testing machine: XLW (PC) -500N-50N, Shandong Jinan Languang Electromechanical Technology Co., Ltd.;
 Cantilever beam impact testing machine: X CJ, Jilin University Science and Education Instrument Factory.

2.3. Sample Preparation

The production process is shown in Figure 1, and the production temperature is shown in Table 1.

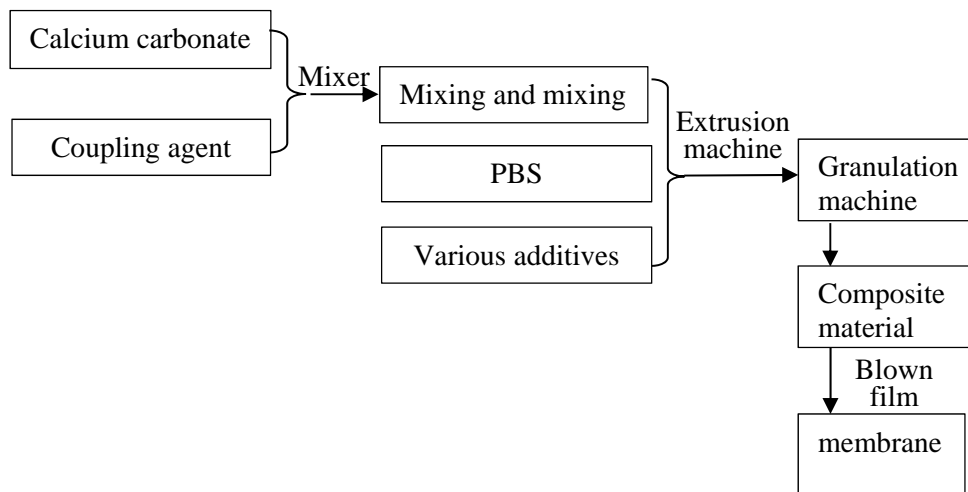


Figure 1. Production process

Table 1. Production temperature of PBS/CaCO₃ composite

1 area/°C	2~4 area/°C	5~6 area/°C	8 area/°C	Machine head temperature/°C	Terminal mode/°C
115~120	120~125	125~130	130~135	135~140	140

2.4. Performance Testing

The tensile properties are tested according to GB/T1040.3-2006, and the sample is type I.

For the spline, the stretching speed was 50 mm/min, and 5 samples were tested in each group. The results were averaged.

The impact performance was tested according to GB/T1843-1996. Each group was tested with 5 samples and the results were averaged.

Degradation performance was carried out by soil-buried method. The sample was cut into (25×25)mm sample. After drying and weighing, it was sandwiched between gauze and buried in the flowerbed soil about 20 cm away from the surface for a certain period of time (28d). After taking out, and calculating the mass loss rate of the sample, the calculation formula is: weight loss rate = (m1-m2) / m1 × 100%, where m1 and m2 are respectively

For the original quality of the sample and the quality after degradation, 5 samples were tested for each group, and the results were averaged.

3. Results and Discussion

3.1. Effect of Coupling Agent Type on Properties of Composites

Experimental conditions: the mass ratio of PBS and CaCO_3 was 7:3; the coupling agent was aluminate, titanate and silane, and the addition amount (calculated as the mass of calcium carbonate, the same below) was 2%.

It can be seen from Figure 2 that the mechanical properties of the composites are different when the coupling agents used are different.

The mechanical properties of the composites with the addition of coupling agent were significantly improved. When the coupling agent was aluminate, the effect was the most obvious. Therefore, the aluminate coupling agent was determined to be the most PBS/ CaCO_3 composite. Good coupling agent.

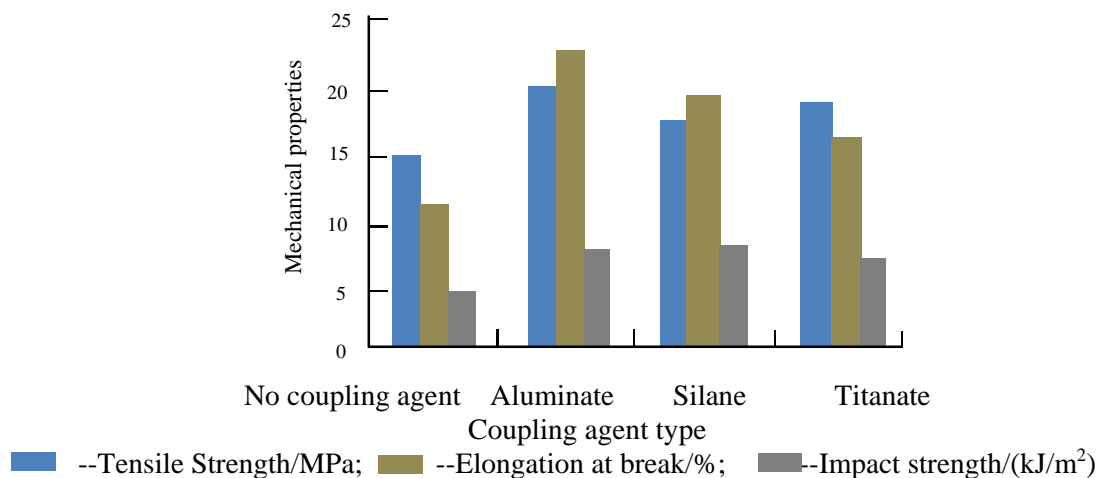


Figure 2.

3.2. Effect of PBS / CaCO_3 Mass Ratio on Properties of Composites

Experimental conditions: the amount of aluminate added is 2% (calculated as the mass of calcium carbonate), The mass ratio of PBS to CaCO_3 was set to 10:0, 9:1, 8:2, 7:3, and 6:4.

When the mass ratio of PBS to CaCO_3 is 6:4, the extruder is often blocked during preparation, and the required temperature is also high. If the temperature is too high, the degradation of PBS will be triggered, indicating that the amount of calcium carbonate added is too high. Therefore, the quality ratio relationship does not continue to be followed up.

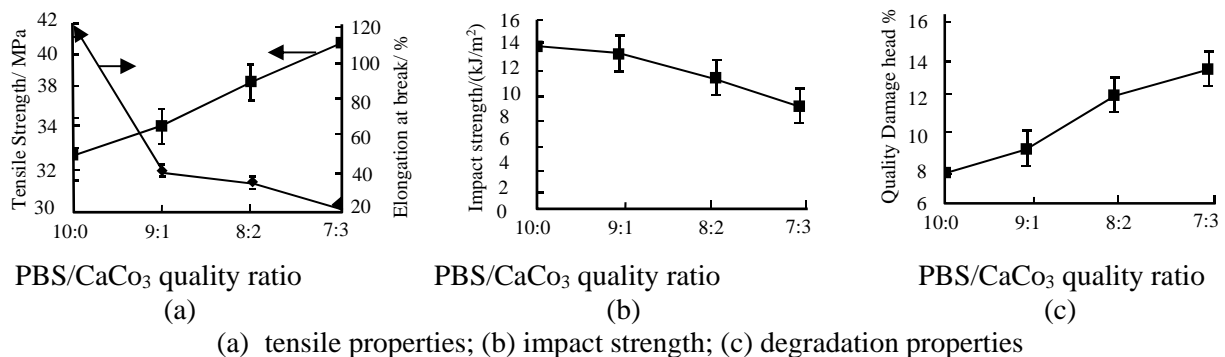


Figure 3. Effect of PBS/ CaCO_3 mass ratio on properties of composites.

It can be concluded from Fig. 3(a) and (b) that as the amount of CaCO_3 increases, the tensile strength of the composite increases, and both the elongation at break and the impact strength decrease. This is because CaCO_3 acts as a filler and can act as a skeleton. When the amount is larger, the tensile

strength of the composite is larger. At the same time, the presence of a large amount of powder limits the movement of the PBS molecular segment, so that CaCO_3 and PBS The bonding strength of the interface is weak, which leads to the decrease of impact strength and elongation at break of the composite. However, when the amount of CaCO_3 is as high as 30%, the elongation at break of the composite is still higher than 20%, indicating that the material still has a high Elongation, and the ultimate goal of PBS filled fillers is to minimize the cost of the product while maintaining performance. It can be concluded from Fig.3(c) that the mass loss rate of the composite increases linearly with the increase of CaCO_3 dosage, which is much higher than that of pure PBS. This is due to the filling effect of CaCO_3 , which makes the microorganisms more susceptible to erosion. The inside of the material [7-9], so the ratio of PBS/ CaCO_3 was determined to be 7:3.

3.3. Effect of Coupling Agent Amount on Properties of Composites

Experimental conditions: the mass ratio of PBS to CaCO_3 is 7:3, The amount of the amount of the aluminate (calculated by the mass of the calcium carbonate) was 1.0%, 1.5%, 2.0%, 2.5%, 3.0%.

It can be seen from Fig. 4(a) and (b) that as the amount of aluminate increases, the tensile properties and impact strength both appear to rise first and then tend to be gentle. This is because CaCO_3 has poor affinity with PBS matrix resin [10-13], and the performance of the composite material is deteriorated due to uneven dispersion. The addition of coupling agent can improve the surface properties of CaCO_3 , starting from composite materials. The effect of the binder can effectively improve the compatibility of CaCO_3 with the PBS matrix and increase the interfacial bonding strength of the two, but the amount of the coupling agent is not as good as possible [14-15]. For a long time, there will be an interference effect, and the excess coupling agent will not only fail to achieve the coupling effect, but will become an impurity of the system and increase the production cost of the composite material[8]. It can be seen from Fig.4(c) that when the amount of aluminate is different, the degradation performance is not much different. Considering the cost of the coupling agent and its addition amount to the mechanical properties of the composite. It can be seen from Fig. 4(c) that when the amount of aluminate is different, the degradation performance is not different. Considering the cost of the coupling agent and the amount of the addition agent on the mechanical properties and the degradation properties of the composite material, the effect is better when the amount of the aluminate is 1.5%.

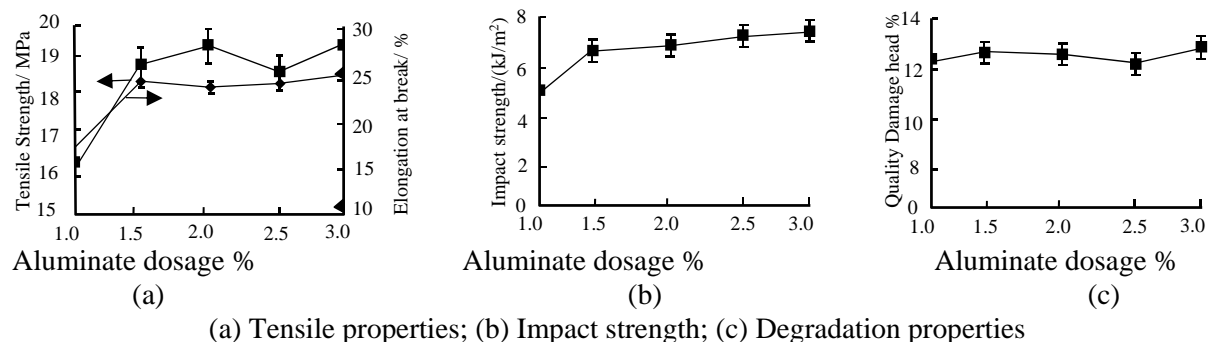


Figure 4. Effect of the amount of aluminate on the properties of composites

4. Conclusion

The aluminate coupling agent has the most obvious effect on the performance of the composite; when the amount of CaCO_3 is increased, the tensile strength and degradation performance of the composite increase, the elongation at break and the impact strength decrease; the effect of the amount of aluminate on the degradation performance Not large, but when the amount of aluminate is increased, the tensile properties and impact strength first rise and then tend to be gentle.

When the mass ratio of PBS and CaCO_3 is 7:3, and the amount of aluminate is 1.5%, the composite material has better comprehensive performance, which can meet the requirements of use, and can

reduce the yield by nearly 30% compared with pure PBS. The cost of its promotion and further application.

5. References

- [1] C.N.CHUI, T.J.HAUNG and Y.HE, “*Study on Aging Performance of Poly (butylene succinate)/Calcium Carbonate Composite*”. Plastic technology, Vol.41 No.11, pp.74-77.2013.
- [2] Z.C.LIAO, “*Research Progress of Biodegradable Plastic PBS*”. Plastic technology, Vol.38 No.7, pp.93-98.2010.
- [3] TACHIBANA Y, MASUDA T, FUNABASHI M, et al. “*Chemical synthesis of fully biomass-based poly (butylene succinate) from inedible-biomass-based furfural and evaluation of its biomass carbon ratio*”. Biomacromolecules, Vol.11 No.10, pp.2760-2765.2010.
- [4] Y.C.SONG, Z.P.WANG and XCHENG. “*PreParation and PorPerties of Starch/BS Blends*”. China Plastics, vol.20, no.4, pp.65-67, 2006.
- [5] J.LIU, H.J.JI, W.ZHANG, “*Development in blending modification of biodegradable Poly (butylene succinate) and natural biodegradable polymer*”. New Chemical Materials, Vol.41 No.8, pp.1-3.2013.
- [6] Z.DING, Q.LING, and X.S.PEN. “*Toughening Research Progress in Completely Biodegradable Polylactide by Blending*”. Plastic, Vol.45 No.2, pp.95-97.2016.
- [7] B.YANG, Y.XIU, H.J.JI, “*Application of Double-coated Surface Modification of Calcium Carbonate in Highly Filled Composite Material*”. Plastic, Vol.43 No.1, pp.4-7.2014.
- [8] L.B.GAO, “*The Study on Modification of Fully Biodegradable Poly (butylenes succinate)*”. Beijing Technology and Business University, 2006.
- [9] K.K.YING, “*Study on modification of biodegradable Poly (butylenes succinate)*”. Wuhan University of Technology, 2011.
- [10] X.LI, D. H.LIU and Y.H.HUANG, “*Performance of Calcium Carbonate Modified by Aluminate Compound Coupling Agents*”. Yunnan Chemical Technology, Vol.30 No.5, pp.3-6.2003.
- [11] L.X.LUN, Z.F.LUO, “*Study of the surface modification of heavy calcium carbonate*”. Journal of China University of Mining & Technology, Vol.40 No.2, pp.269-272-6.2011.
- [12] Y.X.MA, P.ZHOU and H.M.LIU, “*Preparation and Properties of PLA / NPCC Composite*”, Plastic, Vol.44 No.5, pp.25-28.2015.
- [13] H.YANG, L.ZHANG and X.LU, “*Study on Isothermal Crystallization Kinetics of the Calcium Sulfate Whisker/PBS Blends*”, Plastic technology, Vol.41 No.5, pp.8-12.2013.
- [14] Q.WEN, “*Study on blending modification of biodegradable plastics PBS*”, Hunan University, 2011.
- [15] T.LI, H.Z.LI and J.B.ZENG, “*Microbial Degradability of Thermoplastic Starch/PBS Blends*” Chemical Research and Application, Vol.31 No.7, pp.994-997.2019.