Synthesis and properties of phenolic modified enzymatic hydrolysis Lignin-epoxy Resin/epoxy resin Composites

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Abstract: With the enzymatic hydrolysis lignin (EHL) as the raw materials, And the phenol-sulfuric acid method was used to modify EHL. Under alkaline conditions, lignin-epoxy resin (L.EP) was Synthesized by phenolated lignin (PL) reacted with Epichlorohydrin (ECH). The structure of EHL and its modification and the synthetic resin were by FT-ir. The effects of factor reaction conditions on the process of phenolation were discussed. The results indicate that the effect of modification s the best under the condition of 3.0 h, 95 C, and 4 ml/g H2so4 (2 MOL/L), and the content of phenolic hydroxyl group reaches 4 632, which increases by 42% compared with EHL. The effects of different LEP adding amount on the mechanical properties and thermal properties of L-ep/epoxy E-51 Composites were investigated. The results show this tensile strength of L-ep/epoxy E-51 Composites is the best when amount of L-EP is 5%, which increases by % The compared with the pure E-51 epoxy resin. The increase in thermal stability of L-ep/epoxy E-51 composites is enhanced. The Non-thermal method is used to analyze the curing kinetics of epoxy E-51 and L-ep/epoxy E-51 composites. The results reveal that L-EP has a certain effect on the curing of L-ep/epoxy resin Composites.

Keywords: enzymatic hydrolysis lignin; Epoxy Resin; Composites; mechanical properties; thermal properties

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Epoxy (EP) has good mechanical properties, binding, Electrical insulation and chemical stability, to be used as adhesive, paint and composite resin matrix, in construction, Mechanical, Electrical and electronic, fields and aerospace applications wide1, but its synthetic raw material double phenol A comes from non-renewable petrochemical products, with Petroleum capital source scarcity and its price rising, Finding and utilizing renewable assets source instead of bisphenol A As the raw material for the preparation of epoxy resins, has become for the current urgent need to resolve - problem. Lignin (L) is from " benzene propane structural unit through carbon carbon key (C-C) and ether
keys (C First 0- C ) connected three-dimensional mesh polymer material, is nature only renewable biomass with aromatic ring structure, Its content is only times over cellulose, every year in our country, we have a large number of wood for pulping waste Discard form emitted or burned, cause tremendous resources Waste[4].

A wide range of lignin sources, The molecular structure of the contains alcohol hydroxyl groups and phenol hydroxyl, also contain aromatic ring structure, can be used with Epichlorohydrin alkane (ECH) occurrence of epoxidation, generate high thermal stability, rigid epoxy. But due to lignin reactivity low in the use of lignin instead of BPAA synthetic epoxy before, requires Modify it, increase its reactivity[5 6], phenol as a kind of important modifier, can increase the content of the phenol hydroxyl group in lignin structure, has been widely used in the modification of lignin. podschun etc[1] to Beech solvent type lignin, to its phenol modified, Increase the number of potential cross-linked points, and Analysis Effects of different reaction conditions on the degree of phenol :Ma etc[1 7] phenol modified rice husk acid insoluble lignin, explores the optimal modification of condition Alonso, and so on [all] studied oxalic acid as a catalyst, Phenol Structure of modified Cork lignosulfonate, Analysis of reaction conditions to Effects of phenol product performance, And get the best phenol condition, Yang etc[1] Phenol in four different lignin under alkaline conditions modifier, through two-dimensional nuclear magnetic resonance (hsqc NMR ) and phosphorus -NMR ( To P NMR) analysis before phenol The structural characteristics and active parts of lignin after are.

enzymatic hydrolysis of lignin ( EHL ) is enzymatic hydrolysis of corn straw preparation can Source ethanol or bio-natural gas residue after a relatively mild process from. compared to the traditional paper waste liquor extraction of the lignin ratio, enzymatic hydrolysis lignin preserves the lignin active group, therefore has high reactivity. This study was based on the previous work of the former Foundation[1 7], using phenol - Sulfuric acid method for phenol in enzymatic hydrolysis of lignin Modify, Modified phenol process and optimized phenol condition, to increase The content of phenolic hydroxyl in its molecular structure; under alkaline conditions, Modified ECH and ,, reactive Synthetic bio- Epoxy, Research on its pair of Bisphenol A shadow of the thermodynamic properties and solidification kinetics of epoxy resins ring, Research results for reproducible enzymatic hydrolysis residues in thermosetting epoxy resins The effective use of the provides theoretical basis.

1. Experimental materials and methods

1.1 raw materials

EHL , Industrial, Shandong Longyuan Biotech Co., Ltd. (Remnants sugar <3%, ash <5%, Purity >8 %.

Phenol , concentrated sulfuric acid, Na 0 H , Concentrated hydrochloric acid, acetone is divided into Analysis Pure , Nanjing Chemical Reagents Co., Ltd.; ECH , Parse Pure, on Hailing Chemical Reagent Co., Ltd., four methyl bromide, analysis Pure, Group Chemical Co., Ltd.; HUF, Hefei Blog American Biotech Co., Ltd.

1.2 Experiment Method

1.2.1 Phenol enzymatic hydrolysis of lignin ( PL ) synthesis

under the catalysis of acid, lignin Styrene-propylene unit side chain a bit the carbon atoms on the form a carbon cation because of the proton, phenol class substances subjected to a carbon-cation attack with a lignin side chain condensation, the right or adjacent position of phenol hydroxyl group with C _ C The shape of the The type connects to lignin.

Concrete steps: take 3. g EHL, one Set volume 2 mol/l h2so4 solution add to 1 ML three-mouth flask, warming up through 8 C , Heat-stirring 1.5H, Join 4.5g phenol, following continue warming to set temperature, reaction period. end of reaction, Centrifuge, Remove upper layer acid, then rinse with deionized water, remove residual acid and phenol @ C Vacuum dry 24 h, get phenolic wood Vegetarian (PL), reaction equation as shown in figure 1 shows[1].

1.2.2 phenol lignin - Synthesis of epoxy resins

To call 5. g/PL , G ECH , 55, Four methyl ammonium bromide Catalyst, Add to ml three -Port flask, Stir warm up to 6 C, drop in G Na 0H, Insulation Response
2. 5 H . end of reaction, cool , with 1 mol/l on HCI Solution Adjustment Products PH to Neutral , rotate evaporation to remove residual ECH, products washed after distillation ,Centrifugal , Wood Quality after drying - Epoxy ( L - EP ). reaction equation diagram 2 : !.

tests and representations

Phenol Hydroxyl content determination : using the method of Fu-phenol ( FC Method ), with phenol as a standard to draw a standard curve 1).

Determination of epoxy value : with hydrochloric acid - Acetone method for chemical drop set [1] 1. Hydrochloric acid can be combined with a woody lignin-based epoxy resin, the epoxy base Group occurrence reaction , Excess hydrochloric acid by a certain concentration of Na 0 H solution to titration .

Infrared Spectral analysis : takes the KBr Tablet method, in the United States PE Company's FT - IR -360 analysis on the Type Infrared Spectrometer , To determine
Range is 4 ~ cm-1 , scan times Times .

Molecular Weight : first to the lignin and phenolic lignin samples into the row acetylation , with four tetrahydrofuran ( THF ) for elution , will acetylation samples after fourTetrahydrofuran, The concentration is approximately 1 mg/ml. mining with us Agilent 1100 gel chromatograph test , velocity to 1 ml/min, the Sample quantity is June . with polystyrene (PS) as a sample to correct the molecular weight of the Samples , on the resulting molecular weight distribution curve Line points , get count molecular weight Mnand the heavy-weight numerator On Mw.

tensile performance test : to combine phenolic lignin with different content to epoxy add to E-51 Resin , based on theoretical value Add polyamide 593 curing agent . goes through three curing stages in turn :

c , 2 H ; c , 3 H ; c , 1 H . follow GB/t 1040.2 -2006(1) with ; Zhu Chun xin er si material testing company's Universal tester for tensile performance test .

TG Test : using the United States TA Company's TGA Q5000 Type thermogravimetric Analyzer , sample about each time 3 ~ 5 mg , temperature scan fan surround ~ c ,warming rate 10 c/min , nitrogen flow rate

Ten ml/min .

Scanning electron microscope test : will L-ep / Epoxy Composite solid spline stretch cross section , on conductive glue , is sprayed with after , United States FEI Company'sQuanta $ Ambient scanning power Sub-microscope ( SEM ) to observe the morphology of the epoxy composite cross-section .

DSC Test : using the German Netzsch Company's DSC F 3 type differential scanning calorimeter , test sample approximately each time 5 ~ MG , temperature Scan range ~ C , N2 flow rate $ ml/min.

2. Results and discussions

2.1 phenol lignin - Structure of epoxy resins

EHL , PL and L-ep The IR spectra of are shown in Figure 3 shows . to see ,EHL on 3 404 cm-1 is strong 0-H Flex Peak , on 2 940 cm-1 Place to methyl , methylene

C - H Flex Vibration Peak , in the 1 126

benzene ring vibration Peak , 1 035 cm -1 for the more invasive Mukifang ring c-h bending vibration peaks of .

and EHL comparison , PL on 753 cm -1 , 691 cm -1

An absorption peak of two new single substituted benzene rings appears at , This is EHL The result of a condensation reaction of the side chain of the to the ortho-position of phenol ; 3 cm-1 near 0- H Scaling Vibration peaks widening , and Low wave offset , Description of phenol modified , enzymatic hydrolysis of lignin 0- H content increased .

and PL compares , L - EP structure and PL is similar , says Ming PL Participate in the reaction of the substance , 1513 cm-1 at Asymmetric deformation of epoxy group vibration peak ,1 246 cm-1 at C -0 [ ] and C=0 asymmetric Flex peaks , 915 cm-1 Place feature absorption peaks for epoxy groups , above description successfully synthesized L- EP
2.2 Process optimization of phenolic modified lignin

phenol concentration (C) - absorbance curve like Figure 4 shows. can look at out of, phenol concentration and 760 nm There is a linear pass between the absorbanceDepartment, its equation is: A = 0.0111C + 0.08211 correlation only $^2=0.9948$, to use the line as the determination of phenol in modified lignin the standard curve for hydroxyl content.

diagram 5 is the reaction time (H), reaction temperature (C) and, H2SO4 usage (ML/G, relative to EHL) phenol-hydroxy lignin in phenol-hydroxyl

Phenol and the absorbance
The effect of the base content.

by Diagram 5 (a) Know, with the extension of the phenol time, modified Wood quality phenol hydroxyl content rises first and then lower, response 3.0h, phenol hydroxyl content reaches maximum. with phenol time extension phenol The greater the reaction is, the more complete the, the phenolic hydroxyl content increases. But when phenol time is too long, partially phenol lignin with condensation, phenol the hydroxyl content decreases. The result indicates that the, reaction time is 3.0h best.

from Diagram 5 (b) Know, as the phenol temperature increases, phenol-Wood quality phenol hydroxyl content rises first and then decreases, When phenol temperature is then C when, phenol hydroxyl content reaches maximum. with phenol temperature elevation, The more complete the phenol reaction, phenol hydroxyl content rising high; When the phenol temperature is too high, The partially phenol lignin itself will With condensation, so phenol hydroxyl content is gradually reduced. so, wood The phenol temperature control of the element in C more appropriate. by Diagram 5 (c) Know, with h2s04 Increase in dosage, Phenol the phenolic hydroxyl content of lignin increases first, then down, h2s04 amount to 4ML/g when, % phenol hydroxy content reaches maximum. h2s04 on anti should be used as a catalyst, so as its dosage increases gradually, Catalytic phenol. The more complete, so phenolic hydroxyl content increases. when H2S 0 dosage exceeding 4ML/g when, under conditions of high temperature strong acid under lignin easy condensation, affects phenol reaction, and acid dosage overlarge, increased dissolution of phenol lignin, causes phenol hydroxyl reduction small, so select H2S 0 4. The amount of is 4 ML/g.

is known by the above analysis, reaction time 3. Oh, reaction temperature 2 c, mol/l H 2S 04 dosage of solution is 4 ml/g when, best phenol. tested four groups of best conditions for parallel experiments with phenol -Modified lignin phenol hydroxyl content, get an average of 4 632 mmol -g$^{-1}$. enzymatic hydrolysis of lignin phenol hydroxyl group is 3. 257 mmol -- 1, after phenol-modified processing, lignin phenol-hydroxy The base content is increased by the 42%.

2.3 Relative molecular weight of lignin

enzymatic hydrolysis of lignin (EHL) and phenol lignin (PL) count Molecular weight $M_w$ and weight-average molecular weight $M_w$ test results for table 1 "show." can see,enzymatic hydrolysis of lignin modified by phenol, No on weight average molecular weight, or number of homogeneous molecular weight and enzymatic hydrolysis ligninto decrease, scatter smaller, indicates phenol reduction The molecular weight and structural complexity of enzymatic hydrolysis of lignin.

2.4 Wood Quality - Epoxy (L - EP) Epoxy value L - EP The epoxy value of E evaluates:

(V-VI) C
where: V for blank test consumption NaOH the volume of the standard solution (ML); V1 consumes for sample tests NaOH the volume of the standard solution (ML); C is NaOH the molar concentration of the standard solution (mol/L); W is L-ep Quality of (G).

L-ep The epoxy value data for the is the table 2 shows . unknown , Group Ping rows with less results , data Reliable , L-ep The average ring for Oxygen value 1. mmol/g .

Table 2 Phenol modified lignin - Epoxy resin value

Table 2 Epoxy value of phenolic modified lignin-epoxy resin

Experiment 12 3
Epoxy value/(mmol g⁻¹) 1.52 1.57 1.56

2.5 L-ep / Epoxy E-51 Tensile properties of composites

diagram 6 is L - EP / Epoxy E -51 tensile strength of composites and modulus of elasticity. can see , with L -EP Increase content , L -EP / E -51 The tensile strength of the composite increases first and then decreases by . loop Epoxy resin composite tensile strength in L-EP Add to 5% reaches maximum , increase to 26% , over 5% start on Drop. This is because L-EP contains more aromatic rings , its plus Adds the number of rigid chain segments in a blend solidify , composite rigidity increases , tensile strength increases [1]; But because the L - EP Lower Epoxy value for , and E -51 Epoxy Compatibility worse , low cross-linked when curing , causes its content to be greater than 5%after L - EP / Epoxy E -51 The tensile strength of the drops . other , can to see with L-EP Add amount ,L- EP/ epoxy E -51 Composite modulus of elasticity no significant change. These results tables Ming , Add an appropriate amount of phenol modification L- EP can effectively improve bisphenol A epoxy tensile strength , and affect its modulus of elasticity less.

2.6 L-EP/ Epoxy E-51 Composite thermal stability

diagram 7 is different L - EP Add Quantity L - EP / Epoxy E - I Thermal weightlessness curves for composites . L-EP/ Epoxy E-51 Composite Initial degradation temperature ,maximum decomposition temperature and ,OC residual charcoal rate data such as tables 3 are shown in . can see , with L-EP Add amount Increase , L - EP / Initial degradation of epoxy resin composites ( loses heavy 5%) temperature rising , This is because the L - EP has macromolecules structure , heating not breaking down , and E -51 resin formed after cross-linking so that the duplicate The initial degradation temperature of the composite material is increased . and maximum thermal decomposition temperature inadd 5 % -EP Maximum , also indicates the composite resin that is formed at this time The three-dimensional network structure of the solidified material is most tightly stable. other , also

See , with L - EP increased content , Thermal weightlessness of a cured substance decrease , residual quality increase , The high temperature stability of the solidified material high. This is because L-EP The contains a large number of aromatic ring structures, as well as polar groups , increases the force between solidified molecules , and L-EP The structure of hindered phenol in molecule has the process of trapping thermal degradation The function of the free radicals formed by , can effectively increase the heat of the Cure stability [2].

2.7 L-EP and L-EP / section appearance of epoxy Resin curing object Chart 8 to pure E-Wuyi Resin spline and add 5%L- EP , L- EP / Sectional Morphology of epoxy resin composite splines . and pure E-51 Comparison of fracture surface morphology of resin , add 5% L - EP for L - EP / The cross section of the epoxy composite has a river-like crack , and have more branches . description L-EP /E-51 break before to resist greater Force , Therefore the tensile strength of the composite is higher .

2.8 Curing Kinetics of epoxy resin system
Kissinger equation \(^1\)
to
\[
\ln \left( \frac{T_p}{\bar{C}} \right) = \ln \left( \frac{T}{T_p} \right) - R \cdot \frac{E}{R} \\
\ln \left( \frac{R}{A} \right) - \ln \left( \frac{T}{T_p} \right) = 0
\]
Flynn - Wall - O Zawa equation \(^1\)
to
\[
D \left( \frac{N}{E} \right) = 1.052 E^2 \\
D \left( \frac{1}{T_p} \right) = -R \cdot \frac{E}{R} \\
Crane \(^1\)is
\[
D \left( \frac{1}{T_p} \right) = \ln \bar{A} \\
D \left( \frac{1}{T_p} \right) = \frac{R}{E}
\]
the above equation: \(T_p\) is DSC Curve Peak temperature \((K)\); is heating rate \((K \cdot \text{min} - R\) is an ideal gas constant \((8 \cdot J^* (\text{mol} \cdot K)^{-1})\); \(E, E_2\), AE for apparent activation energy \((kJ \cdot \text{mol}^{-1})\); \(A\) is a table-pointing front factor; is the reaction progression.

Diagram 9 is an epoxy E - I and add 5% L - EP for L - EP / E -51 composite at different heating rates DSC Curve. Set temperature range \(~ / C\), Heating rate is 5, 10, 15, \(K / \text{min}\). available, epoxy E - wuyi and add 5% L-EP L - EP / Epoxy E -51 The peaks of the composite system at different heating rates top temperature \(T_p (K)\), such as table 4 shows. based on data, binding the above equation \(2) - \left( 4, \text{with} \ln (T / T_p^2) \right) \text{and} \ln N / ? \text{to} 1000 / T_p \text{for linear regression as shown ten is shown in}.

Diagram 9 At different heating rates E-51 (a) and 5%epoxy E-51 System (b) for DSC Curve
Fig. 9 DSC curves of E-51 (a) and 5%epoxy E-51 system (b) at different heating. Rates
diagram E-51 and 5% ep/epoxy-51 Composite System (b) fitting curves for different equations Fig. Ten Fitting lines of E-51 (a) and 5% L.ep/epoxy E-51 composites system (b) through different equations

consists of the Kissinger equation \(2)\) slope and intercept in \(\ln (\text{Ai}^0)\), ln- form \(2)\) can get apparent activation energy \(^,\) the refers to the Previous the factor lnA. fromFlynn-Wall -Ozawa the slope of the equation. 0.052 E / I, Generation \(3)\) To get the apparent activation energy E 2, and then the \(^,\) and E 2 The average value of the two activation energies as activation energy \(E\), Generation into \(4)\) available reaction progression. The results of the above parameters are calculated as table 5 is shown in. can see, add 5% L - EP after, composite material The activation energy required to solidify the material system is reduced by, This is because the L-

EP has a structure of macromolecules, and Epoxy E -51 resin cross-linking Make it easier to form a three-dimensional mesh structure. This description adds the right amountL - EP can effectively promote L-EP/ epoxy E -51 Composite solidify.

3. Conclusion

(1) Infrared analysis and determination of phenolic hydroxyl content indicate that, Phenol after modification, the structure of lignin is effectively connected with phenol, phenol hydroxy content increase, reactive activity increased; the resultant product
The epoxy group was successfully introduced in the, and structure in the lignin phase is similar to.

(2) The single factor experiment determined the best phenol process: 3. Oh, 95 C, 2 mol/l h2so4 dosage 4 ML /g. best conditions products with phenol radical content up to4 632 mmol / G, more than the original enzymolysis the lignin increase 42%.

(3) Gel chromatographic analysis indicates that, modified by phenol, enzymatic hydrolysis lignin Molecular
weight reduction, Scatter reduction.

(4) Add a moderate amount of phenol lignin - epoxy (L-ep), can enhance L- EP/ epoxy E -51 resin tensile performance, when l-ep Add to 5% when the tensile strength of the composite is increased by the, 26%.


(6) Dynamic Analysis results show that, L - EP can reduce duplicate Consolidated apparent activation of the system, to L - EP / E -51 Epoxy The curing process for the composite has the effect of___.

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