Free radical scavenging ability of sodium lignosulfonate and its application in food grade polypropylene

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Sodium lignosulfonate (SL) was prepared from waste of cotton lignin (CL) through hydrothermal reaction method. Orthogonal experiment was designed with value of OIT as objective function. Polypropylene (PP) is a polymer produced by the addition polymerization of propylene. It is a white waxy material with a transparent and light appearance, which is widely used in food and pharmaceutical packaging. The results of GPC and TG analysis revealed that SL has stable thermal properties, which means that SL has the potential to be an antioxidant for PP materials. In addition, the scavenging effects of CL and SL were studied. The obtained results exhibited that the SL can obviously increase the scavenging effect on free radicals and it is a kind of new synthetic antioxidant with antioxidant property, which could effectively delay the oxidation of PP. Subsequent rheological experiments proved that the SL/PP sample can improve the heat-resistant oxygen performance of PP under the thermal oxygen shearing environment. Combined with the effect of SL on the mechanical properties of PP before aging, SL has a stabilizing effect on PP thermal oxygen aging.

Keywords: cotton lignin, sodium lignosulfonate, free radical scavenging, antioxidant properties, food grade PP.

INTRODUCTION

Free radicals are molecules or ions with unpaired electrons and are the products of biological metabolism. Certain concentrations of free radicals are one of the necessary conditions for the human body to conduct normal life activities, which can show unique physiological effects. Many redox reactions of metabolic processes can produce free radicals. In the food packaging industry, PP is a commonly used material, and its oxidative degradation is an autocatalytic free radical chain reaction in which many free radicals are involved[1]. However, too much of radicals are harmful to the human physical health, causing disease such as aging, cancer and heart disease, resulting in physiological and pathological changes. There are many free radicals in the degradation process of PP, such as ROOH, HO·, ROO· and RO·etc[2-5].

In view of the importance of free radicals, the search for efficient, inexpensive, low-toxic, and even non-toxic antioxidants has caused much concern. At present, most of the antioxidants commonly used in domestic food packaging materials are synthetic, commercial antioxidants such as butyl hydroxyanisole (BHA), 2,6-di-tert--butyl-4-methylphenol have been widely used due to their strong antioxidant properties. Unfortunately, these antioxidants have strong antioxidant properties, but they have a variety of potential side effects and are toxic to the body's enzyme system. Therefore, the search for natural, high-efficiency, low-toxic antioxidants from plants has become an inevitable trend in the development of antioxidants, and has attracted more and more attention from biologists and pharmacologists[6]. The study[7] found that under certain conditions, sodium lignosulfonate has good antioxidant capacity and free radical scavenging ability, anti-cancer, anti-mutagenic and inhibit the natural oxidation and depolymerization of cellulose, so it has the potential to be widely used in food, cosmetics and medical industries. Therefore, research on new, safe,

stable and natural antioxidant substances is extremely important for people's lives.

The cotton straw is mainly composed of cellulose, hemicellulose and lignin, of which lignin accounts for about 25%. Xinjiang is rich in cotton resources, the amount of cotton that can be harvested is about 1.68×10^7 t, and the yield of cotton straws is 4~6 times that of cotton. However, the current situation is that most cotton straws are handled in simple manner such as smashing, burning or disposal, and there is no resource utilization at all. Due to the shortage of resources per capita in China, Xinjiang is located in arid areas and faces objective limitations of structural water shortage and fragile ecological environment. Cotton straws should be used in high-efficiency and high value-added on-site to avoid resource waste and environmental pollution caused by simple processing. Therefore, it is of great practical value to separate lignin from cotton straws and prepare SL as a natural antioxidant.

In this work, SL was prepared from waste of cotton straw by the method of hydrothermal reaction. The optimum preparation process of SL was determined by single factor and orthogonal experiment. The structure of SL was analyzed by FTIR. GPC and TG analysis were used to study the thermostability of CL and SL. The scavenging ability of CL and SL on HO-DPPH and their iron ion reduction ability were also investigated, so as to provide some basis for the further study of SL. Static rheological experiments and mechanical properties were used to further verify the antioxidant properties of SL in PP.

EXPERIMENTAL

Materials

A sample of cotton (Kashgar, Xinjiang, China) lignin isolated via the method of ionic liquid[8] at laboratory was used as the starting source. Anhydrous sodium

sulfite (Na_2SO_3) and sodium hydroxide (NaOH) were offered by Kelong Chemical Reagent Factory, Chengdu, China. Anion exchange resin and cation exchange resin were purchased from Yuanye Biotechnology Co., LTD., Shanghai, China. The solvent for adjusting pH value was hydrochloric acid solution (HCl) from Alfa Aesar. A lubricant, under commercial name of Calcium stearate, was purchased from Aladdin. Food grade PP powder was purchased from the research institute of Dushanzi Petrochemical Company of China, and the melt flow rate was 5.999 g/10 min (200°C/ 5.4 g). Other chemicals and reagents (analytical grade) used for other analyses were obtained from Aladdin.

Synthetic of SL and design of single factor and orthogonal experiment

The purified CL was modified according to the method of hydrothermal reaction. The specific operation process is shown in Figure 1. More specifically, CL (2.5~3.5 g) and Na_2SO_3 (5 g) were added into water and dissolved completely at room temperature. The pre-prepared solution was put into hydrothermal reactor and reacted for several hours (4~7 h) at high temperature (150~180 °C). The schematic diagram of synthesis of SL is presented in Figure 2[9]. Then HCl solution (1 mol/L) was added to adjust the pH value (11~14) of the mixture. After filtration, pure SL powder was obtained by vacuum drying. Through a series of experiments, it was found that the reaction time and temperature, mass ratio and pH value have a great influence on the OIT after SL mixed with PP.
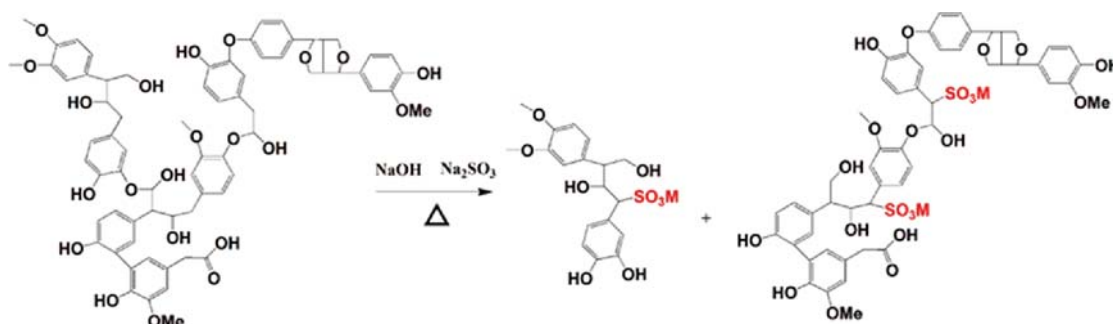
Samples preparation and determination of OIT

PP powder, calcium stearate (0.1 wt%) and SL (0.3 wt%) were injection molded into standard and tensile splines by using an injection molding machine (XL-400VI, Ningbo, China). The experimental flow chart is shown in Figure 3. Taking OIT as the objective function, the optimal conditions were obtained by orthogonal experiment. The OIT was measured by DSC (Q-2000, TA, USA) instrument. Approximately 10~15 mg of SL/PP samples were weighed directly into the crucible to ensure complete contact with the bottom of the crucible. Firstly, the air discharge operation was carried out for 50 min at a gas flow rate of 150 mL/min under a nitrogen atmosphere. Then, the nitrogen flow rate was changed to 50 mL/min and the temperature was raised to 200°C at a heating rate of 20°C/min. After reaching the temperature, the sample was kept at a constant temperature for 10 min in a nitrogen atmosphere. The nitrogen flow was immediately switched to a 50 mL/min oxygen stream and the temperature was continued until the samples were completely oxidized, ending the experiment.

Characterization of lignin

FTIR analysis: The structure of the CL and SL was characterized by FTIR spectrometer (Bruker Equinox 55, Karlsruhe, Germany). All samples were dried prior to measurement. Samples were prepared by standard KBr pellet/disk technique and the wave number range was determined to be 4000–400 cm^{-1}.

GPC: CL is insoluble in organic solvents and it is necessary to carry out the acetylation process. The

Figure 1. Synthesis process of SL
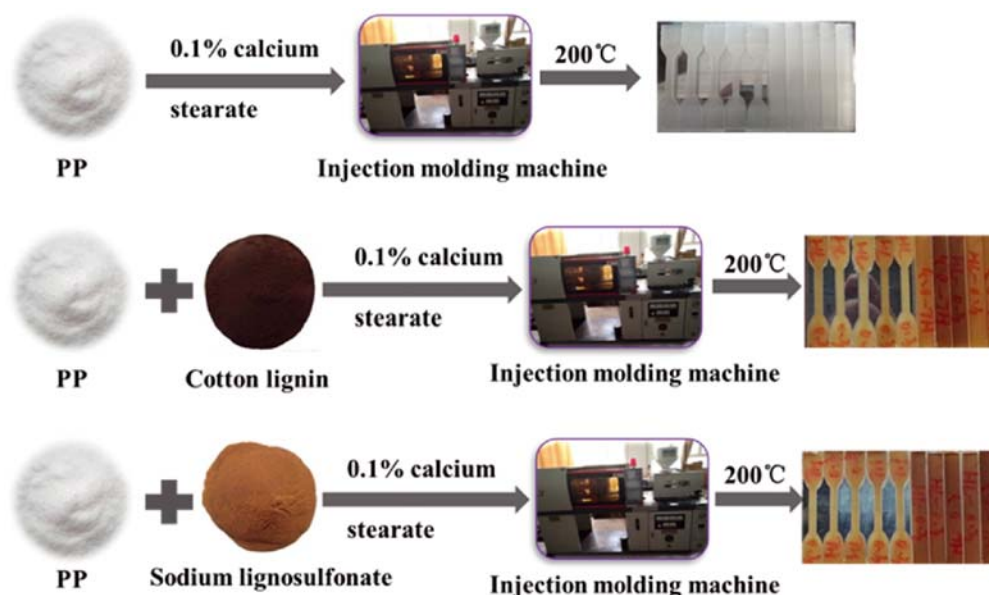

Figure 2. Synthesis of SL

Figure 3. PP and lignin molding process

0.1 g of CL was dissolved in a mixture solution of 1 ml pyridine/acetic anhydride (1:1), and then reacted for 72 h at room temperature in the dark. Then the lignin was centrifuged and washed with ether and dried to obtain acetylated lignin. GPC column (300×7.5 mm, VARIAN, Inc.) eluent, flow rate in DMF was 0.7 ml/min, column temperature was 40°C, polystyrene set as standard and detector temperature was 30°C, which was conducted on Agilent 1260 high performance liquid chromatography equipped with a refractive index detector. The SL was dissolved in an aqueous solution, the flow rate of the aqueous phase instrument (Water 1515 Isocratic HPLP pump/Waters 2487 Dual Absorbance Detector, American Waters Corporation) was 0.5 mL/min, and the column temperature was 30°C.

TG analysis: TG analysis was performed on an Integrated thermal analyzer (HCT-1, Hengjiu, Beijing). Weigh the appropriate amount of CL and SL separately into the crucible, using nitrogen as the carrier gas, set the flow rate to 100 mL/min, slowly heat at 10°C/min, and increase from room temperature to 600°C.

The antioxidant capacity of CL and SL

The factors leading to polymer degradation can be divided into internal and external factors. The internal factors are mainly related to the molecular structure of the polymer, such as the C-F bond energy of polytetrafluoroethylene is 500 kJ/mol, and the C-H bond energy of polypropylene is 410 kJ/mol. In addition, in the polymer oxidation reaction, the rate of hydrogen abstraction from the carbon atom in the oxidation reaction depends on the type of C-H bond, and the C-H intensity is arranged as follows: primary hydrogen > secondary hydrogen > tertiary hydrogen. The C-H bond in the PP molecule belongs to the tertiary hydrogen, so it is easily oxidized. The molecular structure of PP is related to the synthesis process. Generally, its antioxidant activity is mainly sought from external factors. Among the external factors, the most important is thermal oxygen or photooxygen degradation. In the oxidative degradation reaction, there are two periodic reactions (see Fig. 4).
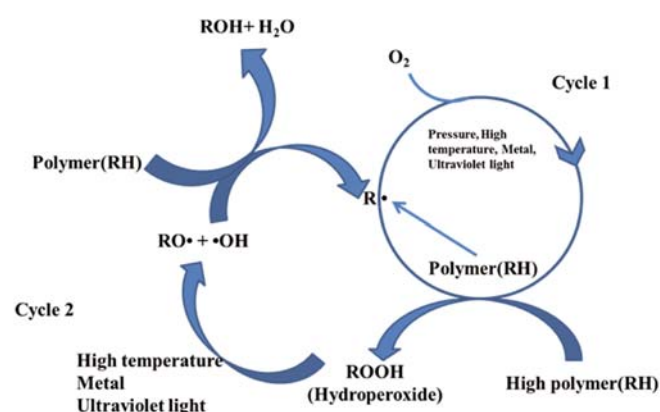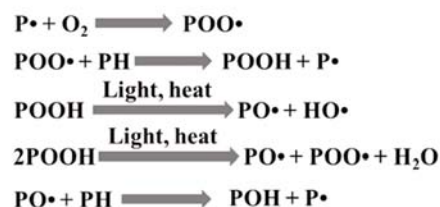

Figure 4. Oxidation cycle of PP

In two cycles, the high molecular polymer is continuously oxidized to form a large number of low molecular compounds, and the reaction process is generally divided into three stages: chain initiation, chain growth (or chain transfer, chain branching) and chain termination:
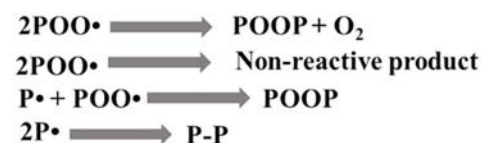

In the above formula, pH represents a polymer, and P· represents a polymer macromolecular radical. In cycle 1, a chain initiation reaction and an oxidation re-

action mainly occur. In cycle 2, a chain growth reaction (ie, an increase in free radicals) occurs mainly. Thus, the macromolecular chain undergoes decomposition, and the molecular weight is greatly reduced, resulting in a decrease in physical and mechanical properties; On the other hand, in the process of reaction, due to disordered cross-linking, disorder control is often formed. The network structure increases the molecular weight and causes the polymer to become brittle, hard, and elastic. Based on this theory, the effect of sodium lignosulfonate on the oxidation process of polypropylene will be discussed next.

Determination of scavenging activity of HO·

The activity of scavenging HO· was determined by reference[10, 11]. 2 mmol/L $FeSO_4$ solution and 2 mmol/L salicylic acid ethanol solution were added to a 10 ml colorimetric tube, 1 ml of a sample solution of different mass concentration. 1ml of 0.05 % H_2O_2 was finally added into the tube and subjected to a water bath for 60 min under 37°C. Using absolute ethanol as a blank control, the absorbance of each concentration sample was measured at a wavelength of 536 nm to be A_0. The sample solution was replaced with 1 ml of deionized water and the above operation was repeated to measure the absorbance A_1. Replace H_2O_2 and sample solution with 2 ml of deionized water and repeat the above procedure to measure absorbance A. The hydroxyl radical scavenging rate was calculated by the equation (1):

$$\text{Hydroxyl radical scavenging rate} = \left[\frac{A_0 - A_1}{(A - A_1)}\right] \times 100\% \qquad (1)$$

Determination of scavenging activity of DPPH·

The antioxidant activity was determined by the radical scavenging activity method using DPPH· as described by a number of literature reference[12–18]. Absorb 2 ml of sample solution, then 2 ml of 1 mg/mL DPPH· and ethyl alcohol mixture solution was added. After incubating the mixture for 30 min, and the absorbance of the sample solution A_i was measured at 518 nm. 2 ml of sample solution mixed with 2 ml of anhydrous ethanol to determine the absorbance of the solution A_j. 2ml anhydrous ethanol was mixed with 2 ml DPPH· ethanol, and the absorbance A_0 of the solution was determined. The radical scavenging activity was calculated by Equation 2:

$$I\% = \left[1 - \frac{A_i - A_j}{A_0}\right] \times 100 \qquad (2)$$

Where A_0 is the absorbance of the control group, A_i is the light absorption of sample group, and A_j is the absorbance of blank group. The antioxidant activity expressed as the clearance rate (I%).

Determination of reduction capacity of CL and SL

The reduction capacity of CL and SL was determined by the method described in the literature[19–22]. Take 2 ml samples of different concentrations, then add 0.2 mol/L phosphate buffer solution (pH = 6.60) and 25 ml 1% potassium ferricyanide solution respectively. In the next step, 2.5 ml 10% trichloroacetic acid solution, 2.5 ml deionized water and 0.5 ml 0.1% ferric chloride solution were added in 50°C water bath after 20 min rapidly cooled to room temperature. The absorbance was measured at 700 nm after 10 min of setting.

The rheological properties and processing stability of SL/PP samples

Static rheological experiment (Minilab II, HaaKe, Germany): Use 6 g pure PP and SL/PP samples (0.3~0.9%), respectively. Barrel temperature to 200°C, speed setting to 30 r/min, the running time is 10 min.

Mechanics Performance Testing

According to ISO 527:2012, the tensile specimens were tested at room temperature with a crosshead speed of 100 mm/min using a computer-controlled universal testing machine (CMT6104, China). σ can be calculated by Equation (3):

$$\sigma = \frac{P}{bd} \qquad (3)$$

in which is tensile strength in MPa; P is maximum load and b and d are the width and thickness of the sample in mm, respectively.

The elongation at break (ε, %) can be calculated by Equation (4):

$$E = \frac{L - L_0}{L_0} \times 100\% \qquad (4)$$

L and L_0 are the length and initial length of the tensile break of the sample in mm, respectively.

RESULTS AND DISCUSSION

Single factor and orthogonal experiment

The optimal preparation process of SL was determined by single factor and orthogonal test with CL and sodium sulfite as initial raw material by using hydrothermal reactor. CL was dispersed into sodium sulfite solution [C(CL/Na_2SO_3 (g:g))= 1:5~4:5] contained in a 50 ml hydrothermal reactor. Following, the reactor was kept under high temperature (150~180°C) in vacuum oven for at least several hours (4~7 h). Next, adding 1mol/ml HCl to neutralize the pH value (11~14) of the mixture. The mixed liquor were dried by vacuum drying oven at least for 2~3 days for obtaining powder products. The effect factors for the orthogonal experiment included respective reaction temperature (A), reaction time (B), mass ratio (C) and pH value (D) of solutions, which are shown in the Table 1.

Table 1. Factor level of the orthogonal experiment L9(34) of preparation for SL

Factor			
Levels	A[°C]	B[h]	C[CL/Na_2SO_3[g:g]	D[pH]
1	170	7	3.5/5	13
2	165	5	2.5/5	12
3	175	6	3/5	11

Through a series of experiments, it was found that the reaction temperature, reaction time, CL/Na_2SO_3 (g:g) ratio and pH value have a great influence on the OIT of SL/PP samples. The following is a discussion of the single process factors based on the basic data of experiments.

The influence of different reaction temperatures on the OIT of SL/PP materials is shown in Figure 5(a). The OIT of the SL/PP samples was studied by changing the temperature (150–180°C) with keeping the other conditions constant. As can be seen in Figure 5a, the
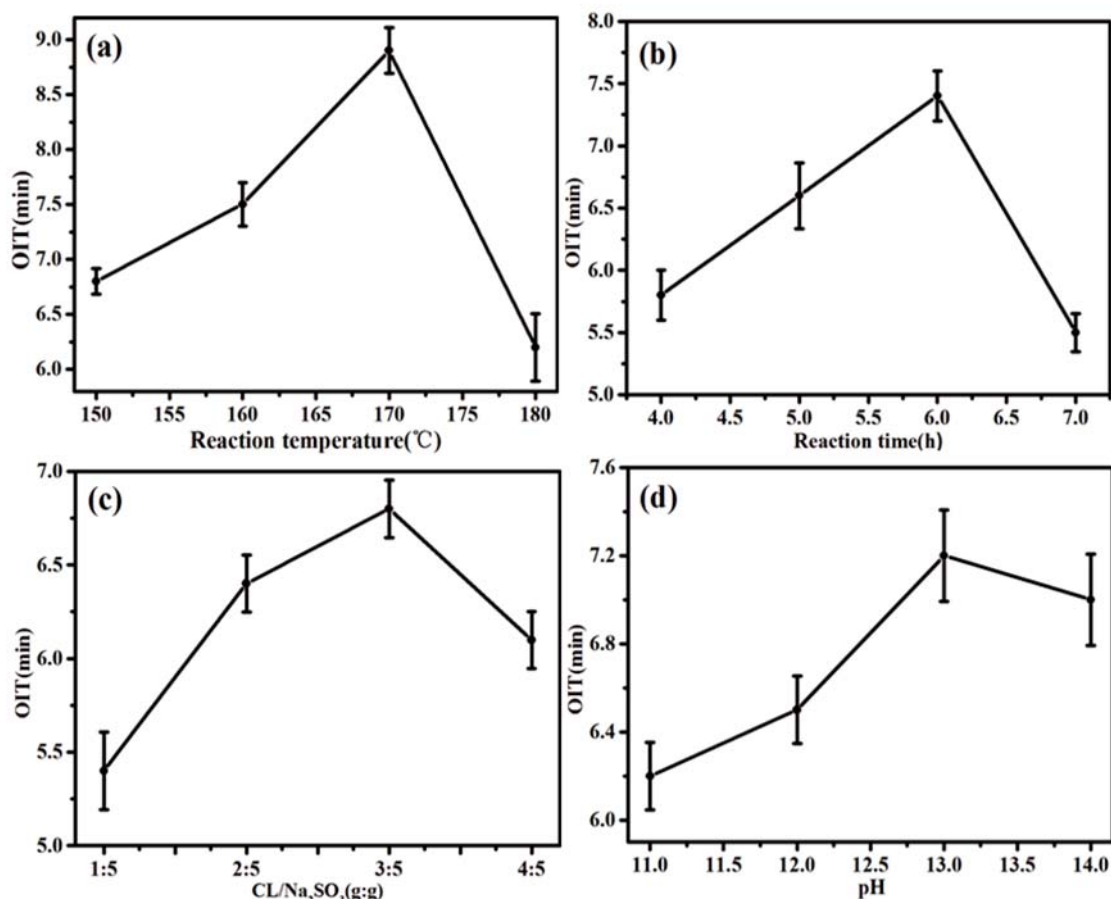
Figure 5. Single factor test results (a) reaction temperature, (b) reaction time, (c) CL/Na$_2$SO$_3$ (g:g), (d) pH

temperature has a very significant effect on the OIT of the SL/PP samples. As the test temperature increased, the OIT of the SL/PP sample first increased and then decreased, and the OIT reached a maximum of 8.9 min at 170°C. At the end, as the temperature increases, the OIT of SL/PP samples decrease continuously. The reason may be that at higher temperatures, SL/PP samples react with oxygen to generate hydroperoxides[23] at a faster rate, thus increasing the consumption rate of SL in PP samples. Therefore, obvious oxidative exothermic phenomenon appears in a relatively short time, at the meanwhile, a suitable test temperature can produce test data with better resolution.

The effect of different reaction times on SL/PP samples is shown in Figure 5(b). As can be seen from the figure, the reaction time has a great influence on the OIT of the SL/PP material. With the increase of reaction time, the curve shows a trend of first rising and then falling, the OIT reached maximum at 6 h, i.e. 7.4 min. When the reaction time reaches a certain value, the OIT of PP material added with SL begins to shorten, which may be because the presence of some macromolecules and other small molecules in the product affects the oxidation process of PP, thus shortening the OIT of PP.

The influence of different ratios (CL/Na$_2$SO$_3$) on SL/PP samples is shown in Figure 5(c). Since PP has melted during OIT testing, the effect of sample quality on its OIT is almost negligible[24]. It can be seen that the amount of sodium sulfite remains unchanged. With the increase of content of CL, the OIT of SL/PP samples first increases and then gradually decreases. When CL/Na$_2$SO$_3$ ratio was 3.5/5, the maximum OIT reached

6.8 min. This may be due to the SL produced under this condition was added to the PP, the internal oxidation occurs obviously, making OIT longer; But the large amount of SL added to PP, oxidation often happens on the surface, the internal oxidation reaction is not significant, making OIT shorter[25].

The effect of pH value is shown in Figure 5(d). The OIT increases first and then decreases with increasing pH value. The final OIT decreased less than the previous three factors. The maximum OIT was 7.2 min. This may be because the color of SL reduces the OIT of PP. After adjusting the pH with hydrochloric acid, the color of lignin will change. On the one hand, the addition of pigment (contained in CL) accelerated the degradation of PP, and in order to capture the consumption of the free radicals generated in the degradation process of PP, SL as antioxidant agent was added[26]; On the other hand, pigments in lignin can also reduce the stabilizing effect of phenolic antioxidants[27].

The data presented in Table 2 exhibited that the influence of each variable on the OIT of SL/PP samples is in sequence: B>D>A>C. The optimal combination is A$_3$B$_1$C$_2$D$_2$. The best modified combination was verified by the sample, and the OIT was 9.1±1.025 min, which was higher than that of other combinations in the orthogonal table. Therefore, this combination was determined to be the best preparation technology of SL, and a lot of modification experiments were should be carried out in the following work.

As can be seen in Figure 6, compared with the pure PP sample, the OIT of the PP sample increased after adding 0.3 wt% CL and SL to the PP. The data show

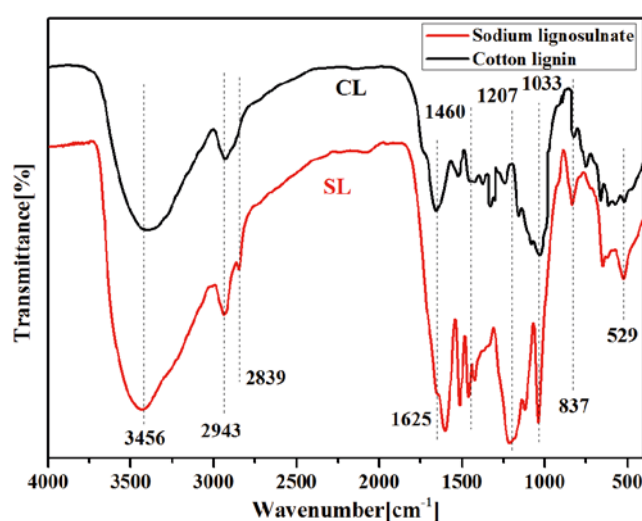**Table 2.** The orthogonal experiment results of preparation for SL

Number	Factors				OIT
	A[°C]	B[h]	C[CL/Na$_2$SO$_3$(g:g)]	D[pH]	
1	170	7	3.5/5	13	7.1
2	170	5	2.5/5	12	7.2
3	170	6	3/5	11	6.9
4	165	7	2.5/5	11	8.3
5	165	5	3/5	13	5.2
6	165	6	3.5/5	12	7.4
7	175	7	3/5	12	8.9
8	175	5	3.5/5	11	7.8
9	175	6	2.5/5	13	7.6
K1	21.3	24.3	22.3	19.9	
K2	20.9	20.2	23.1	23.5	
K3	24.3	22	21.1	23.1	
k1	7.1	8.1	7.4	6.6	
k2	7.0	6.7	7.7	7.8	
k3	8.1	7.3	7.0	7.7	
R	1.1	1.4	0.4	1.2	
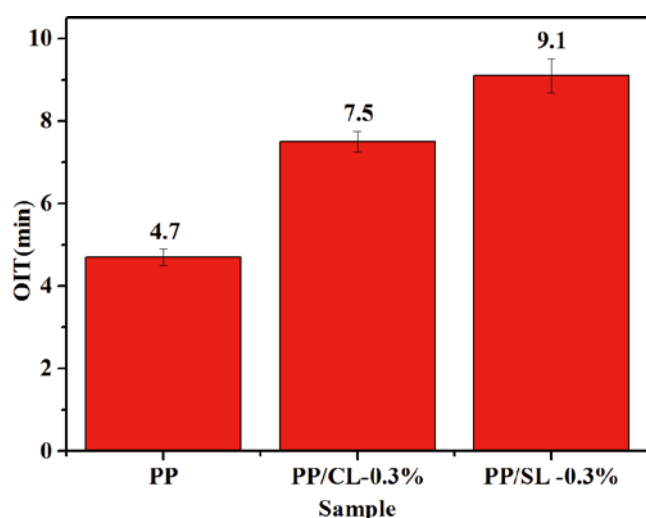
Figure 6. The OIT of PP, PP/CL and PP/SL sample

Figure 7. Infrared spectra of CL and SL

that CL can delay the oxidative degradation of PP in oxygen-rich and high-temperature environments. Although compared with SL, it has a lower ability to delay the oxidative degradation of PP, but it also has a certain antioxidant effect. The literature[28] suggest that the natural polyphenols scavenge PP radicals mainly by transferring hydrogen atoms from phenolic hydroxyl groups to active radicals and quenching the active radicals to stabilize the degradation of PP. This is the reason that cotton lignin and sodium lignosulfonate can delay PP aging.

Characterization of the CL and SL

Figure 7 shows FTIR spectra of CL and SL. The spectra of both samples showed strong absorption peak at 3456 cm^{-1}, attributed to O–H stretching vibration of alcohols, due to a lot of hydroxyl groups in the structure of CL. Another obvious stretching vibration region appears at 1600–1000 cm^{-1}, which are the region of aromatic skeletal vibration of guaiacyl (G) and syringyl (S) units of CL structure. Both of them showed aromatic ring skeleton vibration bands at 1625, 1515 and ~ 1100 cm^{-1} which correspond to sulfonate group. In the region, the characteristic peak at 1600 cm^{-1} is due to the stretching vibration of the benzene ring skeleton, the absorption at ~ 987 cm^{-1} can be assigned to the substituents on the aromatic ring and the band at 837 cm^{-1} can be attributed to C–H stretching vibration[29]. It is due to that primary units of CL have phenylpropane structures, including benzene

rings and carbon chains. The peaks at 2943, 2839 and 1454 cm^{-1} were assigned to the C–H bond vibration of methoxy groups, combined with benzene ring by C–O–C bonds. The above evidences proved that the SL under high temperature and strong alkali environment kept the most representative CL structures and not damaged. The characteristic peaks at 1207, 1033 and 529 cm^{-1} were assigned to the sulfonic groups[30]. As can be seen in Figure 7, compared with cotton lignin, these three peaks of SL have been significantly strengthened, so it can be proved that the sulfonic groups were grafted with CL successfully[31]. The absorption peak of methylene C-H stretching vibration in cotton lignin appeared at 2943 cm^{-1}, and the absorption peak was obviously weakened after sulfonation, indicating that CL was affected by sulfonation reaction. Furthermore, compared with CL, the peaks strength of methyl and methylene at 2928 and 2851 cm^{-1} were enhanced, indicating that the lignin was degraded to a certain extent after modification.

Table 3. Average molecular weight and polydispersity index (M_w/M_n) of CL and SL

Lignin	M$_w$[g/mol]	M$_n$[g/mol]	Polymer dispersity index [PDI]
CL	6948	4062	1.71
SL	4098	3339	1.23

The molecular weight of lignin has an important influence on its antioxidant properties. This work further demonstrates the effect of CL on the oxidation resistance

and thermal stability characteristics of different molecular weight distributions before and after modification. The molecular weight and distribution coefficient of lignin are important criteria for studying its structural characteristics and evaluating the activity of degradation modified products. At the same time, many physical and chemical properties of lignin are not only closely related to the molecular weight, but also restricted by the molecular weight distribution. Therefore, combining the best process conditions of sodium lignosulfonate discussed in the previous sections: The lignin ratio is 2.5/5, the reaction temperature is 170°C, the reaction time is 7 h, and the pH is 12. The molecular weight change of lignin degradation products under the conditions of GPC was used to measure the antioxidant effect of lignin. As can be seen in Table 3, the average molecular weight (M_W) of cotton lignin decreased from 6948 to 4098 and the PDI has decreased significantly. This is possibly caused by the higher syringyl unit content in the lignin and the low M_w indicates small molecules of lignin were extracted. $-HSO_3$ was added to the modified lignin macromolecular side chain, but did not cause too much structural change. As compared with CL, the SL presented lower molecular weight (M_w = 4098) with narrow range of PDI. This shows that during the catalytic degradation process, the connecting bonds between the lignin structural units were partially broken, which caused the original lignin macromolecules to become relatively small molecules. In addition, compared with the original cotton lignin, the dispersion coefficient of SL also decreased from 1.71 to 1.23. It shows that after microwave hydrothermal reaction, the molecular weight distribution range of lignin becomes narrower, and it tends to be more uniform, which will be conducive to the industrial high-value utilization of lignin. The size of the molecular weight obviously cannot

meet the requirements of direct industrial applications, and the molecular weight distribution is also relatively broad, which needs to be uniformized.

Figure 8 demonstrates the molecular weight distribution in further effect on the antioxidant thermal stabilization of SL. As shown in Figure 8, the CL has a single steep degradation stage from 220 to 600°C. The slight weight loss observed over the temperature range of 60–120°C (3 wt%) is due to the volatilization of adsorbed water and light volatiles. At this temperature the weight loss amounted to 60% for all the cotton lignin preparations. The current results are in good agreement with the thermal stability of lignins, in which the lower molecular weight lignin fractions showed better antioxidant properties and thermal stability than unfractionated lignin[32]. As for SL, SL has a stable single steep degradation stage in the region of 251–600°C. There is no obvious weight loss happened between 100–180°C, which indicating that there is no absorbed water and light volatiles exist. The maximum decomposition temperature ranged about 251°C. In the process of degradation, a total of 30% of the weight is lost. TG analysis further proves that SL as a new type of antioxidant is expected to participate in the PP molding process.

In the Figure 8(a), CL has a certain weight loss in the temperature range of 100–135°C. This is caused by the free water in CL, combined with evaporation of water, etc. In the range of 210–270°C, lignin lost 18%. At the same time, it can be known from the DTG curve that the weight loss rate of lignin keeps increasing in this interval and reaches a peak at 370°C. The easily decomposed sugars in the lignin and some small molecular weight lignin groups are rapidly degraded and volatilized. In the temperature range of 350–500°C, the lignin still maintained a high weight loss rate, but the
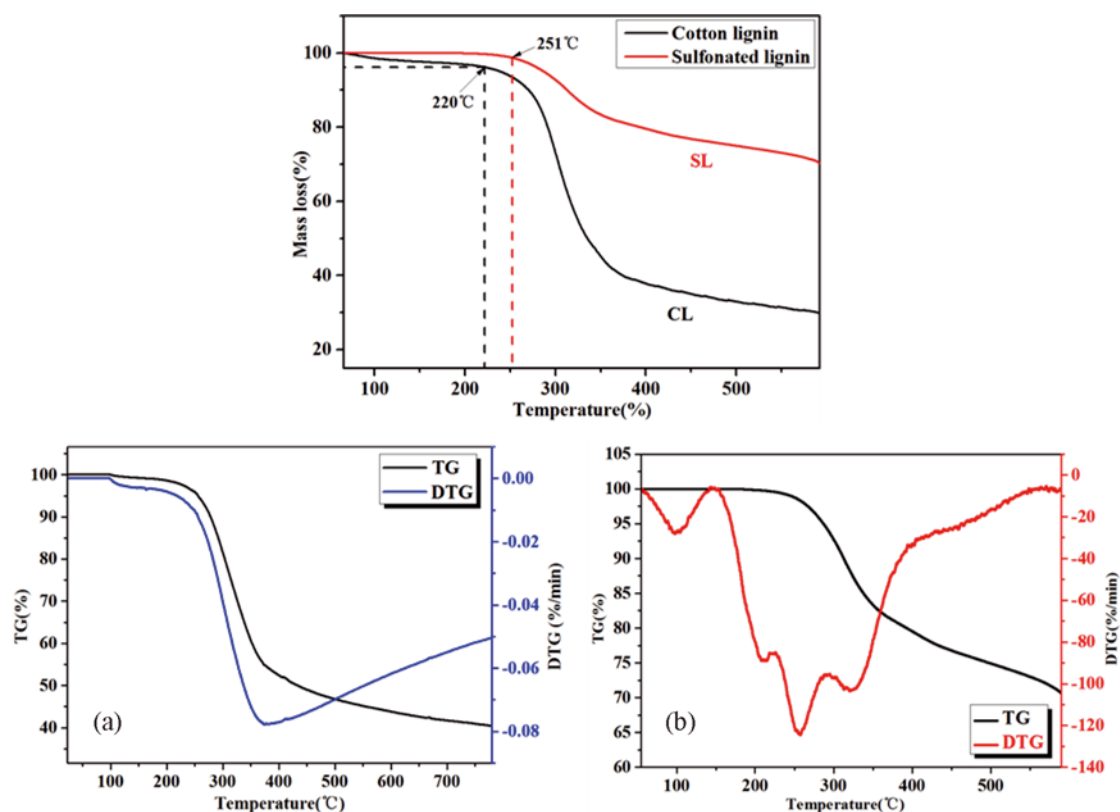

Figure 8. TG-DTG spectra of CL and SL powder under oxygen atmosphere: (a) TG-DTG spectra of cotton lignin; (b) TG-DTG spectra of sodium lignosulfonate

trend was gradually slowing down. This is mainly due to the oxidative degradation of lignin macromolecules combined with air to small volatile molecules. After 500°C, the decomposition of inorganic substances in lignin was occurred. When the temperature reaches 700°C, the weight loss tends to balance, and the residual rate is 39%, indicating that the content of ash impurities in cotton lignin is small.

In the Figure 8(b), SL has a certain weight loss in the temperature range of 26–135°C. This is also caused by the free water in SL, combined with evaporation of water, etc. In the range of 150–200°C, lignin lost 25%. At the same time, it can be known from the DTG curve that the weight loss rate of lignin keeps increasing in this interval and reaches a peak at 250°C. The easily decomposed sugars in the lignin and some small molecular weight lignin groups are rapidly degraded and volatilized. In the temperature of 260–400°C, the lignin still maintained a high weight loss rate, but the trend was gradually slowing down. This is mainly due to the oxidative degradation of lignin macromolecules combined with air to small volatile molecules. After 400°C, the decomposition of inorganic substances in lignin. When the temperature reaches 600°C, the weight loss tends to balance, and the residual rate is 8%, indicating that the content of ash impurities in SL is small.

THE ANTIOXIDANT CAPACITY OF CL AND SL.

Determination of scavenging activity of HO·.

Figure 9 displays the radical scavenging ability of CL and SL. The maximum hydroxyl radical scavenging rate of SL can reach about 98%. In comparison to SL, unmodified CL showed moderate antioxidant activity. These phenomena are trace back to the experimental principle of salicylic acid method for determination of hydroxyl radical scavenging ability. Hydroxyl radicals are produced by Fenton reactions: $H_2O_2 + Fe^{2+} = ·OH + H_2O + Fe^{3+}$; Salicylic acid was added to the reaction system, and the hydroxyl radical generated by Fenton reaction reacted with it, and a special absorption peak of 2,3-dihydroxybenzoic acid would appeared at 536 nm as the above formula shows[33]. As the hydroxyl radical scavenger is added to the reaction system, the hydroxyl radical will be reduced and the production of the colored compound
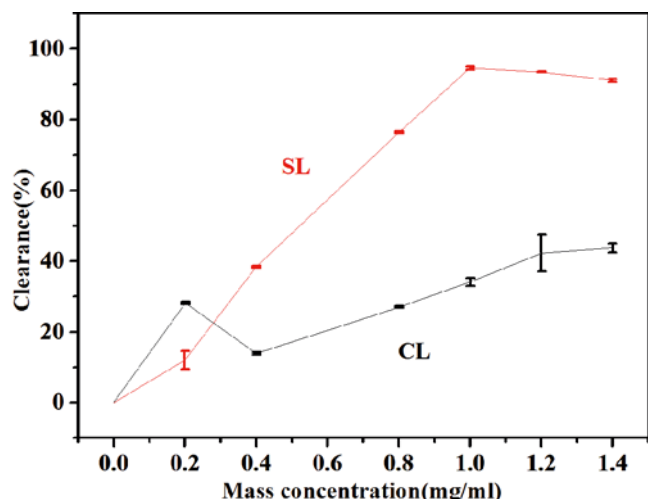
will be correspondingly reduced. However, the addition of SL makes the reaction system clear more free radicals and generate less colored compounds. Although the scavenging activity of SL was ∼ 12% at 0.2 mg/mL, its remained lower than that of CL in the concentration range measured. However, at a subsequent concentration of 0.4 mg/ml, the clearance rate of CL decreased sharply from 28 to 13.83% and then increased gradually, but never exceeded SL. Moreover, the clearance rate of SL has been rising from beginning to end, and there has been no ups and downs. Therefore, this suggests that SL appears to be a more moderate HO· scavenger than CL and the data presented here indicated that markedly antiradical ability of H·. It has been proved that the SL has stronger ability of scavenging hydroxyl radical than the original CL. The HO· is involved in the degradation process of PP, and it is a kind of active oxygen radical with strong oxidation ability, which can easily oxidize various biological macromolecules with high oxidation efficiency and fast reaction rate[34]. As we can see from the picture, SL as a new kind of synthetic antioxidant, which can significantly improve the scavenging rate of HO· and delay the oxidative degradation of PP in the following work.

Determination of scavenging activity of DPPH·

The antioxidant activity of all twelve samples (original CL and SL) was studied using the DPPH· method. DPPH· is a stable free radical with a maximum UV absorption at 518 nm, which is widely used for antioxidant measurements of plant extracts and food supplements, additives, and lignin[35, 36]. Figure 10 graphically presents the radical scavenging ability of the CL and SL as a functional concentration. SL has the best scavenging effect on DPPH· than CL, the maximum clearance rate can up to 45%. In the previous work, some researchers have devoted to studies of the radical scavenging properties of lignins, which are realized as efficient antioxidants of natural origin. However, the research of the radical scavenging properties of CL and SL has not been discussed yet. In general, the free radical scavenging efficiency of DPPH· under homogeneous conditions can be determined by ESR method and spectrophotometry. The spectrophotometry has been selected to explore the radical scavenging ability, which proved that CL as natural antioxidant has
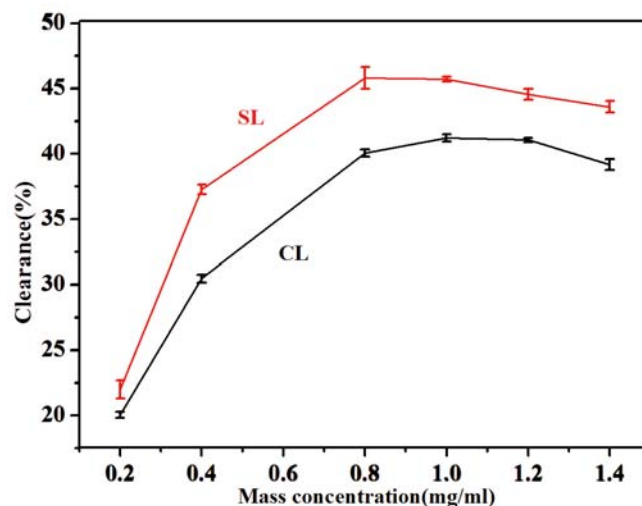
Figure 9. Hydroxyl radical scavenging ability of CL and SL

Figure 10. Results of DPPH· scavenging by CL and SL

good removal rate may be due to some structure activity relationships, including hydroxyl groups in the side chain for increasing scavenger activity. Through the analysis of the interaction rate constant of lignin-DPPH·, the contribution of molecular weight and p-conjugate system of lignin polymer to free radical scavenging was revealed[37].

CL and SL are both polyolefin antioxidants. It can be seen from the Figure 10 that when the concentration of polyolefin antioxidants is low, the DPPH· clearance of both polyolefin antioxidants increases as their concentrations increase. When the concentration of polyolefin antioxidant exceeds 0.8 mg/ml, as the concentration of polyolefin antioxidant increases, the clearance rate decreases with the increase of antioxidant concentration of polyolefin. When the concentration of polyolefin antioxidant is the same, the clearance rate of SL antioxidant is higher than that of CL. This is because SL is an alkyl polyphenol antioxidant, which contains far more antioxidant functional groups (phenolic hydroxyl groups) per 1 mol of molecule than CL, which can more effectively capture free radicals. In addition, the polyolefin antioxidant molecules are small, the diffusion effect in the system is good, and the probability of capturing free radicals is higher. Therefore, this is the reason why the polyolefin antioxidant SL has a higher DPPH· clearance than CL, and has a small content and high antioxidant performance.

Determination of reduction capacity of CL and SL

The reduction capacity of CL and SL are shown in Figure 11. Antioxidants can block free radical attack and resist the damage caused by them. How to correctly and truly evaluate the reduction capacity of iron ions in antioxidants has become the primary problem to be solved. Determination and analysis of reduction capacity of iron ions in antioxidants, based on the principle of redox reaction, antioxidants reduce Fe^{3+} ferrocyanide into Fe^{2+} form, and determine the amount of reduced Fe^{2+} by detecting the formation of Prussian blue at 700 nm, so as to show the reduction capacity of various antioxidant[38]. It is obvious that the reduction capacity of SL is better than that of CL. As the concentration increases, the absorbance of each substance increases, which indicates that the antioxidant capacity of SL is stronger than that of CL.
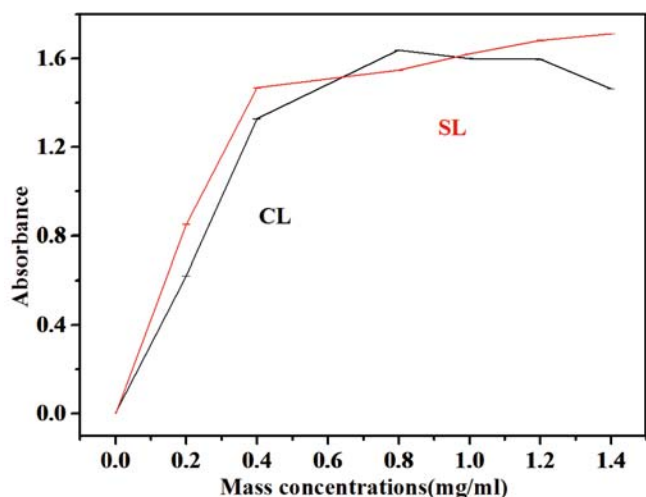
All in all, SL acts primarily in the oxidation cycle 1 of PP. On the one hand, SL acts as an antioxidant or prevents oxidative stress damage by directly removing peroxides or free radicals; On the other hand, SL can also exert its antioxidant function by limiting the formation and level of superoxide and corresponding reactive oxygen or nitride. As an antioxidant, SL can capture the free radicals P· and POO· formed in the chain reaction stage so that they do not cause a destructive chain reaction. The antioxidant is also capable of decomposing the hydroperoxide POOH to form a stable inactive product. Since the –OH of SL is subject to steric hindrance, H atoms are easily detached from the molecule, and peroxide radicals (POO·), alkoxy radicals (PO·), and hydroxyl radicals (HO·) in the degradation process of PP. The chain reaction is terminated by the combination of the inactivation, so that the thermal oxygen aging chain reaction is terminated.

Effect of CL and SL on rheological properties

Figure 12 showed that pure PP sample has poor heat resistance and oxygen performance. At barrel 200°C temperature environment and screw shearing action happened hot oxygen aging degradation behavior, reduce its flow resistance and viscosity, in the picture show the torque is reduced. Adding SL can increase the torque of PP sample and alleviate the thermal oxygen degradation of PP at high temperature and under the action of screw shear. With the increase of rheological time, the torque of modified PP sample changes little and the rheological curve is relatively gentle, indicating that adding SL can maintain the heat resistance and oxygen resistance of PP sample for a long time. Among them, PP samples with SL addition of 0.9 (wt%) had the highest performance of torque value initially. This may be because in the rheological test process, SL and PP were remixed at high temperature and under the rotation of twin screws, so that the mixture was more even and the antioxidant efficiency of SL was improved. However, after the rheological time exceeded 2 min, the torque value decreased sharply, indicating that the thermal stability was not stable when the addition amount was 0.9 (wt%).When the addition amount were 0.3–0.7 (wt%), the torque values decreased to varying degrees, but all of them were higher than the torque value of pure PP sample. This indicates that different addition amounts
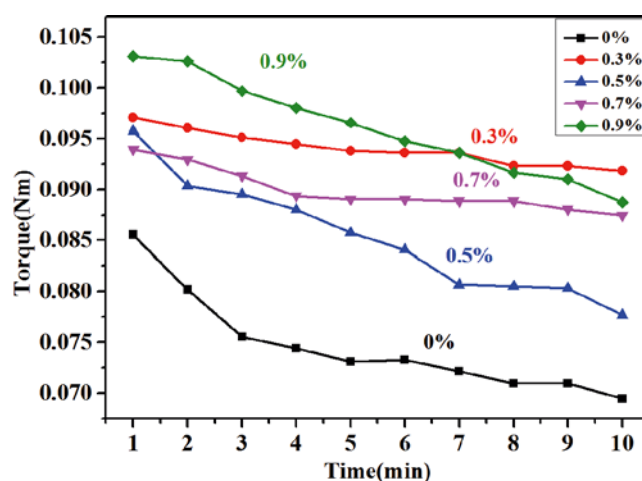

Figure 11. Reduction ability of CL and SL

Figure 12. Effects of SL on PP rheological properties

have certain antioxidant properties, but when the addition amount is 0.3 (wt%), the change of torque with time is the most stable, close to a straight line, and the torque value is relatively high. At the meantime, OIT performed the best. Therefore, SL had certain heat-resistant oxygen performance in PP forming process.

Effect of SL on PP mechanical properties

Table 4 demonstrated that the tensile strength trend of each sample is basically the same. The data showed that SL had a stable effect on the mechanical properties of PP, and the antioxidant capacity increased first and then decreased with the addition of SL. The antioxidant capacity of PP was the best when adding 0.3 (wt%). The results were in consistency with the rheological data and the OIT.

Table 4. Effect of SL on mechanical properties of PP sample

Sample number	Tensile strength/Mpa	Elongation at break/%	Impact strength/kJ·m^{-2}
PP-0%	34.51	724.02	21.90
PP-0.3%	35.67	708.13	21.63
PP-0.5%	34.95	723.28	21.13
PP-0.7%	33.17	571.06	22.88
PP-0.9%	30.54	494.20	22.20

CONCLUSIONS

The preparation of SL was optimized by single factor and orthogonal experiment by using OIT as objective function. In addition, OIT is also used to measure the antioxidant properties of PP, CL/PP and SL/PP samples. The preparation of SL was successfully determined by infrared analysis. The stable thermal degradation properties of SL were preliminarily studied by molecular weight determination and TG analysis. The data confirmed that SL can be added to the molding process of PP as a new synthetic antioxidant without affecting the original properties of PP. The free radical scavenging experiment further demonstrated that SL, as an antioxidant, could scavenge free radicals generated during the degradation of PP materials. The higher the scavenging rate, the better the antioxidant performance. The results showed that SL had higher antioxidant capacity than CL. From a macroscopic point of view, vitamin E has a significant effect on the melt stability, color stability and thermal oxygen effect (embrittlement) of PP during processing, thereby improving the processing stability and service life of plastic products. When 0.3 (wt%) of SL was incorporated into PP, heat resistance and oxygen resistance were significantly improved as compared with the starting PP, and it was further confirmed that the addition of SL did not affect the original properties of the PP material, or even improved the mechanical properties of PP materials. It is provides a basis for the rational development of SL, which as new antioxidant can effectively delay the oxidation of PP.

ACKNOWLEDGEMENTS

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