

Impact of natural antioxidant systems on the oxidation resistance and mechanical properties of polypropylene

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This paper describes the separation of oxidation resistant components from the seeds of pomegranate (PSA), grape (GSE) and sea buckthorn (SSE). The anti-oxidation properties of the resultant extracts, used as the natural anti-oxidants for polypropylene (PP), were compared with Irganox1010. The effects of these natural antioxidants on the antioxidant levels of PP samples were estimated by thermal oxidative aging and micromixed rheology, OIT, XRD, SEM, TEM and mechanical properties tests of samples before and after aging. The results show that adding PSA, GSE and SSE can obviously increase the mechanical properties of PP. In addition, the molding stability of polypropylene raw material is prolonged and improved. Moreover, the mechanical properties of the PP samples after 240 h of thermal oxidative aging indicates that, the best results, closest to the anti-oxidation ability of Irganox1010, can be obtained when the additive amount is 0.5% (wt%) for PSE or 0.7% (wt%) for GSE.

Keywords: Polypropylene; Natural antioxidants; Thermal oxidative aging; Oxidation induction time; Grape seeds

INTRODUCTION

Polypropylene (PP) has become one of the most important thermoplastics in the industry, and the amount of PP is also the highest among various synthetic materials¹. PP is widely used in textiles, packaging, home appliances, electromechanical, transportation, construction and other industries due to its excellent mechanical properties, low cost, and processability. It can produce woven bags, boxes and containers, automotive plastic parts, and electronic appliances, plastic films, pipes and fiber products, etc^{2, 3}. The unstable helical conformation of PP and the tertiary carbon atoms in the structure are relatively sensitive to oxidation, and are prone to be oxidatively degraded by thermal oxygenation during processing and use, which affects the practical application of PP. In order to make the PP material durable, antioxidant treatment of PP is necessary^{4, 5, 6, 7}. At present, the synthetic antioxidants added in PP are excellent in performance but there is a potential safety hazard that cannot be ignored. With the increase in the amount of PP used in food-contact objects and medical products, higher requirements are placed on the safety performance of PP materials⁸⁻¹³. Natural antioxidants with high safety and no toxic side effects provide a new direction for polymer. In the oxidizing environment, organisms generate a series of free radicals¹⁴. In order to reduce the amount of reactive oxygen species and free radicals, organisms synthesize various substances with strong antioxidant effects^{15, 16, 17}. These substances are widely present in the roots, stems and leaves, and fruits of plants, and their anti-oxidation reaction mechanism is similar¹⁸. So far, this area has mainly studied the effects of carotenoids, natural polyphenols, and lignin as natural antioxidants on various polymers. Carotenoids can react with alkyl groups, alkoxy groups, and peroxy groups in polymers^{19, 20}, eliminating free radicals via a single electron transfer mechanism²¹. Carotenoids effectively scavenge alkyl and alkoxy groups at low oxygen concentrations, impeding the oxidation of

polyolefins, but their efficiency is limited^{19, 22, 23}. Natural polyphenols are polyphenolic hydroxy compounds that are abundant in various plant species. The presence of phenolic hydroxyl groups gives it antioxidant activity, and the free radical scavenging action of polyphenols mainly utilizes the dehydrogenation of phenolic hydroxyl groups to eliminate free radicals²⁴⁻³⁰. Researches using the free radical scavenging capacity of the phenolic hydroxyl groups of lignosulfonate as the polymeric stabilizers have been extensively tried. Most of the experimental results also proved the anti-oxidation effect of lignin³¹⁻³⁵.

In this paper, we use waste processing residues, from beverage factories and wineries, as raw materials to extract a large number of active antioxidant species from fruit seeds, and applied them as PP antioxidants via melt-blending with PP, by which the inducing time of the PP material through oxidation has been significantly increased. Rheological and mechanical properties were measured to evaluate the effect of natural antioxidants on the molding processability of polypropylene. The effect of various antioxidants on the crystal structure of PP was analyzed by XRD. The apparent morphology of the sample was used to determine the stability of different antioxidants in PP thermal oxygen aging. A comparative study on the anti-oxidation effects of commercial antioxidants and natural antioxidants on PP was conducted, screening out the natural antioxidants with the best anti-oxidation effect on PP, providing a variety of active antioxidant species for polypropylene.

EXPERIMENTAL

Materials

PP (T30S, Homopolymer spinning grade, MFR 1.8~3.0 g/min, $\overline{M}_n = 7\sim 24 \times 10^4$ g/mol) was supplied by China Petroleum Dushanzi Petrochemical Company; MFR experimental parameters: load is 2.16 kg; temperature is 200°C (polypropylene molding and processing

temperature); samples are taken once every 30 s for a total of 6 times; each adding amount is 4–5 g. Polyphenol antioxidant Irganox 1010 (purity quotient of $\geq 98\%$) was supplied by Aladdin, China; Pomegranate seed extract (PSE), Grape seed extract (GSE), and Sea buckthorn seed extract (SSE) originate from the waste residue of beverage plants (Pijaman Pomegranate Manor, Xinjiang, China) and wineries (Kashmir Moulin Wine, Xinjiang, China), and are extracted using a hydro alcoholic solution.

Extraction process of the natural anti oxidation components

The waste seeds were washed, dried and grinded before sifting through an 80 mesh sieve. The active anti-oxidant components were extracted via ultrasonic-assisted extraction (wave frequency = 40 KHz, electric power = 250 W). The resultant extractions were concentrated under vacuum and dried at 40°C to give the natural anti-oxidants. The best results were obtained using 20% v/v ethanol with a solid-liquid ratio of 1:25 at 55°C for 40 min, in the case of PSE, giving 6.843 ± 0.930 mg/g of polyphenol; Using 60% v/v ethanol with a solid-liquid ratio of 1:25 at 55°C for 40 min, in the case of GSE, giving 10.073 ± 1.130 mg/g of polyphenol; And using 30% v/v ethanol with a solid-liquid ratio of 1:25 at 45°C for 60 min, in the case of SSE, giving 9.606 ± 0.320 mg/g of polyphenol.

Preparation of the standard sample

The accurately weighed PP and different antioxidants (The amount of antioxidant 1010 in polypropylene is generally 0.1%–0.5% and PP use for experiment contains 0.3 wt% of AO because China Petroleum Corporation stipulates that the addition amount of antioxidant 1010 in T30S is 0.3%) in a certain ratio (Table 1) were mixed in a high speed mixer for 15 min, and then extruded through a twin-screw extruder (TE-20, Keya company China) at temperatures of 150, 190, 200, 210 and 200°C, before injection molded at temperatures of 200 and 210°C into dog-bone type specimen by plastic injection molding machine (XL-400 VI: Ningbo China).

Extruder for melt blending extrusion granulation, process conditions: The machine head temperature is

200°C, the first stage temperature is 220°C, the second stage temperature is 200°C, the third stage temperature is 195°C, the fourth stage temperature is 215°C, the melting temperature is 180°C, the main machine frequency is 14.0 Hz, the feeding frequency is 14.0 Hz. The pellets are then injection molded into standard dog-bone type specimen. The injection process conditions are as follows: the first stage temperature is 200°C, the second stage temperature is 190°C, the injection pressure is 85 bar, the sol pressure is 80 bar, the holding pressure is 70 bar, and natural cooling for 24 hours.

Determination of anti-thermal-oxidation property in polypropylene

Oxidation induction time (OIT): OIT is the measurement of the time when the sample begins to undergo automatic catalytic oxidation under high temperature (200°C) oxygen, and is an indicator to evaluate the thermal degradation capability of the material in molding, storage, welding and use. The principle is that the plastic sample is placed in a differential thermal analyzer with an inert reference (such as alumina), which rapidly replaces the inert gas (such as nitrogen) in the sample chamber with oxygen at a certain temperature. The oxidation induction time of different PP samples was measured by DSC (Q-2000, USA 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 afterwards, 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.

Capillary rheological test: Capillary rheometer is mainly used for testing the rheological properties of polymer materials; The torque value of the samples (Before starting the experiment, cut PP, PP-AO, PP-PSE1, PP-PSE2, PP-PSE3, PP-GSE1, PP-GSE2, PP-GSE3, PP-SSE1, PP-SSE2 and PP-SSE3 samples respectively into 6 g, these samples before and after aging were placed in the charging barrel and mixed for 10 min) at different time slots were obtained by a micro mixing rheometer (MiniLabII,

Table 1. The compound proportion of PP samples and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO)

Sample	PP (wt%)	PSE (wt%)	GSE (wt%)	SSE (wt%)	AO-1010 (wt%)
PP	100	0	0	0	0
PP-AO	99.7	0	0	0	0.3
PP-PSE1	99.7	0.3	0	0	0
PP-PSE2	99.5	0.5	0	0	0
PP-PSE3	99.3	0.7	0	0	0
PP-GSE1	99.7	0	0.3	0	0
PP-GSE2	99.5	0	0.5	0	0
PP-GSE3	99.3	0	0.7	0	0
PP-SSE1	99.7	0	0	0.3	0
PP-SSE2	99.5	0	0	0.5	0
PP-SSE3	99.3	0	0	0.7	0

Germany Haake), using co-rotating twin-screw with a rotation rate of 30 r/min at 200°C (set value of the charging barrel). Collect 10 minutes of torque and time data, and take the average value every 60 seconds as a point to draw the torque time curve.

Indoor thermal oxygen aging test: The standard tensile sample was placed in the blower oven, and continuously aged for 240 h. The aging process was monitored by doing performance testing for the samples taken every 48 h.

Mechanical properties: 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 (1):

$$\sigma = \frac{P}{bd} \quad (1)$$

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 (2):

$$E = \frac{L-L_0}{L_0} \times 100\% \quad (2)$$

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

Analysis

The XRD curves of the samples were obtained using the X-ray diffraction analysis (XRD, D8 advance Bruker, Germany) Cu-K α radiation with p-Ni filter (U = 40 kV, A = 40 mA) in the 2θ range of 10° to 60° at a scan rate of 6°/min. Transmission electron microscopy (TEM) images were obtained using the transmission electron microscopy (TEM, JEM-2100, Electronics Co, Ltd. Japan) to observe the dispersing effect of additives in PP, while the accelerating voltage was 100 kV. Scanning electron microscopic (SEM) images were obtained using the scanning electron microscopy (SEM, JSM-5600LV, JEOL, Ltd. Japan) to observe the surface morphology before and after aging of sample.

RESULTS AND DISCUSSION

X-ray diffraction (XRD)

The XRD scans for different PP samples are indicated in Fig. 1. With the addition of different extracts, the overall intensity of the XRD peak increases in turn. The spectrum of each sample is very similar, and the obvious diffraction peaks are all PP α crystals. In contrast to the Irganox1010 (commercially available antioxidant) added PP, the β -crystal diffraction peaks appeared at 2θ of 16.2° for the PSE, GSE and SSE added PP samples. The existence of β crystalline form reflects that, all kinds of extracts act as beta crystal nucleating agents in the PP matrix, thus indicates the increase of tensile strength and impact strength in the sample.

Oxidation induction time

The OIT test is a method for evaluating the thermal stability of a polymer in an atmosphere of oxygen at a temperature higher than the melting point of the poly-

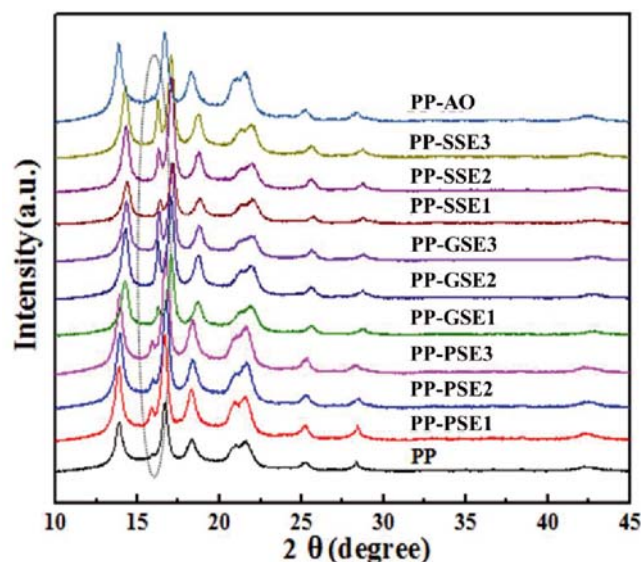


Figure 1. XRD curve of PP samples and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO) before aging

mer. This method can easily and intuitively determine the effect of antioxidant on the thermal stability of PP. The antioxidants in the sample can increase the oxidation induction time, and subsequently delay the thermal oxygen degradation of the sample.

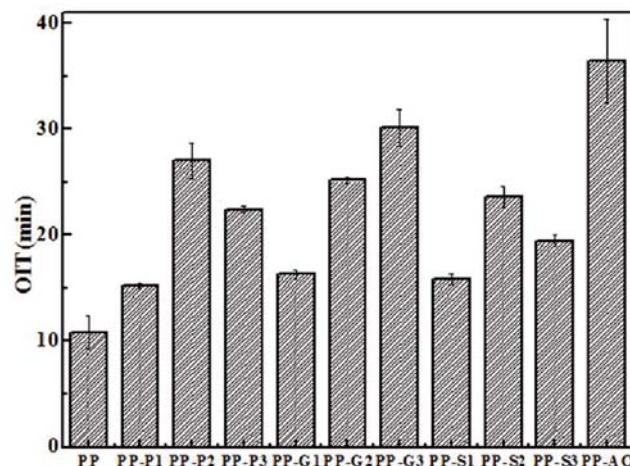


Figure 2. OIT curve of PP samples and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO) before aging

The OIT data (Fig. 2) shows that, adding various types of extracts to PP can significantly increase the oxidation induction time of PP, and different extracts have different lifting capacities. PSE, GSE and SSE can delay the oxidative degradation of PP in oxygen-enriched and high-temperature environments. The OIT of PSE, GSE and SSE increases with the added amount. Although compared with Irganox 1010, all the natural antioxidants slow down the ability of PP to oxidize and degrade, but they also play a certain role in anti-oxidation. Most of the literature suggests^{36, 37} that the removal of PP radicals by natural polyphenols happens mainly through the hydrogen transfer from the phenolic hydroxyl group to the reactive free radicals and quenches the active radicals to stabilize the degradation of PP.

Effect of antioxidant on the rheological properties of PP before and after aging

The degree of aging and degradation of the polymer was determined by analyzing the relationship, through a micro mixed rheology test, between the change in the torque values of the PP samples before and after thermal oxidation. Figure 3 indicates that, while the rotation rate of screw is 30 r/min and the temperature of the charging barrel keeps at 200°C, the torque values of all samples, in the first 1min of the aging process, fall into the range of 0.198 Nm~0.205 Nm, indicating the samples having very similar molecular weight and initial torque values. After 10 min of shearing process, the torque value of the pure PP sample falls from 0.198 Nm to 0.136 Nm (torque retention rate = 68.7%). However, torque retention rate of all the anti-oxidant added samples keeps within 80%–90%, illustrating the ability of the natural antioxidants (as for the synthetic antioxidant) to enhance the molding stability of polypropylene. The initial torque values of the pure PP sample are 0.104 Nm and 0.087 Nm after 96 h and 240 h of thermal oxidation, respectively; declined 47.5% and 56.1% comparing to the PP sample before aging. This is because the continuous thermal oxidation attack results in the degradation and molecular chain breaking of the polypropylene, leading to the decrease of molecular weight and the subsequent

change of torque. On the other hand, even the natural antioxidant added PP sample with the lowest anti oxidation property, PP-SSE1, shows a decline of only 17.1% in torque value after 96 h of aging. It can be seen from the relation curve of the torque value and time after 240 h of aging that, the initial torque value of PP-SSE1, the SSE sample with a molecular fraction of 0.3%, got close to the pure PP sample, indicating the lost of its anti-oxidation property after 240 h; while the PP-PSE2, PP-PSE3 and PP-GSE3 samples still retain the anti-oxidation ability comparable with PP-AO.

Mechanical properties before and after aging analyses of PP samples

It can be seen from Table 2 that, both the tensile strength and the elongation at break of the PP sample have increased after the addition of PSE, GSE and SSE. This is because the toughness and strength of the PP sample have been enhanced by the appearance of β -crystal diffraction peak (Fig. 1) after the addition of the natural anti-oxidants. At the beginning of the thermal oxidative aging process, except PP-PSE3, the tensile strength of other samples slightly increased with the passage of aging time. It began to keep declining at a later stage, especially for the pure PP sample.

The reason for this variation is due to, at the beginning of the thermal oxidation, the breaking of the PP's mole-

Figure 3. Capillary Rheology of PP samples and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO) before aging and after 96 hours and 240 hours of aging

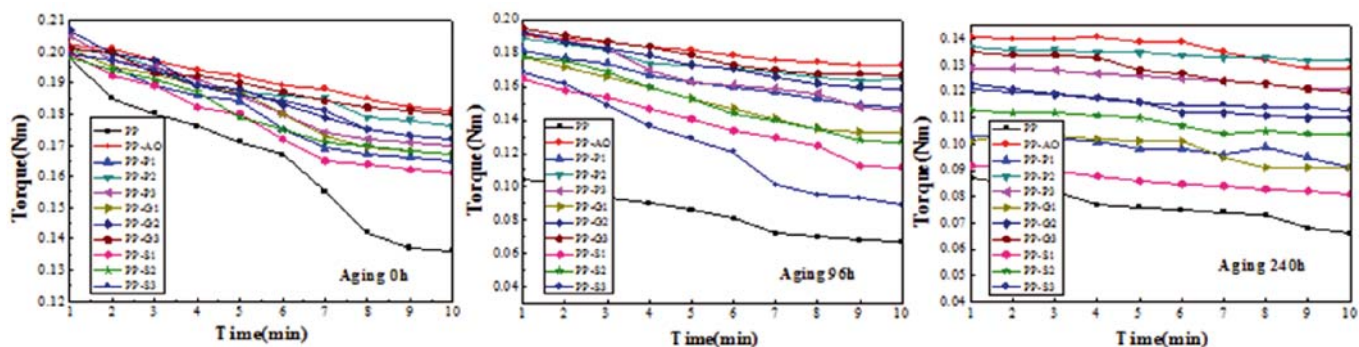


Table 2. Effect of Antioxidants (0.3–0.7 wt% content PSE, GSE, SSE and AO) on mechanical properties of PP samples before and after aging 48, 96, 144, 196 and 240 hours

Sample	Tensile strength (M Pa) /Elongation at break (%) /Young's modulus (M Pa)					
	0 h	48 h	96 h	144 h	196 h	240 h
PP	40.1/514.2/282.37	42.9/394.5/336.89	43.6/242.4/330.27	41.9/198.1/322.50	40.1/169.9/307.15	38.1/126.1/305.81
PP-AO	40.6/520.7/329.49	41.4/488.1/368.42	42.4/388.7/340.30	42.8/408.7/336.25	40.3/245.7/309.48	39.8/215.0/251.03
PP-PSE1	41.5/521.2/379.41	41.8/413.9/399.21	42.2/312.5/370.60	42.8/232.1/346.30	41.4/186.9/331.53	39.4/167.7/268.64
PP-PSE2	41.6/527.1/350.84	42.4/466.8/362.92	42.9/375.7/336.70	41.2/292.2/325.35	40.4/216.9/309.95	40.1/206.4/263.39
PP-PSE3	42.4/529.7/355.98	40.3/441.4/344.97	42.6/345.3/340.72	40.8/266.7/334.14	40.1/228.7/322.08	39.3/211.2/268.21
PP-GSE1	42.7/523.2/412.25	44.3/420.7/557.85	45.7/325.3/502.81	45.1/242.8/475.42	43.8/194.1/419.27	40.4/176.1/363.53
PP-GSE2	43.0/539.4/377.19	45.6/459.8/485.15	46.4/378.1/434.99	43.4/300.6/428.01	41.9/220.1/425.40	40.0/209.8/421.43
PP-GSE3	43.5/535.1/368.25	45.3/476.1/545.72	45.9/375.7/459.12	43.3/322.0/433.38	42.4/233.9/430.37	40.3/211.9/393.80
PP-SSE1	42.5/532.0/387.37	44.4/402.6/516.09	46.1/327.8/507.12	45.6/241.3/481.33	43.6/187.7/425.68	39.5/159.6/423.74
PP-SSE2	42.9/541.3/371.70	45.6/420.5/524.29	48.6/358.4/518.44	46.5/284.9/465.05	44.8/213.7/356.10	39.1/186.7/345.92
PP-SSE3	43.4/546.6/336.35	44.9/411.0/517.55	46.4/339.1/516.09	46.3/253.3/507.21	43.5/194.3/460.56	40.3/152.9/403.01

cular chain under a thermal oxygen process, leading to the increase in the tensile strength of the sample via the formation of a partial network through the crosslinking effect between the free radicals. At the later stage, the partial network structure is destroyed by the cleavage and branching of the molecular chain, resulting in the increasing number of active free radicals, which lead to the continuous activation and accelerated degradation of the molecular chain. After a 96 h of thermal oxidation, the elongation at break of a pure PP sample was maintained at 47.1%. For the PP samples after the addition of synthetic or natural antioxidants, the elongation at break retention rate values are 71.9%, 60.1%, 68.0%, 66.0%, 62.2%, 70.1%, 70.2%, 61.7%, 66.0% and 71.9% for PP-AO, PP-PSE1, PP-PSE2, PP-PSE3, PP-GSE1, PP-GSE2, PP-GSE3, PP-SSE1, PP-SSE2 and PP-SSE3, respectively. These results indicate that, the pure PP sample becomes brittle and completely loses its application value after continuous placement in oven at 60°C for 96 h, while the addition of natural antioxidants can obviously increase the heat and oxygen resistance of the PP sample. And the anti-oxidation ability of the natural anti-oxidants is comparable to the synthetic antioxidant Irganox 1010.

Before aging, the Young's modulus of each samples were basically low. This may be because after the polypropylene molding process, the internal thermal molecular movement slowly affects the crystallinity and causes the Young's modulus to decrease; However, the significant improvement after 48 hours of aging is probably because aging improves the intense movement of thermal molecules inside the sample, improves the crystallinity and thus the Young's modulus. With the increase of the aging time, the Young's modulus gradually decreased, and the value appeared the lowest at 240 h compared with 48 h. And it is consistent with the change trend of tensile strength, which gradually decreases with the decrease of strength.

Submicroscopic or ultrastructural analysis of PP samples

Through the study of the TEM analysis of each samples (Fig. 4) show that the dispersibility in the PP matrix is best when the PSE addition amount is 0.5% (wt%). When the amount of PSE added exceeds 0.5% (wt%), PSE particles will agglomerate in the matrix, resulting in stress concentration, so that the sample does not have a toughening effect, and fine cracks and plastic deformation will occur during the stretching operation, causing Stress cracking occurred in the specimen, and the ultimate elongation at break was shown. At the same time, with the increase of thermal and oxygen aging time, PSE could not effectively capture free radicals due to the agglomeration phenomenon, which reduced the molecular migration speed of PSE, so that PSE could not better delay the degradation of PP.

By observing the dispersion of GSE in PP matrix (Fig. 4), it can be seen that compared with PSE, GSE is a round particle with uniform and similar size. At low content, GSE can be evenly dispersed in PP matrix. When the content is 0.7% (wt%), it has the best dispersion in PP. With the increase of GSE, agglomeration will occur, which shows that elongation at break decreases. On the other hand, agglomeration can also affect the speed

of molecular migration, not only can't GSE effectively capture free radicals, but also can cause resource waste.

The dispersion state of SSE in PP matrix can be observed visually by projection electron microscope. As same as PSE, the SSE content is 0.5% (wt%), which has the best dispersion in PP. Increasing the amount of SSE did not improve the antioxidant efficiency of SSE, but only resulted in agglomeration, thus affecting the antioxidant capacity of SSE.

To sum up, the TEM results (Fig. 4) reveal that, the solid particles agglomerate in the PP matrix as the amount of natural antioxidants increases. While the mass fraction is 0.7%, the order of agglomerate rate is PP-SSE3>PP-PSE3>PP-GSE3. Hence the anti-oxidation efficiency of the PP-PSE3 and PP-SSE3 samples at the later stage of the thermal oxidation process is obviously lower than PP-GSE3, which is probably due to the better dispersivity of the grapeseed extract.

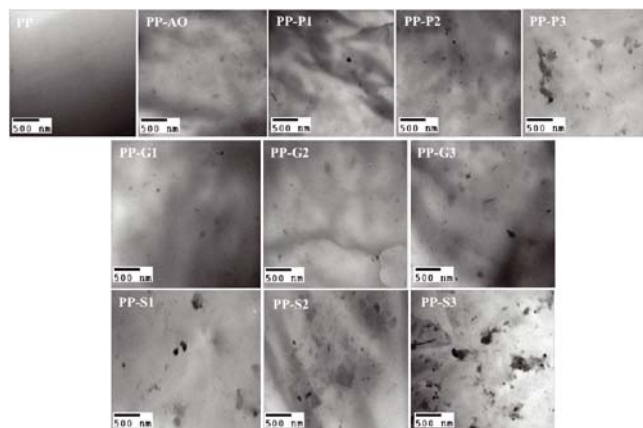


Figure 4. TEM images of PP samples and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO)

Analysis of the morphology of PP sample after indoor exposure aging

Figure 5 shows the SEM images of different PP samples before and after thermo-oxidative aging. PP-0d is an unaged pure PP sample. PP-10d is a pure PP sample that has been aged for 10 days. All the other samples are ten days old. The surface of the unaged PP samples was smooth and wrinkle-free, and after accelerated aging by indoor hot oxygen cracks with criss-cross patterns appear on the surface. This is a macroscopic representation of the oxidative degradation of PP, and the crack elongation of PP samples will continue to decrease, resulting in the drop of mechanical properties. Adding antioxidants to the PP sample can effectively reduce the formation of surface cracks. The PP sample (PP-AO), to which Irganox 1010 was added, had no cracks on the surface after thermal oxygen aging, but the surface became uneven. Except for a small amount of little cracks in PP-PSE1, the other samples of PSE-added PP were crack-free, and the surface was roughened by the influence of temperature and oxygen. Among them, the surface roughness of PP-PSE2 sample was the lowest. PSE can delay the embrittlement and aging of PP, so that the sample can maintain certain toughness, and the mechanical properties of PP can be maintained for a longer time in a hot oxygen environment. The addition of GSE to the PP matrix can reduce or eliminate the appearance of cracks.

The surface of PP-GSE3 sample is relatively smooth with only a few spots and wrinkles. For the PP-GSE1 sample, there are a few minor cracks appeared on the surface. As to the PP-GSE2 and PP-GSE3 samples, the surface becomes rough. Combined with X-ray diffraction analysis, it can be concluded that, GSE promotes the generation of β crystals, which, comparing to α crystals, can significantly increase the toughness of the PP material in the PP matrix. Moreover, the GSE added PP sample has a stable oxidation resistance, so the surface of the sample after aging has no obvious cracks. The surface of the SSE added PP sample, on the other hand, became rough after aging. The same as GSE, SSE promotes the formation of beta crystals in the PP sample, thus increases the toughness of the material. Although the antioxidant capacity of SSE is lower than that of GSE and PSE, it still can effectively stabilize the PP sample to a certain extent, delaying the brittle aging of PP, which causes brittle fracture.

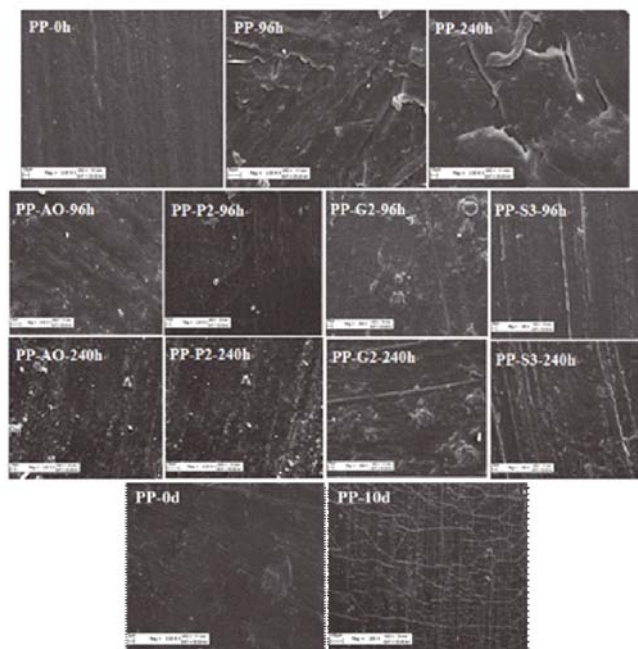


Figure 5. SEM images of PP sample and PP with 0.3–0.7 wt% anti-oxidant content (PSE, GSE, SSE and AO) after aging 96 and 240 hours

CONCLUSIONS

In this work, various natural extracts were obtained from fruit seeds and are used as PP antioxidants. It was found that, after adding into the PP sample, GSE and SSE caused the material to exhibit significant β crystal diffraction peaks and β crystal nuclear function. All three natural antioxidants studied, PSE, GSE and SSE, can increase the oxidation induction time and the stability of the PP sample in hot oxygen environment, and subsequently delay the oxidation and degradation of PP. PSE, GSE and SSE can effectively maintain the mechanical properties of PP even after indoor thermal oxygen aging. However, the anti-oxidation properties of these natural antioxidants are not directly proportional to the amount of addition. Best results of this study were obtained when the addition of PSE is 0.5% (wt%) or the addition of GSE is 0.7% (wt%) to the PP sample. And among these natural antioxidants, GSE has the

uniform particle size and the best dispersity in the PP matrix. While the addition of GSE is 0.7% (wt%) in the PP sample, the anti-oxidation effect is comparable to Irganox 1010.

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