

lignin / structure and performance of polylactic acid composites

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Abstract: lignin is produced by melting blending and injection molding / Polylactic acid composites , and through the differential scanning calorimetry analysis , Mechanical Performance Test , Vicat Softening Point temperature measurement , scanning electron microscope , The effects of lignin content on the structure and properties of composites are studied by means of water absorption tests . The result shows that , lignin / polylactic acid The crystallinity of the composites decreases first and then increases with lignin content . as the lignin content increases , composite tensile strength decreases , Impact Strength render first increase and then decrease the trend , modulus of elasticity increasing . when lignin content is 5%~10% when , Composite has relatively good overall mechanical properties . Add a small amount of lignin to help improve the wood quality / The fiber-softening temperature of polylactic acid composites . as lignin increases , Initial contact angle of composites increase , that's hydrophilic drop . But after immersion, the water absorption of the composite increases with the lignin content. ,-- absorbent can improve .

Keywords: Polylactic acid ; lignin ; Composite ; crystallinity ; Mechanical Properties ; hydrophilic

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Poly(lactic acid) (PLA) has good biodegradability , no poison sex , and has good mechanical properties , can be processed in a variety of ways processing , is considered to be the most promising biodegradable polymer material [1]. current PLA apply to agricultural mulch film , Food wrapping film , dining utensils , Biomedical , Electronic Product shell etc Collar field [2,3] , But they still have high production costs , poor heat resistance and flush strike Low performance , greatly restricted PLA The application and development of . so , further enhanced PLA Performance Research has become biodegradable Hot topics in the material field [4,5].

in Nature , lignin reserves second only to cellulose , also has a raw Object biodegradability . annual pulping and papermaking Industry isolate fibers from plants Suyo1. 4 million ton , Also get lignin by-products 5000 million ton left Right . but so far , separated lignin treated by incineration Super past % , not only cause great waste ,and aggravate the environment Dirty . over the years people on lignin in synthetic resins , adhesives , Surface use of areas such as active agent although there has been some research results [6] , but use it as a filler material enhancements PLA performance reports are relatively low . so , exploring lignin enhancement PLA the possibility of ,not only helps promote Efficient use of lignin , Also reduces costs to help PLA base Application and popularization of composite materials .

for this , This article uses lignin as the enhancer , blends with molten and injection molded lignin with different lignin /PLA Duplicate Close material . with DSC, Mechanical Performance test , SEM, Contact angle Test methods such as studied lignin content on lignin / PLA composite Knot structure and performance impact .

1. Experiment Section

1.1 experimental raw materials

PLA: $T_m = 171.21^\circ \text{C}$, Model 6252D, United states Nature Works company ; lignin : Zinan-Saint-Quanque Group Co . , Ltd.

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1.2 Sample Preparation

will PLA and lignin in C Vacuum Drying H , and then According to the quality of lignin score is 0% , 5%,10%, 15% and 20% the ratio of to lignin and PLA to add to CTR - typetorque rheometer (Shanghai Chang Kai Electromechanical Technology Co., Ltd.) in , on 180 C with r/min rotational speed of blending 5 min . and then the chopped particletake dhy -5 Mini Injection molding machine (Shanghai De Hong Rubber and plastic machinery Co.) Make dumbbell-shaped and rectangular spline . injection conditions :barrel temperature 190 C, stencil temperature C , injection Pressure 0. 5 MPa, Inject time ten s , pressure-holding time Ten s .

1.3 Sample Testing and characterization

1.3.1 DSC analysis and crystallinity calculation : Use modulateddsc 2910 type differential scan calorimeter (MDSC , US TA Instrumentation company) measuring lignin / PLA The melting and crystallization behavior of composites . sampling 4~ 8 mg, Keep gas flow \$ mL /min , with ten C / min The heating rate of the will sample from the C heats up to 190C , record Hot

enthalpy of change with temperature curve , To get a glass transition temperature (T_g) , Cold crystallization temperature (T_c , melting temperature (T_m) and molten heat enthalpy (ΔH_m) parameters .

Wood Quality / PLA The crystallinity of the composite is in type (1) evaluates :

x - Muscle

(1-y) ΔH_c

type : x . ---- crystallinity ; ΔH . --- melting enthalpy ;----- Woody

Quality Score ; A H C-- P L A The enthalpy of the When fully fused , its value

is - 6 j/g.

1.3.2 Mechanical Performance Test : tensile performance with 5969 type In - Stron Electronic Universal Material testing machine (US Instron Company) Press photo GB/ T 1447-???? Standard tensile tests on materials , Stretch speed to 2 mm/min . Impact Performance xjjud\$Q suspension arm beam pendulum impact tester (Chengde Couth Scientific Testing Co., Ltd.) Press GB/T1843- 2008 standard cantilever notch impact test Check . 1.3.3 topography View : with Quanta 250 Environment Scan electron microscope (ESEM,FEIHong Kong Limited) view compound The shape structure of the impact section of the material .

1.3.4 Vicat Softening temperature test : takes the XWB E Hot-Change shape & vicat softening point temperature Tester (Chengde Test Machine Limited company follow GB / T1 633 - To Standard , test material Vicat Soften temperature . test payload 1 kg, heating rate is 2 °c/min .

1.3.5 Contact Corner test : Use model OCAMicro Full automatic video Micro contact angle meter (Germany dataphysics Duke Division) , measuring different lignin /PLA Contact angle for composite materials .

1.3.6 Water absorption test : to different lignin / PLA Composite Sample to weigh the dry mass of the product after drying it is then put into the deionized Water Soak , check out daily weigh its quality to W_{wa} , Take advantage of (2 test) Test composite water absorption (W).

$W = (w_{wt} - w_{dry}) / w_{dy}$ ()

2. Results and discussions

2.1 DSC analysis

Fig . 1 compares lignin in different lignin / PLA Complex Combined materials DSC curves , The relevant data obtained by IS listed in d ah 1. by D ah 1 knowable ,, content of lignin to Composite's melting point T_m Basic no impact describes the , andPLA in the preparation process No significant thermal degradation occurred . and pure PLA Crystal degree (8. (\$) compared to , Add 5% after the lignin , crystallization of composites The degree is lowered to

4.66%. But as the lignin content increases, composite material crystallinity of the material increases with it, when lignin content reaches 20%, Composite All materials crystallinity reached 1048%, is above a pure PLA crystallinity of (8.95%). This is because the lignin structure is complex and irregular, belongs to Non-crystalline three-dimensional reticular natural polymer, Its main chain and its horizontal to a certain extent, the rigid groups in the cross-linked structure are limited P L- A Molecular chain movement, cause composite crystallization capability and crystallization rate Rate affected by, So add a small amount of lignin after the composite crystallization degree drops. but, lignin can also be induced as nucleating agent PLA crystallization [7]. increase lignin content, Its effect as nucleating agent Force Greater, the crystallinity of the composite exhibits a higher trend., and in lignin up to The crystallinity of the 20% exceeds the pure PLA.

Fig. 2, Fig. 3 and Fig. 4 compares different lignin content on the lignin /PLA tensile strength of composites, break elongation, Play sex modulus and impact strength. You can see from the diagram, the presence of lignin produces varying degrees of tensile and impact properties of composites effect.

consists of the Fig. 2 Know, Pure PLA the tensile strength and elongation at break are divided into no, MPa and 7.01%, But after the lignin is added, two decreases, and decreases as lignin levels increase. where, when lignin content is 10% when, tensile strength of composites to Wuyi. MPa, break elongation is 2.61%, than pure PLA lowers the 205% and 62.8%, and when lignin content is further increased through 20% when, The tensile strength of the composite is only, MPa, Break split elongation to 1.79%, respectively compared to pure PLA to Lower 31.9% and 745%, indicates that the Addition of lignin reduces the tensile strength of the material and the Break elongation. This is mainly due to the presence of lignin particles., destroy up PLA The formation of a long-range continuous phase of a molecule, cause lignin / PLA

consists of the Fig. 3 Know, The addition of lignin increases to some extent The elastic modulus of composites. with lignin content increasing, wood quality /PLA The elastic modulus of the composite also increases continuously., where, when lignin content 10% when, The modulus of elasticity of the composites reaches the 3.00 GPa, than pure PLA increased approximately 5.63%; and when the lignin contains to further increase to 20% when, The elastic modulus of composites reaches 3. GPa, than pure PLA improves about 10.21%, This description, has _ The addition of a rigid structure to the lignin enhances the overall composite of the stiffness and modulus.

consists of the Fig. 4 Know, when lignin content <10%, Composite The impact strength of the increases as the lignin content increases, and when Woody content >10%, impact strength of composite decreased gradually, When the lignin content is 10% when, Composite impact strength reached the most Large value, to 4.3 MPa, than pure PLA raised approximately 5%. This says "" When the lignin content is not high, the hedging caused by the addition of lignin the promotion of energy absorptive capacity dominates, make composite material toughness Improve; but with lignin content _ Step Increase, lignin for Structural defects, So when lignin content exceeds 10% After, Composite impact strength is declining, when lignin content 20% when, lignin / PLA Composite impact strength is even lower on a pure PLA.

Consolidated Fig. 2 ~ Fig. 4 to discover, when lignin content is in 5% ~ 10% around, lignin / PLA Mechanical properties of composites relatively well.

2.2 Vicat Softening temperature analysis

Tab. 2 The shows lignin in different lignin / PLA dimensional card softening temperature for composites. as an Important indicator of material thermal performance and production product quality, vicat The higher the softening temperature, The material's the better the thermal deformation ability. from D ab 2 can see, when composite material lignin content 5% when, Its D-card softening temperature is 3 °C, relative to pure PLA for 7 °C has some improvement, describes lignin the excellent heat resistance of the itself helps improve lignin / PLA complex, Overall heat resistance. But as the lignin content increases, complex The dimension of the material's softening temperature begins to decrease, and the lignin content up to up to 15% less than pure PLA, This may be because with

the increase in lignin more , hydrogen bonding between lignin molecules strengthens to occur reunion , form structural defect the , makes the composite's card softening temperature decrease .

Tab . 2 Vicat softening temperature to lignin/pla com -
posites With different contents of of lignin

Content of lignin/% 0 5 10 15 20

Vicat Softening temperature/c 62.7 68.3 63.1 62.2 59.7

2.3 SEM parsing

Fig . 5 is lignin with different lignin / PLA Composite Material material SEM Chart . You can see from the diagram , when lignin content is lower when , distribute lignin evenly across PLA Matrix , interface Knot better , This is mainly due to the phenol hydroxyl group in lignin and the in PLA the carboxylic acid can form hydrogen bonds , so lignin is more compatible with PLA good [9] . But as the lignin content increases , lignin and PLA Base The gap between the bodies becomes more , interface Less binding ,This is because There are more hydroxyl groups in the wood the quality , with strong intramolecular and intermolecular hydrogen Key action , lead to easy reunion between lignin , and reunion of lignin does not spread evenly across PLA base , makes lignin and PLA in Microscopic separation of each other . at the same time ,SEM also support PLacomposite material

The mechanical properties and heat resistance of the material decrease strictly when it contains more lignin bad , and The massive agglomeration of lignin affects larger structural defects ,

heavy Behavior -- as the lignin content increases , lignin and PLA eventually results in a significant reduction in mechanical properties and heat resistance of composites .

The matrix cannot be well compatible with , Composite interface Changes

2.4 hydrophilicity Analysis

The contact angle refers to the gas , Liquid , The gas that is made at three intersection points - Liquid The tangent of the interface through the liquid and solid - The angle between the liquid lines 0, Yes measures of wetting degree . Fig. 6 is different lignin / PLA composites Initial contact Angle comparison Chart , from Fig .6 You can see ,with lignin Increase in content , lignin / PLA Composite Initial contact Contest the gradient, is the hydrophilicity drop . This is mainly because lignin except with the "" has polar hydrophilic hydroxyl groups outside the , also has hydrophobic non-polar phenyl propane skeleton . in test lignin /PLA Composite with Tentacles , Because the time is shorter , The hydroxyl group in the lignin, and so on. has not yet effectively adsorbed water molecules , The hydrophobicity occupies the dominant at this time .

Fig . 7 is lignin with different lignin / PLA Composite Material A comparison of the water absorption of a material soaked in deionized water . from Fig. 7 to to see , with soaking time extended , Water absorption curves for five materials start with a significant increase , then increase gradually decrease . under the same soak time , lignin / P LA Composite water absorption rate with wood Increase quality content . This is due to the existence of a lignin structure more hydroxyl , A that can form intermolecular hydrogen bonds with water molecules with the wood increased quality content , after soaking long enough to adsorb more water molecules . also , from SEM Results , lignin content more High time , occurrence of agglomerated lignin granules with PLA interface knot between the matrix Fit Difference , The interface produces more pores , after full soak more water molecule access to material inside , This is also causing the lignin content to increase The reason for the enhanced water absorption of the composite after " _ M.

3. Conclusion

(1) The addition of a small amount of lignin will make the lignin / PLA Composite Material The crystallinity of the material has decreased , But with the lignin content further mentioned high , The crystallinity of the composite increases

gradually. . when lignin content is up to to 20% when , composite crystallinity greater than pure PLA.

(2) increases with lignin content , lignin / PLA Composite the tensile strength and elongation at break gradually decrease , and the modulus of elasticity is reduced by up +, impact strength increases first and then decreases , when lignin content in 5%~10% when , composites have relatively good mechanical properties .

(3) The addition of a small amount of lignin helps improve lignin /pla dimensional card softening temperature for composites , But with lignin content in a Step increased ,composite card softening temperature decreasing again .

(4) when lignin content is low , lignin / PLA Composite interface better , But with lignin content increasing , Composite interface difference between degrees of change .

(5) increases with lignin content , lignin / PLA Composite Initial contact angle increase , that's hydrophilic drop . But after soaking the composite material the water absorption of the material increases with the lignin content , : , water absorbent-enhanced .

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