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 dis cussed.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 thecontent of phenolic hydroxyl group reaches 4 632 , which increases by 42% compared with EHL. The effects of different L-EP adding amount on the mechanical properties and thermal properties of L-</b3 1>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 I s 5 %,which increases by % The compared with the pure E-51 epoxy resin. withthe Increase Intheamountofl-ep,thermal stability of L- ep/e-51 composites s enhanced. The Non-sothermal method is used to analyze the curing kinetics of epoxy E-51 and L-ep/e-51 compos</b32 >ites. The results reveal that L-EP has a certain effect on the curing of L-ep/epoxy resin Composites.</b20 >

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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 wide [ ]. 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 8]. phenol as a kind of important modifier , can increase the content of the phenol hydroxyl group inlignin structure , has been widely used in the modification of lignin . podschun etc [] 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] 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 [] 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 [,]] , 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 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 $h2s0_4$ 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 []] .

1.2.2 phenol lignin - Synthesis of epoxy resins

To call 5. $_g$/PL ,. G ECH , . 55_g 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 HCl 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 [ ].

Determination of epoxy value : with hydrochloric acid - Acetone method for chemical drop set []]. 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 M_w .

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[ ] 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

2.1phenol 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

Compound .

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 . 01111C + 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 risinghigh ; 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 h2s0$_4$ Increase in dosage , Phenol the phenolic hydroxyl content of lignin increases first, then down , h2s0 $_4$ amount to 4 mL/g when , % phenol hydroxy content reaches maximum . h2s0$_4$ 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$_4$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 H$_2$ S 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 0$_4$ 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_n 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

1 ooow

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 NaOHThe 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 ,3 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	1	2	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 [?] ; 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 %l-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 materialhigh . 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-likecrack , 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 [/] to

Ln (/?/Tp) = Ln (fees) a Shan (1/Tp) (2)

Flynn - Wall - 0 Zawa equation [/] to

D (ln") = 1. 052 E 2 ()

D (1/Tp) -- ~R ~ ()

Crane '] is

D (ln/?) = one AE ()

D ($1/T_p$) $^-$[R] ()

the above equation : Tp is DSC Curve Peak temperature (K); is heating rate (K . min - R is an ideal gas constant (8 . J * (mol • K)$^-$. ; E,E2 ,AE for apparent activation energy (kj • mol- 3 ; 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 Set temperature range ~/C, Heating rate is 5, 10, 15, K /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 Tp(K), such as table 4 shows . based on data , binding the above equation (2)~(4, with ln((/?/ Tp^2) and LN /? to 1000/T_p for linear regression as shown ten is shown in .

diagram 9 At different heating rates E-51 (a) and 5%l-ep/epoxy E-51 System (b) for DSC Curve
Fig. 9 DSC curves of E-51 (a) and) %L-ep/epoxyE-51 system (b) at different heating. Rates

diagram E-51 and 5% l-ep/epoxye-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 ^(Ai/^), In- form (2) can get apparent activation energy ^ , the refers to the Previous the factor InA . fromFlynn-Wall -Ozawa the slope of the equation 1. 052 Ez / 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 £ , 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 $h2s0_4$ 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%.

(5) thermogravimetric Analysis show , add different content L - EP , to enough enhancements L- EP / E -51 Thermal stability of epoxy resin composites .

(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 _ . .

References

1. Auvergne R , caill0l s,david g,*et al.* biobased thermosetting epoxy : Present and Future[j]. Chemical reviews, 2014, 114 (2): 1o82-1115.
2. Gao Kun , Shan , Sun Baogang , , and so on . Hot and humid aging on fiberglass / Epoxy Effects of composite performance []. Journal of Composite Materials , 2016,6:1147-1152.

GA0 K,shi H Q,sun B g,*et al.* Effects of Hydro-ther mal aging on properties of Glass Fiber/epoxy composites[j]. Acta materiae compositae sinica , 2016 , (6): 1147-1152 (inchinese)

3. as ADA C, BASNET S, 0TSUKA M , *et al.* Epoxy resin synthesis using low molecular weight lignin separated from various lignocellulosic [J]. International Journal of biological macromolecules,2015 ,74:413-419.
4. laurichesse S,aver0us L. Chemical modification of lignins</ b20>: towards BioBased polymers[j]. Progress in polymerscience,2014, 7:1266-1290.
5. Liu Wenjun , Meng Lingjun , Lu Ling , , and so on . alkali lignin hydroxyl methylation modified []. East North Forestry University journal ,2013, 6: 130-134.

LIU W J , MENG L J , LU Q , *et al.* Soda ligninhydroxym-ethylation [J]. Journal of Northeast forestry University, 2013, 41 (6): 130-134 (Inchinese).

6. Yang L, WANG X F, CUI Y , *et al.* Modification of renewable Resources-lignin-by three chemical methods and its applications to polyurethane foams [J] polymers for Advanced Technologies , 2014 , (): 1089-1098.
7. SUN y s,qiu X q,liu y Q. Chemical reactivity of alkali lignin modified with laccase[j]. Biomass & Bioenergy,2013, : 198-204.
8. PAN H,sun G,ZIIA0 T. Synthesis and characterization of aminated lignin [J]. International Journal of biological macromolecules,2013 , 2 (): 221-226.
9. P0dschun J, saake B, Lehnen R reactivity enhancement of organosolv lignin by Phenolation for improved bio-based]. European polymer Journal, 2015, : 1-11.
10. MA Y J , ZHA0 X « CHEN X, *et al.* An approach to improve the application of acid-insoluble lignin from Rice hull in PHE-

Nol-formaldehyde Resin[j]. Colloids and Surfaces A-physico- chemical and Engineering Aspects, /b11> on, [* * []] 377 (1-3):

284-289.

11. al0ns0 M V , 0LIET M , R0driguez F,*et al.* moditi-cation of ammonium lignosulfonate by Phenolation for use in phenolic resins [J]. Bioresource Technology, on $, 9:

1013-1018.

12. Yang S , WEN J L , YUAN T Q , *et al.* characterization and phenolation of Biorefinery technical lignins for lignin-Phenol-formaldehyde Resin adhesive Synthesis [J]. RSC advances, 2014, 4 (): 57996-58004 .
13. P0dschun j,stucher a,saake b,*et al.* Structure function Relationshipsin the phenolation of Lignins from </ b11> different sources [J]. ACS Sustainable Chemistry & engi-neering, 2015,3 (Ten): 2526-2532.
14. Sail , Huangpingping , Guo Minghui . Study on the method of improving lignin phenol hydroxyl content into show []. Journal of Southwestern Forestry University , 2014, 6 (): 98-103.

ZHANG F,huang p p, GU0 M. Progress in increasing phenolic hydroxyl content of lignin[j]. Journal of Southwest forestry University, 2014, (6): 98-103 (in Chinese) .

15. Li Wenting . Ionic liquids [Bmim]cl Synthesis of lignin lignin-based epoxy resins in and cured [D]. Huainan : Anhui Polytechnic University , 2015.

LI W-Synthesis of lignin-based epoxy resin in ionic liquid [BMIM]CL and Characterization[d]. Huainan: Anhui University of Science and Technology , 2015 (in Chinese).

16. Raiyurong , Zhang Zeng , yellow thousand strong , , and so on . FC method for determination of phenolic hydroxyl in lignin and paper plasma base []. China paper Journal ,2007, 1: 54-58.

LAI Y r,zhang Z,huang G Q,et Al Determination the content of phenolic hydroxyl groups in lignin and pulp wit H Fc-method[j]. Transactions of Pulp and Paper, 2007, 22 (1): 54-58 (Inchinese).

17. Zhao Jianbing , Wang Shibing . optimization of synthesis conditions for lignin epoxy resins []. Chemical and Bioengineering , 2015, 2: 63-66.

zha0j B,wang B. 0ptimization of Synthenic Conditions of lignin epoxy resin[j]. Chemistryand Bioengineering, 2015, 2: 63-66 (Inchinese).

18. China National Standardization Administration Committee . Determination of tensile properties of plastics : GB/t 1040- 2006[s]. Beijing : China Standard Publishing house , 2006. Standardization Administration The "for" tensile properties of plastics : GB/ T 1040-2006[s]. Beijing:standards Press of china,2006 (in Chinese).
19. Ferd0sian f,zhang Y S,yuan Z s,*et al*. Curing Kinetics and mechanical properties of bio-based epoxy composites Comprising lignin-bised epoxy resins [J]. European,2016, polymerjournal : 153-165.
20. XIA0 X, LU S,qi b,*et al*. Enhancing thermal and mechanical properties of epoxy resins by addition of a hyper-</ b30>branched aromatic polyamide grown on microcrystalline cellu lose fibers[j]. Rscadvances,2014, 4 (+) : 14928-14935.
21. CHEN M Q , LIU S M , I F , *et al*. The study on curing kinetics of lignin-based epoxy resin system using Non-isother- MALDSC method[j]. Advanced materials, 2013, 788:223-227.
22. Li Xiaoying , Chai Chunpeng , Li Changfeng , , and so on . non-isothermal DSC Research Adding class liquid Crystal pbpcs Curing Kinetics of modified epoxy resins [].Journal of Polymers , 2013 (9) : 1190-1196.

lixj , CHAICP , LICF, etal. Non-isothermal Cure kinet ICS to mesogen-jacketed liquid crystal polymer pbpcs Modi</b3 1>fied Epoxy resin[j]. Acta Polymer sinica, 2013 (9):11901196 (inchinese)

23. Li Heng , Wang Dehai , Chan Xiaqing . non-isothermal DSC Study of epoxy resin system solid Kinetics []. Solid rocket technology , 2013, (2): 266-270.

LI H,wang D H , QIAN X Q. Curing Kinetics of epoxy resin by non-isothermal DSC method [J]. Journal of Solid rocket Technology , 2013 , (2) : 266-270 (in Chinese).