

Effects of coupling agent on antioxidant properties and structure of PP/ cotton stalk lignin composites

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In this paper, the effects of coupling agent and lignin extracted from waste cotton stalks in Xinjiang on thermal-oxygen aging properties of polypropylene (PP) composites were studied. The melt index test and indoor thermal oxygen aging test was carried out on the samples treated with coupling agent. The mechanical properties, surface micromorphology, rheological properties and element composition of the materials before and after 30 days of aging were studied. The results showed that the titanate coupling agent was the best for improving the melt index and mechanical properties of PP/cotton stalk lignin composites. After the 30-day thermal oxygen aging test, the samples with 2% lignin had the best impact strength and retention rate of fracture elongation, reaching 68.9% and 77.3% respectively. The sample with 3% lignin content had the smoothen surface, no crack appeared. After aging, the increase of C=O was the least, and the crystal peak area decreased less.

Keywords: polypropylene, coupling agent, cotton stalk lignin, composite material.

INTRODUCTION

Lignin is an important natural high molecular compound, which is an aromatic polymer with phenylpropane monomer as the skeleton and an amorphous powder with reticular structure. It is also an organic substance containing hydroxyl group, carboxyl group, methoxy group and other active groups, among which phenolic hydroxyl group and alcohol hydroxyl group are reactive, cohesive and antioxidant^{1, 2}, which can replace fossil resources and be applied to synthetic materials of resin materials, plastic additives and other fields. Xinjiang is the main cotton production base in China, and the amount of cotton straw resource fluctuates with the change of cotton output. According to the statistics in the past two years, the cotton output of Xinjiang is about 2.06×10^6 t, and the amount of cotton straw resource that can be collected is about 1.68×10^7 t, which is a kind of “inexhaustible” bio-based renewable resource^{3, 4}. Therefore, the efficient utilization of lignin in cotton straw has important practical significance in China. The content of lignin in nature is second only to cellulose, but the application of lignin is less than 5% of its recycling amount, and over 90% of lignin is directly accumulated or burned as waste, causing serious damage to the ecological environment. Lignin has a complex structure and a large number of active groups on its surface. In recent years, studies on lignin modified resin, rubber and other materials are also increasing. Biofiber polymer composites (BFPC) are materials made from a thermoplastic or thermoset resin (substrate) with cellulosic fibers as fillers or reinforcement. They are currently used in a variety of products ranging from building materials, automotive parts, packaging, consumer goods, active pharmaceutical ingredients (API) and landscaping products^{5, 6, 7, 8}. The application of lignin as a filler in resin is of great significance to improve the utilization rate of biomass resources and the sustainable development of the natural environment⁹. Polypropylene is one of the most widely used general-purpose plastics, but antioxidants are often added to avoid degradation by heat and oxygen during its processing,

storage and use. At present, the most commonly used antioxidants are blocked phenols, but in recent years, more and more antioxidants in food packaging materials appear easy to migrate and toxic safety issues¹⁰. It is of great social significance to search for a kind of natural antioxidants with high safety, non-toxic side effects and good antioxidant properties for PP. Therefore, using cotton stalk lignin as PP filler to prepare composites is not only an effective way to develop and utilize lignin, but also can reduce PP cost and improve weather resistance¹¹. However, the strong polarity of lignin leads to poor compatibility with non-polar polymers, strong intermolecular hydrogen bonding between lignin makes it easy to aggregate, poor interfacial bonding strength between filler and matrix, and poor performance of composite materials¹². The coupling agent, as a material containing two parent groups, can effectively improve the compatibility between polar lignin and non-polar PP resin, and build a bridge between the two, thus effectively improving the uniformity of the composite after blending. One of the most widely used and effective functional groups for grafting a coupling agent (CA) to a cellulosic fiber is the anhydride functionality. Chemical structure, molecular weight and functional groups per mole of a coupling agent have strong impact on the mechanical properties of composites¹³. In this paper, three coupling agents of silane coupling agent KH-550, KH-792 and titanate coupling agent NDZ-201 of which the active functional groups are all alkoxy groups were used as surface modifiers of cotton stalk lignin to study the melting index and mechanical properties of PP/cotton stalk lignin composites. After judging the melting index and mechanical properties, NDZ-201 titanate coupling agent and composite material with different content of lignin were used for a 30-day indoor thermal and oxygen aging test.

EXPERIMENTAL

Material

PP (D(Y)-W0723F: Homopolypropylene, melt flow rate is 1.8 g/3.0 min and molecular weight is 70,000~240,000) was bought from China Petroleum Dushanzi Petrochemical Company and Baling Petrochemical. Coupling agents KH-550 (molecular weight is 221.4), KH-792 (molecular weight is 222.4) and NDZ-201 (molecular weight is 1310.0) were purchased from DongGuan KangJin New Material Technology co., LTD. Calcium stearate was purchased from ShangHai ShanPu Chemical co. LTD. Cotton stalk lignin was extracted from waste cotton stalks collected from Tashkurgan, Xinjiang by ionic liquid method¹⁴.

Sample preparation

The raw materials were weighed according to the mass ratio in Table 1 and Table 2 for simple mechanical blending and then added to the twin-screw extruder (TE-20, China Jiangsu (Nanjing) Keya company) for melting extrusion and granulation at temperatures of 170, 190, 195, 200 and 190°C and the feed speed at 10 r/min to obtain PP/ cotton stalk lignin blending granules of different proportions, the screw speed of extruder was 10r/min. Injection was molded into formed impact splines and tensile splines type at temperatures of 230 and 210°C and the screw speed was 30 r/min by plastic injection molding machine (XL-400 VI: Ningbo high Xieli machine Shen Liquor Co., Ltd.) after the granules were dried in the air drying box for 24 h.

Measurement of Tg curve: In the atmosphere of nitrogen, it was tested with a TA INSTRUMENTS model DMAQ800 thermal analyzer by a DMA assay. The type of vibration is curved, the frequency of vibration was 1Hz, the range of scanning temperature was 25~600°C, and the heating rate was 3°C/min.

Melt flow rate measurement: The standard spline prepared according to Tab.1 mass ratio was prepared into fine blocks, and the melt index was measured by melt flow rate meter (KL-MI-BP, DongGuan KunLun Industry). The temperature was set at 230°C according to GB/T3682 – 2000¹⁵, 4–5 g was loaded each time, each formula was measured twice.

Indoor thermal and oxygen aging test: After simple screening of the melt index and mechanical properties of the samples, standard samples treated with titanate coupling agent NDZ-201 were prepared according to Table 2, and were put into dhg-9245a electric air-blast

drying oven (Shanghai yihengshan) for a 30-day indoor thermal and oxygen aging test. The temperature was set at 60°C. Samples were taken at 5 days, 10 days, 15 days, 20 days and 30 days respectively, and the structural and mechanical properties were evaluated by the change of surface morphology, XRD, XPS, impact tests and tensile tests.

Determination of tensile strength: According to GB/T1040.3 – 2006¹⁶, mechanical properties of PP/ cotton stalk lignin samples before and after aging were determined by electronic universal material mechanical testing machine (CMT6104, ShenZhen XinSanSi). The drawing speed is 100 mm/min, the spline spacing is 30 mm, the width is 4 mm and the thickness is 2 mm.

Impact strength measurement: According to GB/T1043 – 2008¹⁷, Izod impact test was used to measure the impact strength of PP/ cotton stalk lignin samples before and after aging by an electronic simply supported beam impact machine (XJJD-50, ChengDe JinJian) at room temperature. The measuring range is 7.5 J, the length of the spline is 80 mm, the width is 10 mm and the thickness is 4 mm.

Surface morphology analysis: The surface morphology before and after aging of samples was studied using a scanning electron microscope (SEM, JSM-5600LV, JEOL, Ltd. Japan). The scanning was performed on the fracture of the samples which were sputter-coated with gold prior to scanning. The acceleration voltage is 20 kv.

Haake Minilab test: The Minilab test was carried out using a miniature mixing rheometer (MiniLab II, Haake Germany). 5.0 g of specimens before and after aging treatment were added to the cylinder at a screw rotation speed of 10 r/min. The machine temperature was set as 200°C and the screw rotated diagonally. The data of 1 minute of static torque and time was collect.

X-ray photoelectron spectroscopy (XPS): XPS(ESCALAB 250Xi, Thermo Fisher. US) was used to explore the surface composition of the before and after aging of PP and PP/ cotton stalk lignin mixed samples. X-ray photoelectron spectra were recorded on a Thermo spectrometer with a monochromatized Al K Alpha X-ray source (1486.6eV photons).

X-ray powder diffraction test: The X-ray powder diffractometer was used to test its structure and morphology. XRD scans were recorded on Bruker D 8 advance using Cu-Ka radiation and a p-Ni filter (U = 40 kV, A = 40 mA) in the 2θ range of 10° to 80° at a scan rate of 6°/min.

Table 1. Melting Index Test Material Dosage

No.	Ω[PP] %	Ω[Lignin]%	Ω[KH-550] %	Ω[KH-792] %	Ω[NDZ-201] %	Ω[calcium stearate]%
PP-0	100	/	/	/	/	0.1
PP-1	98	2	/	/	/	0.1
PP-2	96	2	2	/	/	0.1
PP-3	96	2	/	2	/	0.1
PP-4	96	2	/	/	2	0.1

Table 2. Thermal Oxidative Aging Test Material Dosage

No.	Ω[PP]/%	Ω[Lignin]/%	Ω[NDZ-201]/%	Ω[calcium stearate]/%
PL-0	100	/	/	/
PL-1	97	1	2	0.1
PL-2	96	2	2	0.1
PL-3	95	3	2	0.1

RESULTS AND DISCUSSIONS

Selection of the best performing composites

Figure 1 shows the thermogravimetric curve of sample PP and cotton stalk lignin. As shown in Fig. 1, the apparent weight loss of pure PP started from 270°C, and the apparent weight loss temperature of cotton stalk lignin was 250°C. The mass loss before 250°C was due to heat volatilization of some adsorbed water and other small molecules in cotton stalk lignin. Sample PP and cotton stalk lignin have high thermal stability at high temperature, which was conducive to the processing and forming in the test¹⁸. The raw materials in Tab.1 were injected into standard dumbbell shaped splines. The prepared samples were tested by a stretching machine for tensile strength and elongation at break, and the coupling agent formula suitable for the production of composite materials was selected through mechanical properties and processing properties. Table 3 compares the mechanical properties of various raw materials. Table 3 shows that the tensile strength of PP-2 was the highest, but the elongation at break and melt flow rate decreased significantly compared with PP-0. The melt flow rate and elongation at break of sample PP-3 were higher than that of sample PP-0, but the tensile strength of sample PP-3 was lower than that of sample PP-4. The tensile strength of sample PP-4 decreased somewhat compared with that of PP-0, but the melt flow rate and elongation at break were the highest, and the properties of the sample were significantly improved. These phenomena occurred because lignin is directly blended with PP, the sample compatibility is not good, so the melt index drops. When lignin was mixed with PP by coupling agent, the melt index was increased. After the addition of lignin, the impact performance of the samples was improved, because the addition of lignin

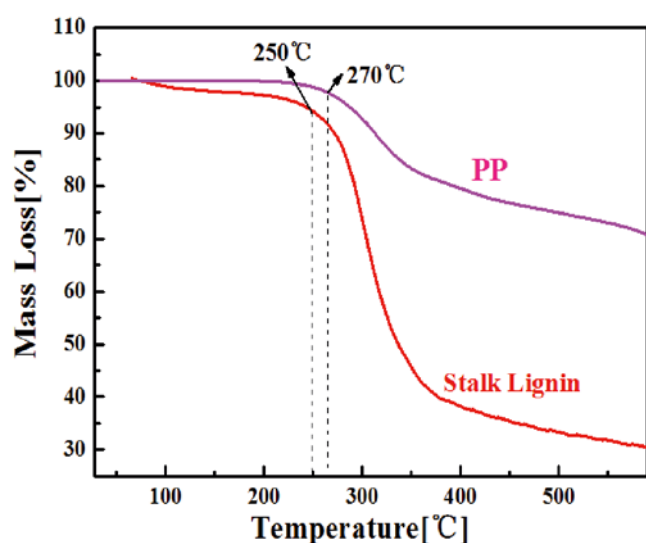


Figure 1. TG curves for different ingredients

Table 3. Melting Index Test Results and Mechanical Properties

	MFR/g · (10 min) ⁻¹	Tensile strength/Mpa	Elongation at break/%
PP-0	1.91	34.5	600.4
PP-1	1.72	37.5	585.8
PP-2	2.03	38.2	525.8
PP-3	1.98	34.7	595.6
PP-4	2.45	37.2	596.9

into the PP matrix changed the crystal shape of PP, so that the spherulites of PP were cut by the elastomer, thus increasing the impact strength of the samples and achieving the purpose of toughening, but the elongation at break of the lignin was decreased because of the low tensile strength of the pure lignin. As the particle size of lignin in PP blends increased, the tensile strength of the samples decreased¹⁹. However, in the production and use of polypropylene, toughness played a very important role. Therefore, PP-4 was selected as the material for indoor thermal and oxygen aging test formulation.

Mechanical properties of samples

Mechanical properties of PP/ cotton stalk lignin samples aged at different times in indoor thermal and oxygen were shown in Table 4 and Fig. 2. As shown in Table 4, the tensile strength of samples first increased slightly with the increase of aging time. Compared with samples aged for 0 days after 5 days of thermal and oxygen aging, the tensile strength of samples PL-0, PL-1, PL-2 and PL-3 increased by 2.6%, 1.8%, 4.0% and 2.7%, respectively. PP is a semi-crystalline polymer and some amorphous regions and crystal incomplete parts in the molecular chain are the defects or imperfect regions between crystals. During the aging test, the molecular chains and chain segments were rearranged under the action of heat. During the first 5 days of aging, the excessive agglomeration in the sample molecules resulted in demoralization, and the molecular weight was slightly reduced. On the contrary, the compatibility of lignin in the blended material was improved, and the tensile strength was increased. With the increase of aging time, the molecular chains in the samples degrade, and the mechanical properties gradually decline^{20, 21}. However, the tensile strength of pure lignin was poor. With the addition of lignin, the particle size of PP blends increased, which eventually lead to the decline of the tensile strength of the blends. And with the increase of aging time, the molecular chains of the samples degrade, the molecular weight decreases and the tensile strength decreases²². As shown in Fig. 2, the impact strength retention and elongation at break retention were calculated compared with unaged samples, which were obtained by dividing the data obtained from the aged samples and the data obtained from the unaged samples. When the aging time reached 30 days, the tensile strength of the samples PL-0, PL-1, PL-2 and PL-3 decreased by 4.9%, 5.7%, 5.4% and 8.5% compared with the samples aged for 0 days, which was caused by the formation of cracks on the surface of the material. Before aging, the elongation rate of the specimen was raised in order to increase the amount of wood quality, and the elongation rate of plin was 637.1%, and the elongation rate was 146.1%, which was because the toughness of pure lignin was good and the grain quality and PP were mixed. The crystal shape of the PP was changed, and the PP ball was cut by the

elastobody, which made the elongation of the PP/ cotton stalk lignin fracture increased, and then achieved the goal of toughening^{23, 24}. After aging for 30 days, the breaking elongation retention rate of PL-2 was the best. The retention rate of impact strength decreased after aging, but it was better than PL-0.

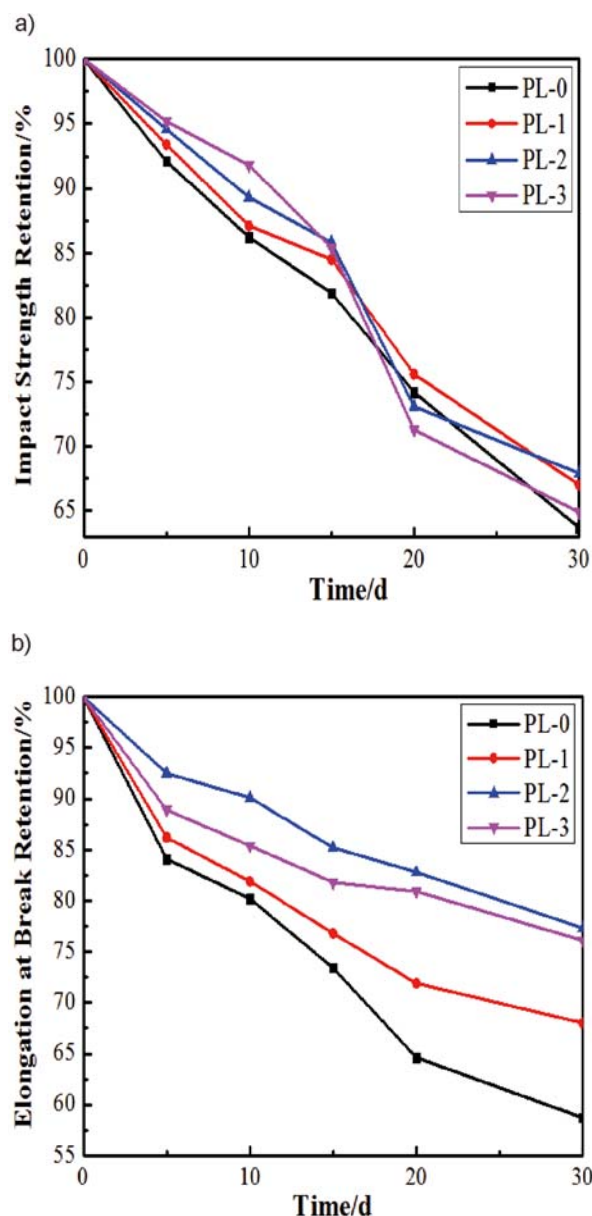


Figure 2. Mechanical properties of PP/Lignin specimens after different time aging: (a) impact strength retention of samples; (b) elongation at break retention of samples

Analysis of surface morphology

It was clearly seen from the SEM photo magnified 2000 times as shown in Fig. 3 that with the increase of aging time, the roughness degree on the surface of samples with different lignin content was also different. After aging treatment, the surface of PL-0 sample became rough with gullies and cracks. A large number of uneven and rough corroded surfaces were formed with slight cracks on the surfaces of PL-1 and PL-2. The surface morphology of PL-3 sample changed from smooth to uneven, no cracks appeared, high mechanical properties could be retained. However, as shown in Fig. 4, the sample of PL-3 aged for 30 days was still resilient as shown by scanning electron microscope magnified by 5000 times, which was consistent with the mechanical properties data. In terms of mechanical properties, the brittle fracture of polypropylene is optimized into resilient fracture. This is because according to the silver-grain shear theory of elastomeric toughening theory, rubber polymers in the blending system are dispersed phase and randomly distributed in the continuous phase of polypropylene, making the large and brittle spherulite of polypropylene become fine and dense spherulite. When subjected to external forces, first of all, silver streaks, cracks or cracks will be generated in polypropylene as the continuous phase, while rubber particles in the continuous phase act as the stress concentration point and continue to induce the production of a large number of silver streaks and shear bands, which can absorb a large amount of energy and thus prevent the passing of cracks. At the same time, rubber particles can also block or even stop the growth of small cracks, so that they do not develop into destructive cracks, so as to achieve the purpose of toughening and improve the aging resistance of polypropylene^{25, 26}.

Capillary rheology analysis

Capillary rheology analysis was used to study the molecular weight of high temperature polymer resin. The static torque of the resin or crosslinked polymers are produced in a closed chamber under the influence of a small amount of oxygen during oxidative degradation of the molecular chain²⁷. Fig. 5 shows the static capillary rheology of PP/cotton stalk lignin samples before and after thermal and oxygen aging test. As shown in Fig. 5.a, the torque of unaged PP/ cotton stalk lignin samples increased in turn with the increase of lignin content at the rheological time of 1 min, which was because that at the beginning of rheology, shear force had a little influence and the molecular weight of the blend was closest to the molecular weight of the unaged sample. The more lignin was added, the higher the molecular weight of the composite material was, and the higher the torque

Table 4. Indoor Thermal and Oxygen Aging Properties of PP/Lignin Blends

Lignin Content %	Mechanical Properties	Aging Time / day					
		0	5	10	15	20	30
0	Tensile Strength/MPa	40.5	41.56	40.81	39.52	38.85	38.51
	Elongation at break/%	491.0	412.9	393.8	360.4	317.2	288.2
1	Tensile Strength/MPa	35.32	35.96	34.87	34.69	34.56	33.32
	Elongation at break/%	581.2	501.1	476.0	446.3	417.9	395.2
2	Tensile Strength/MPa	33.71	35.06	35.94	34.37	33.49	31.89
	Elongation at break/%	593.5	549.0	534.7	505.7	491.4	458.8
3	Tensile Strength/MPa	33.05	33.95	32.91	32.54	31.59	30.24
	Elongation at break/%	637.1	556.4	544.1	521.1	515.4	484.8

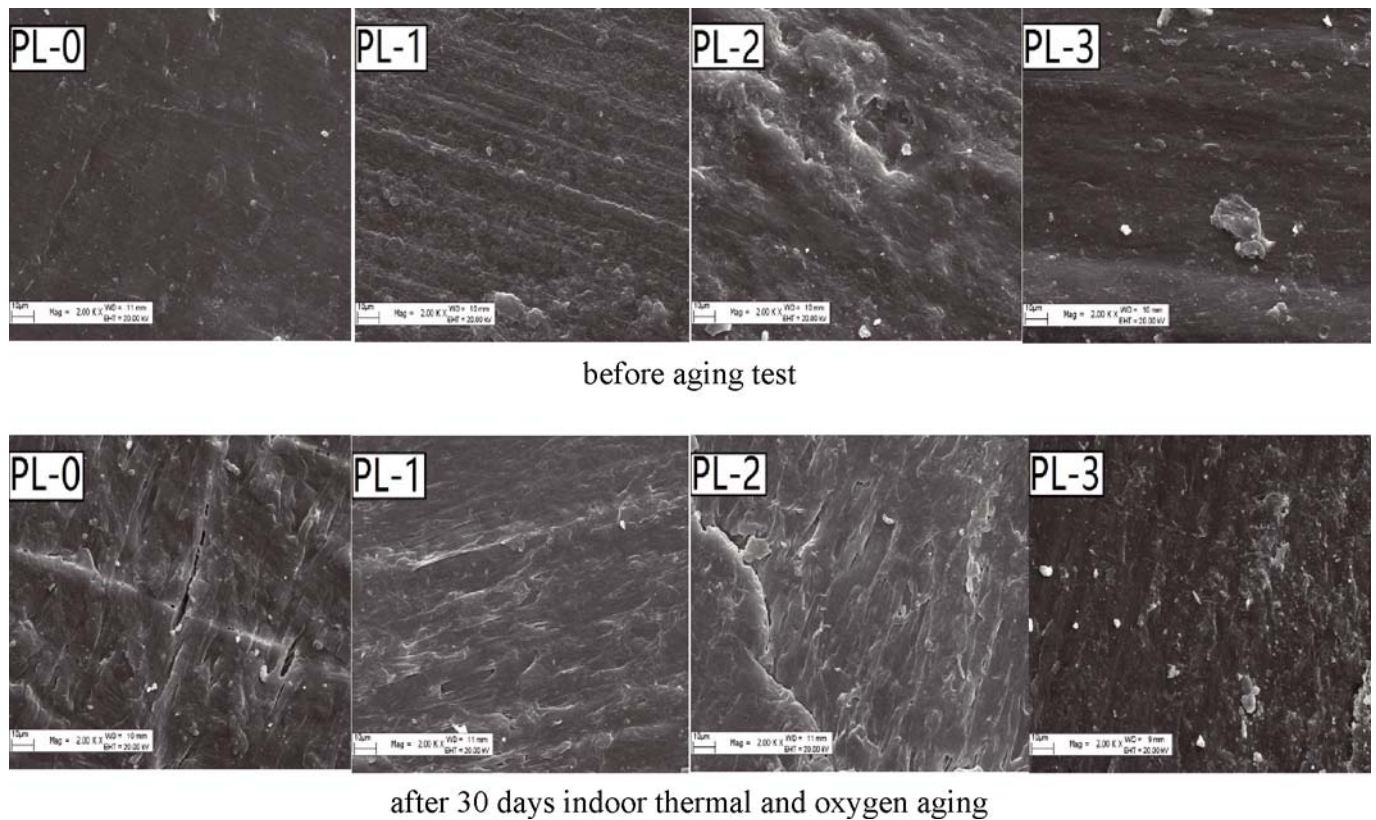


Figure 3. SEM images of PP/Lignin samples before and after aging test

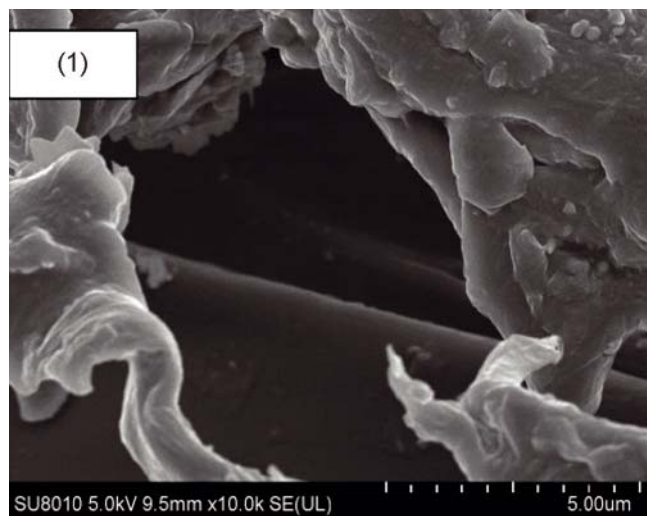


Figure 4. SEM image of PL-3 after 30 days aging

was. With the extension of rheological time, the torque tends to decrease, which was because under the action of shear force, the material flow resistance decreased, the fluidity increased, and the torque decreased²⁸. As shown in Fig. 5.b, compared with the unaged samples, the torque of the aged samples decreased, which was due to the degradation of the aged samples to different degrees. As the rheological time increased, the torques of samples PL-1, PL-2 and PL-3 all decreased first and then was gradual. The torques of the three styles were close to each other, but the changes were not very large, indicating that the aging of samples during this period presented yield deformation. The molecular chain was not completely broken, which had certain utilization value²⁹.

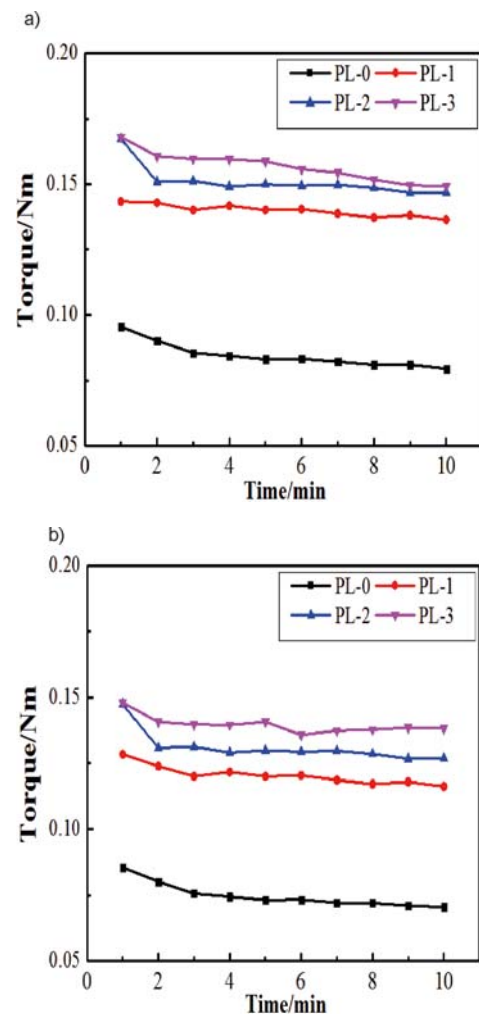


Figure 5. Capillary Rheology of PP/Lignin Samples: a: Unaged PP/Lignin specimens; b: Indoor thermal and oxygen aging 30 days PP/Lignin specimens

Table 5. Comparison of Peak Area of C1s and O1s between Unaged and Aged PP/Lignin Samples

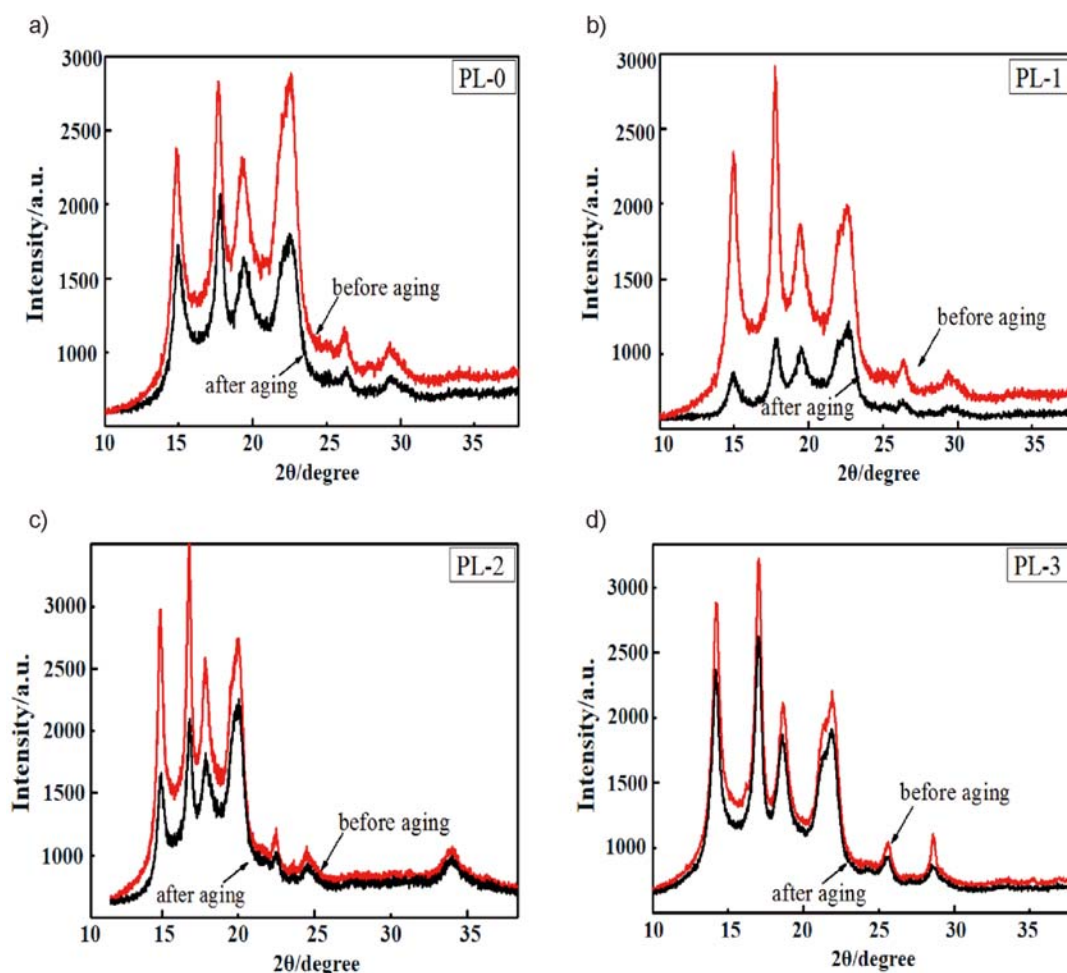
	Before aged				After 30 days aged			
	PL-0	PL-1	PL-2	PL-3	PL-0	PL-1	PL-2	PL-3
C-C/%	96.94	84.22	87.36	89.61	90.87	81.44	83.26	86.09
C-O/%	3.06	3.42	4.05	4.17	5.06	5.94	7.09	7.31
C=O/%	0	3.71	4.09	4.18	4.07	4.81	5.56	5.88

X-ray photoelectron spectroscopy

As shown in Table 5, XPS data shows that after thermal and oxygen aging of PP/ cotton stalk lignin samples, oxygen-containing groups appeared on the surface, mainly C-C content decreased with the extension of aging time, while C-O and C=O gradually increased. The C-O functional groups of PL-0, PL-1, PL-2 and PL-3 at 0 days of aging were 3.06%, 3.42%, 4.05% and 4.17% (caused by thermal aging during injection³⁰). With the increase of aging time, degradation and interaction within the molecular chain were weakened, and the degree of oxidation on the surface of PP/ lignin samples gradually increased. The content of C=O functional groups of PL-0, PL-1, PL-2 and PL-3 increased to 4.07%, 4.83%, 5.56% and 5.88% respectively after 30 days of aging. The PP structure contains a tertiary hydrogen, which can easily generate hydrogen peroxide, thus accelerating the formation of hydrogen peroxide in the main chain. With the increase of lignin content, the content growth rate of C=O functional groups decreased after aging test of PP/ cotton stalk lignin samples. This is because lignin contains a large number of phenolic hydroxyl groups, which can slow down the aging rate of samples^{31, 32}.

X-ray powder diffraction analysis before and after sample aging

The crystal phase structures of PL-1, PL-2, PL-3 and PL-4 samples before and after aging were tested by X-ray diffraction (XRD), and the XRD spectra obtained was shown in Figure 6. As can be seen from the figure, after indoor thermal and oxygen aging, the crystal structure of PP/ cotton stalk lignin sample was basically consistent with that of pure PP, except that the strength and area of crystallization peak changed. Compared with the unaged samples after aging, the corresponding crystallization peak strength of PL-1, PL-2, PL-3 and PL-4 decreased significantly, and the mechanical properties showed that the tensile strength decreased. With the increase of lignin content, the gap between the crystallization peak area of the sample after aging and the corresponding non-aging sample also decreased, which indicated that the addition of coupling agent also made lignin and polypropylene blend better³³, the crystallinity decreased less and the anti-aging ability increased³⁴, which was consistent with the mechanical performance³⁵.

**Figure 6.** XRD scans for PP/Lignin blends before and after aging: a, b, c, d: XRD scans of PL-1, PL-2, PL-3, PL-4, respectively

CONCLUSIONS

The addition of silane coupling agent KH-550, KH792 and titanate coupling agent NDZ-201 can improve the melting index of PP/ cotton stalk lignin samples, among which the titanate coupling agent NDZ-201 had the best effect with an increase of 42.4%. After injection molding, lignin treated with titanate coupling agent NDZ-201 mixed with PP in different proportions was tested and analyzed for tensile properties and impact strength. The results showed that the addition of lignin could effectively improve the mechanical properties of pure PP. When lignin content is 2%, the retention rate of fracture elongation is the best. After 30 days of indoor thermal and oxygen aging test, the addition of titanate coupling agent NDZ-201 could effectively improve the antioxidant capacity of PP/ cotton stalk lignin samples. With the increase of lignin content, the antioxidant capacity of the samples were enhanced. After aging, the degradation in the molecules was reduced, and the surface of the samples became smooth, with less increase in C=O and less decrease in crystallinity.

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