Role of different lignin systems in polymers: mechanical properties and thermal stability

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Lignin was used to study the mechanical properties and thermal stability of polymers. The lignin was blended with three kinds of polymers, and the addition of lignin was 0.5 wt%. Under the condition of thermal oxidation, the thermal stability of lignin/polymer samples varies with the structure of lignin. The effects of lignin on the mechanical properties and thermal stability of the polymers were investigated by oxidation induction time (OIT), rheological properties, mechanical properties and differential scanning calorimetry (DSC). The results show that the effect of lignin on the thermal properties of polymer samples is 2~3°C. It can be inferred that lignin can effectively improve the interaction between polymer molecular chain segments, and improve the crystallization rate and rigidity to a certain extent, so it can be seen that lignin has good compatibility and thermal stability.

Keywords: lignin, mechanical properties, thermal stability, polymer.

INTRODUCTION

In the face of the upcoming food-grade material safety issues, the development and utilization of biomass have attracted great attention. In the process of biomass utilization, lignin is generally abandoned or burned as waste. With the in-depth study of lignin, it is found that lignin is a valuable resource with great potential for use[1]. Lignin is a kind of three-dimensional network macromolecule compound with no definite molecular structure. Because of its complex space network structure, lignin is an amorphous polymer with limited industrial applications. Lignin exists in most terrestrial biomass, but it is not alone in biomass, but coexists with cellulose and hemicellulose, and constitutes the main framework of plants. Xinjiang is the main cotton production area in China, is a kind of inexhaustible, inexhaustible biomass renewable resources. Therefore, the efficient utilization of lignin in cotton straw has important practical significance in Xinjiang[2–5]. Lignin in cotton straw accounts for about 15–20% of the total mass[6–8]. The purity and activity of lignin products are relatively low, which is one of the best conditions for extracting lignin. So in recent years, the research and comprehensive utilization of lignin has become a new trend of global biomass resources research.

Lignin in land plants is mainly composed of guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H). In the molecular structure of lignin, there are active groups such as aromatic group, phenolic hydroxy group, alcohol hydroxy group, carbonyl group, methoxy group, carboxyl group and a conjugated double bond. It can be used to replace fossil resources in the fields of synthetic raw materials of resin materials and plastic additives[9–10].

The chemical structure of lignin also depends on the source of raw materials and extraction and separation methods, which will affect its reactivity, and then affect its application[11]. As an antioxidant, lignin is the most widely used additive in plastics[12–13]. One of the most widely used contents refers to the application of antioxidants in various stages of polymerization, synthesis, granulation, storage, processing and use of plastics[1, 14–17]; The second of the most widely used contents refers to the types of plastic materials with different molecular structures that have appeared in the world today[18], such as polyethylene (PE), polypropylene (PP), polystyrene (PS), engineering plastics, modified plastics and other materials, and the types of plastic materials with antioxidants are the most[19–21]. Li Mingfei et al[22] studied the antioxidant activity of lignin extracted from bamboo, and found that the antioxidant activity of lignin was stronger than that of butylated hydroxytoluene (BHT), and other studies showed that lignin was harmless to skin and eyes[23]. Therefore, the study of different methods of lignin extraction and the impact of lignin on the antioxidant properties of polymers, and ultimately determine the best method of cotton straw lignin extraction, and efficient use of lignins in cotton straw has important practical significance.

In this paper, different kinds of lignin were mixed with PP, LDPE and PS, and the effects of cotton stalk lignin extracted by ultrasonic method (L_1), ionic liquid method (L_2), ultrasonic-assisted ionic liquid method (L_3) and ethylene glycol method (L_4) on the oxidation resistance and thermal stability of PP, LDPE and PS were studied.

EXPERIMENTAL PART

Materials

Polypropylene (PP, T30S, Homo polymer spinning grade, MFR = 2.98 g/min, ϱ = 0.90 g/cm^3), Low Density Polyethylene (LDPE, 2426, MFR = 1.81 g/min, ϱ = 0.912 g/cm^3), Polystyrene (GPPS, 500NT, MFR = 5.52 g/min, ϱ = 0.88 g/cm^3) was supplied by China Petroleum Dushanzi Petrochemical Company; Four kinds of extracted lignin: Extraction of lignin by ultrasonic method (L_1), extraction of lignin by ionic liquid method (L_2), ultrasonic-assisted ionic liquid lignin extraction(L_3), and ethylene glycol extraction(L_4). The cotton stalk was purchased from Kashgar, Xinjiang.

Extraction Procedure and Purity of Cotton Stalk Lignin

Extraction of lignin by ultrasonic method

Weigh 1 g of cotton stalk powder, mix it with 0.7 mol/L KOH and transfer it into a 50 mL conical flask, perform

ultrasonic extraction at 70°C for 80 min, filter, adjust the pH value of the filtrate to 5.5 with 6 mol/L acetic acid, concentrate under reduced pressure, treat the concentrated solution with 3 times volume of 95% ethanol, stand, and filter after complete precipitation. The filtrate was concentrated to remove ethanol, and then 6 mol/L HCl was added to adjust the pH value to 1.5, standing and centrifuging to obtain lignin. The crude lignin was extracted with 1,4-dioxane in an oil bath at 120°C for 6 h in a Soxhlet extractor. Pure lignin was obtained by freeze-drying at –50°C for 5 h, and 1,4-dioxane was recovered by rotary vacuum evaporator.

Extraction of Lignin by Ionic Liquid Method

Weigh 1.00 g of cotton stalk powder, mix with 20 ml of ionic liquid and poured into a 100 ml round bottom flask. Reacting in a magnetic stir oil bath with that reaction temperature set at 150°C for 1 h, and then diluted with 50 ml of deionized water at room temperature and stirred for 1 h. The crude lignin was obtained by centrifuging the filtrate after 2 h, and the ionic liquid was recovered by rotary vacuum evaporator. The purification process is consistent with the above.

Extraction of Lignin by Ultrasonic Assisted Ionic Liquid Method

Weigh 1g of cotton stalk powder, mix it with a certain proportion of ionic liquid: water solution, and pour it into a 50 ml conical flask with ultrasonic frequency of 45 KHz and ultrasonic power of 100 MPa for 2 h at 50°C. The residue was washed at least three times by filtration through a Buchner funnel to remove the residual ionic liquid, which was removed to a total volume of 300 ml. The crude lignin was obtained by centrifuge after the

filtrate was placed for 2 h, and the ionic liquid was recovered by rotary vacuum evaporator. The purification process is consistent with the above.

Extraction of lignin by ethylene glycol

Weigh 1 g of cotton stalk powder, fully mix it with 0.8 mol/L ethylene glycol, transfer it to a 100 mL hydrothermal kettle, keep the temperature at 160°C for 2 h, and cool it to 60°C after reaching the predetermined time. Filter with a cloth and wash three times with ethylene glycol at 60°C. Wastewater generated by washing the residue is used as precipitated lignin. When three times the volume of distilled water is added and stirred at room temperature, a large amount of lignin is precipitated and centrifuged to obtain lignin. The purification process is consistent with the above. Lignin L_1, L_2, L_3 and L_4 were obtained by the four methods mentioned above. The basic structure of lignin is shown in Figure 1.

Sample preparation

The PP and lignin were accurately weighed according to the formula in Table 1, mixed at high speed for 15 minutes in a high-speed mixer, melt blended and extruded in an extruder (TE-20, Keya company China), and pelletized under the extrusion process conditions that the die temperature was 200°C, and the temperatures of the first zone to the fourth zone were 220, 200, 195, 215°C, melt temperature 180°C, host frequency 14.0 Hz, feed frequency 14.0 Hz; Standard tensile and impact splines (XL-400VI: Ningbo China) were prepared by injection molding. The injection temperature of the first stage was 200°C, the second stage was 190°C, the injection pressure was 8.5 MPa, the melt pressure was 8.0 MPa, and the packing pressure was 7.0 MPa.
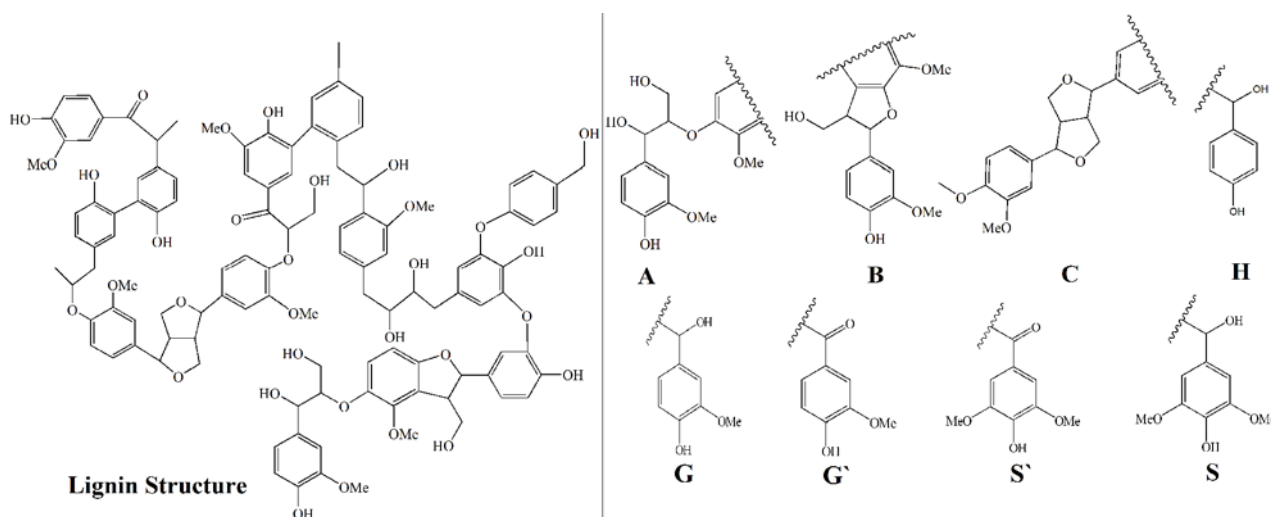

Figure 1. Main substructures observed in cotton stalk lignin: (A) β-O-4 linkages; (B) phenyl-coumaran structures formed by β-5 linkages; (C) resinol formed by β-β linkages; (H) p-hydroxyphenyl units; (G) guaiacyl units; (G`) oxidized guaiacyl units with a Cαketone; (S`) oxidized syringyl units with a Cαketone; (S) syringyl units

Table 1. The compound proportion of PP and lignin

Sample	PP	L_1	L_2	L_3	L_4	CaSt
PP	100	0	0	0	0	0.1
PP-L_1	100	0.5	0	0	0	0.1
PP-L_2	100	0	0.5	0	0	0.1
PP-L_3	100	0	0	0.5	0	0.1
PP-L_4	100	0	0	0	0.5	0.1

(PE, PS are also mixed as shown in Table 6.1)

Oxidation induction time (OIT)

The oxidation induction time of different PP samples was measured by DSC (Q-2000, America TA). Different PP samples (5 mg) were taken, separately, and exposed to nitrogen atmosphere, at a nitrogen flow rate of 50 mL/min and a heating rate of 20°C / min. After reaching a temperature of 200°C, the sample was kept in a nitrogen atmosphere for 10 min. Immediately afterward, the flow of nitrogen was switched to an oxygen flow of 50 mL/min, and the constant temperature was continued until the sample was completely oxidized. Each measurement was repeated three times.

Static rheological experiment (Haa Ke, Minilab II, Germany): 6 g of powdered pure PP and lignin sample (0.3% ~ 0.9%) were used respectively, the barrel temperature reached 200°C, the speed was set at 30 r/min, and the running time was 10 min.

Mechanical performance test

Tensile strength: According to standard GB/T1040.3-2006, the experimental conditions: the tensile rate was 100mm/min. Impact strength: According to the standard GB/T1043-1993, an electronic impact testing machine (type XJJD-50, China) was used for impact test with a 7.5J pendulum at room temperature.

Differential scanning calorimeter (DSC)

DSC test conditions: the mass of the sample is 5 mg, the temperature range is 20~200°C, the temperature rises and then falls (keep it for 3 minutes before cooling), the nitrogen flow is 50 mL/min, and the heating rate is 10°/ min. The thermal oxidation stability of PP and blends of PP with lignin were determined via differential scanning calorimeter (DSC Q2000, America TA) using platinum pans. The running time is 48 minutes and the effective weight change was also been recorded.

RESULTS AND DISCUSSION

Oxidation induction time (OIT) analysis

OIT test is a test method to evaluate the thermal stability of polymers at high temperature above the melting point of polymers in oxygen atmosphere. From Figure 2(a), compared with pure PP, the OIT of PP samples after adding lignin increased significantly, indicating that lignin has a certain antioxidant capacity for PP[24–25]. Due to the different structure of lignin, the thermo-oxidative stability of the polymer is also different[14]. The data show that the antioxidant in the sample can inhibit the thermal oxidative degradation time of the sample, and the longer the sample quality retention time, the better the antioxidant performance of lignin[14, 25]. The OIT of L_2

and L_3 to PP is a little longer, which indicates that the lignin with more phenolic hydroxyl can capture more free radicals to stabilize the degradation of PP. Figure 2(b) shows the effect of different structure lignin on the oxidation induction period of PE. Due to the different thermal stability of lignin with different structures, the protective ability of lignin to plastics at high temperatures, especially at processing temperature, will be different. After adding lignin, the OIT of PE was prolonged to some extent. The OIT of L_2 and L_3 was nearly 7 times higher than that of pure PE, which indicated that lignin could protect the degradation of PE under aerobic condition. The factors affecting antioxidant efficiency are not completely dependent on the number of phenolic hydroxyl in the structure of antioxidants, but also the molecular structure, thermal stability, molecular weight, stability of free radicals and compatibility in PE. Because the molecular weight can affect the migration rate of antioxidant in PE, if the molecular weight is small, it will easily migrate out of the sample matrix, thus affecting its antioxidant efficiency, so it can be inferred that lignin does not belong to small component structure. Figure 2(c) shows the effect of lignin with different structure on the induction period of PS oxidation. In theory, the longer the induction time, the better the antioxidant effect. It can be seen from the figure that the OIT of PS sample extended a little bit after adding lignin, OIT extended from 1.02 min to 2.45 min, and the antioxidant effect had a better trend, but not obvious. Compared with PP and PE, it contributed more to the increase rate of OIT value of PE. Comparing the effect of lignin on OIT of the three polymers, the polymer with more phenolic hydroxyl groups of lignin has better stabilization. The more phenolic hydroxyl, the more free radicals can be trapped, which is more conducive to the thermal and oxidative stability of polymer samples.

Micro mixed rheology test analysis

The thermal stability of plastic materials is one of its rheological properties, which can reflect the phenomenon of molecular crosslinking or chain breaking caused by thermal oxidation at high temperatures. Therefore, the degree of thermal stability of plastic materials can be characterized by the change amplitude of torque and other information. From the curve of Figure 3(a), it can be seen that the torque of pure PP sample decreases gradually with the prolongation of time. The results showed that the thermal oxygen resistance of PP was poor, the thermal oxygen aging degradation occurred during the mixing and extrusion process, and the interaction force between PP molecular chains decreased, which reduced its flow resistance and viscosity, thus increasing the fluidity of PP and reducing the torque.
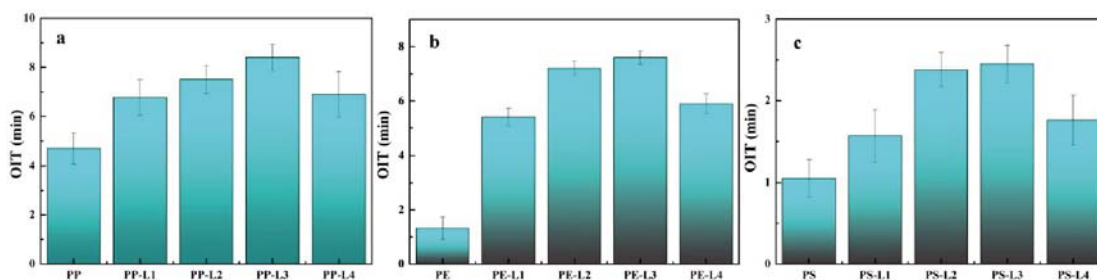

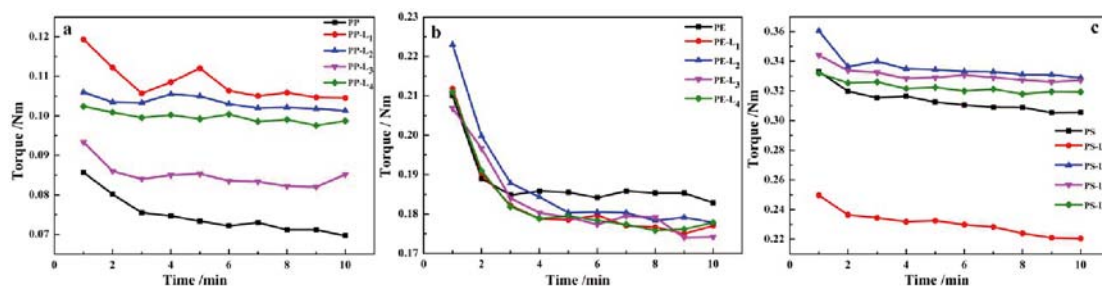**Figure 2.** OIT of different PP, PE, PS samples

Figure 3. Effect of different structure lignin on rheological properties of PP, PE and PS samples

The torque of PP samples with different structure lignin is higher than that of pure PP samples, which shows that lignin can effectively improve the thermal oxidation resistance of PP. This is because the lignin antioxidant can react with the peroxy radical (ROO •) to form the aryl oxygen radical (Ar-O •), which is stable and can capture the active radical, and can further react with the peroxy radical (ROO •) to form the non-radical product (ROO-O-Ar). So as to destroy the radical oxidation chain reaction of PP and realize the thermal stability of the lignin antioxidant in PP; According to the curve of Figure 3(b), the torque of PE decreased rapidly with time at 200°C, which indicated that the crosslinking of molecular chain was the main process of PE thermal oxidation, and the molecular weight decreased, which led to the decrease of torque in the system. The reason for the rapid decrease of torque is that the molecular chain of the sample produces free radicals with phenolic hydroxyl, which makes the molecular chain of PE oxidized and cross-linked; From the beginning of the third minute, the torque basically stabilized, the reason is that the crosslinking reaction of PE chain in contact with air tends to be saturated, resulting in the slowdown of torque; Compared with pure PE, lignin with different structure had no effect on the thermal stability of PE. From the curve of Figure 3(c), it can be seen that the thermal stability and fluidity of the blend of lignin and PS are very good, but the torque of L_1 is much lower than that of other samples and the torque of L_2, L_3 and L_4 on PS samples increases significantly. The reason for the low torque of L_1 may be that the content of phenolic hydroxyl in L_1 is much less than that of other ones; Because the phenolic hydroxyl in lignin forms a hindered phenol structure, which can capture the free radicals in plastics and inhibit the oxidative aging of plastics. In a word, the elements of lignin vary with different plant varieties, places of origin and methods of isolation. Even if the same raw material, the structure of lignin in different parts is different, the molecular weight

is different with different separation methods, and the thermal stability and antioxidant effect of samples are also different.

Mechanical performance test analysis

Table 2 shows that the tensile strength of PP can be slightly improved by adding lignin into PP, and the cross-linking between free radicals formed in the injection molding process of each sample can form a network structure, which can slightly increase the tensile strength of PP; It has no effect on the impact strength, and the elongation at break is less than that of pure PP. This is because the different structure of lignin on PP can show better migration stability and compatibility, play better mechanical properties of PP, due to increasing its thermal-oxidative stability efficiency; The effect of different structure lignin on the elongation at break of PP was obvious. The elongation at break of PP added with different structure lignin was lower than that of pure PP, and the decrease percentages were 4.18%, 2.54%, 3.15% and 4.50% respectively. This may be due to the rupture of PP molecular chains under the action of thermal oxidation, and the formation of network structure between the free radicals formed by crosslinking is destroyed, which makes the elongation at break of PP samples gradually decrease.

Table 3 shows the effect of different lignin structure on the mechanical properties of PE. It can be seen from the table that the tensile strength and impact strength of each sample have the same trend, which has a certain effect on the elongation at break; The results showed that it has effective protection in thermal oxygen environment; The elongation at break of L_2 was a little higher than that of pure PE and the other three samples, which might be due to the cross-linking of the free radicals produced by the phenolic hydroxyl in the lignin structure with the molecular chain segments of the sample, which made the binding ability of lignin and PE better, and improved the elongation at break

Table 2. Mechanical properties of different PP specimens

Mechanica properties	Specimen Number				
	PP	PP-L_1	PP-L_2	PP-L_3	PP-L_4
Tensile strength / MPa	34.41	36.74	36.30	37.50	36.21
Elongation at break /%	676.25	647.96	659.10	654.97	645.81
Impact Strength /kJ · m^{-2}	25.15	25.57	26.15	25.16	25.16

Table 3. Mechanical properties of different PE specimens

Mechanical properties	Specimen Number				
	PE	PE-L_1	PE-L_2	PE-L_3	PE-L_4
Tensile strength / MPa	21.21	20.68	21.81	21.46	21.35
Elongation at break /%	135.18	125.89	142.10	128.87	115.74
Impact Strength /kJ · m^{-2}	8.20	8.75	8.87	8.94	8.33

macroscopically. The other three kinds of lignin reacted with a hindered amine to form hindered phenol, which indicated that lignin had limited ability to protect LDPE in thermal oxidation environment so that the elongation at break decreased.

Table 4 is the effect of different structure lignin on the mechanical properties of PS resin. It can be seen from the table that PS resin has good molding and processing properties and chemical thermal stability, and the addition of antioxidant lignin has little effect on tensile strength and elongation at break. It shows that lignin has good compatibility, but the impact strength is less than that of pure PS, and the impact strength of L_3 is almost the same as that of pure PS. It is possible that the structure of lignin has a great impact on PS molecular chain, and it is also possible that lignin decomposes into small molecules under thermal and oxidative environment, which is prone to cross-linking, affecting the toughness and regularity of PS chain, thus reducing the mechanical properties of materials.

Thermal Performance Analysis

The oxidation resistance of lignin to polymer samples was determined by differential scanning calorimetry (DSC), and the thermal properties of lignin with different structures in three polymers were compared. The melting temperature (T_m) and crystallization temperature (T_C) of the polymer will directly affect the actual use of polymer performance, the processing temperature is determined by T_m, crystallization temperature will affect the mechanical properties of the polymer[26]. Figure 4 is the DSC curve of PP, PE and PS samples with different structure lignin. It can be seen from Figure 4(a) that the melting curve of PP after adding lignin is wide and no other melting peaks appear, which shows that lignin has good thermal stability and good compatibility with

PP; the results also show that lignin can enhance the binding force between PP segments[27]. It can be seen from Figure 4(d) that different PP samples have obvious crystallization peaks at 90°C ~ 120°C, the crystallization peaks of PP samples with lignin are more inclined to high temperature than those of pure PP samples, and their T_C is higher than those of pure PP samples at 2 ~ 3°C. The results showed that the addition of lignin had little effect on the crystallinity and grain size of PP matrix. It was also shown that the chain segment mobility in the lignin interface increased and the lignin had better dispersion in PP as a whole[28]. Figure 4(b) shows that there is a strong exothermic peak at 112°C in the DSC curve, which is the thermal decomposition peak of lignin, mainly occurring the breakage of lignin branches and the dissociation of small molecules such as phenols; At the end of decomposition, an exothermic peak appeared at 124°C on the DSC curve, which was mainly due to the fracture and full combustion of the lignin skeleton. Therefore, cotton stalk lignin has good thermal stability[26]. Figure 4(e) shows that there are two main crystallization peaks in the whole process. The structure of lignin has different effects on the crystallization properties of PE, except L_4. Compared with pure PE, the second crystallization peak is sharper. It is possible that the molecular structure of lignin plays an important role in improving the mobility of PE segments[29]; The crystallization peak width of PE system with lignin was also significantly narrowed, indicating that the addition of lignin improved the crystallization rate of PE, significantly increased the nucleation point of PE molecular chain, and had good heterogeneous nucleation and compatibility for PE crystallization[27]. It can be seen from Figure 4(c) that the melting degree decreases with the increase of temperature, and the melting peak is as wide as that of pure PS; the results showed that the

Table 4. Mechanical properties of different PS specimens

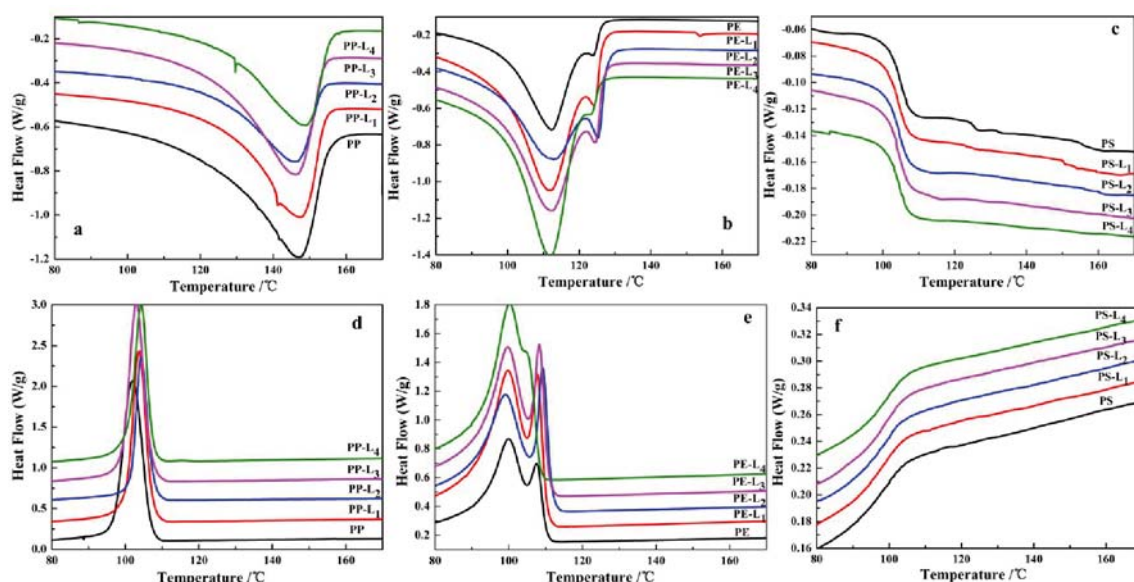| Mechanical properties	Specimen Number				
	PS	PS-L$_1$	PS-L$_2$	PS-L$_3$	PS-L$_4$
Tensile strength / MPa	66.05	64.82	65.21	63.50	64.51
Elongation at break /%	18.60	18.48	18.49	18.47	18.46
Impact Strength /kJ · m^{-2}	8.01	4.91	4.66	7.58	5.33

Figure 4. DSC curve of different PP, PE, PS samples, (a, b, c) Melting curve, (d, e, f) Crystalline curve

effect of lignin on the melting temperature of PS was not obvious, and the lignin did not affect the rigidity and crystallization of PS[30]. It can be seen from Figure 4(f) that lignin does not hinder the crystallization of PS too much, and the crystallization peak of PS sample is very wide, which shows that there is a strong interfacial coupling between PS molecule and lignin surface, which restricts the movement of molecular chain segments to a certain extent, hinders the growth of crystals and forms more imperfect crystals[31].

CONCLUSIONS

Oxidation induction time (OIT), micro-mixing rheology, mechanical properties and differential scanning calorimetry (DSC) were used to study the thermal oxidative stability of lignin on polymer. The results showed that:

(1) The more phenolic hydroxyl in lignin, the more free radicals could be trapped, which was beneficial to the thermal oxidative stability of polymer samples.

(2) The addition of lignin changed the rheological properties of the polymer significantly, and the thermal stability of pure PP, PE and PS was poor. The addition of lignin increased the fluidity and thermal stability of the polymer.

(3) Lignin was added into PP, PE, PS, and the mechanical properties of the samples were studied. The results showed that a small amount of lignin could enhance the tensile strength and impact strength of the polymer, but had a certain effect on the elongation at break.

(4) DSC results showed that the melting temperature and crystallization temperature of PP and PE increased by 2–3°C after adding lignin, but the thermal properties of PS were not affected, which indicated that lignin had good thermal stability and compatibility. In general, lignin had little effect on the thermal properties of PS.

ACKNOWLEDGMENT

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