Research on the Antioxidation of Rosemary in Polypropylene

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Abstract. Effects of Rosemary Antioxidanton, extracted from Rosmarinus officinalis with different solvents, on the antioxidantive properties of polypropylene were evaluated by measuring the oxidation induction temperature. For comparison purposes, the effects of a synthetic phenolic commercial antioxidant Irganox B215, were also analyzed. The results showed that Rao is a more efficient thermal antioxidant for polymers compared to Irganox B215 in low concentration. Rao can be used as a natural antioxidant in place of synthetic antioxidants for polymers. Rao has the characteristic of being harmless and having high activity, good stability and abundant resources to be a good natural antioxidant.

1. Introduction
Polypropylene (PP) is an important thermoplastic resin with many desirable properties including low cost, excellent processing performance and good mechanical properties [1]. However, since the resin is easily oxidized, there is a great need to decrease the antioxidation of PP. The most efficient and convenient method to avoid oxidation and degradation is the addition of antioxidants. The worldwide increase of environmental awareness has brought some newer and higher requirements for hygienic safety to antioxidants that are added in polymer products for food and medicine contact. A growing tendency for the use of natural additives in polymers has been observed during the last several years [2]. Nevertheless, many natural products with antioxidant activity can’t be used in polymers due to their poor thermostability.

Rosmarinus officinalis L., distributed widely in European, used as a spice for thousands of years, has been applied in food, medicine and cosmetics in recent years [3]. Rosemary Antioxidanton (Rao) mainly including diterpenoids, terpenoid and flavonoids compounds [4], extracted from the stems and leaves of Rosmarinus officinalis, have many pharmacological functions in organisms, including relieving cough, removing sputum, inhibiting hypertension, protecting liver, absorbing ultraviolet radiation, antioxidation and antibacterial properties [5-11]. Rao showed a good thermal stability below 200 °C in our previous research, it thus could be used in PP whose processing temperatures is lower than 190 °C. In this report the efficiency of the antioxidant performance of Rao and a comparison with Irganox B215, when added to polypropylene, was evaluated by an oxidation induction temperature test (OIT*).
2. Materials and methods
Isotactic polypropylene (PP, XD-045, powder, MFI: 2.0-6.0 g/10 min and density: 0.41 g/cm3, Yueyangxingchang Petrochemical Co., Ltd., China) was purchased from the Guangzhou Chemical Market. Ethyl ether, ethyl acetate, chloroform, ethanol, petroleum ether, acetone and methanol were analytical-grade solvents.

Dried tender stems and leaves of Rosmarinus oficinalis were mixed with Ethyl ether, ethyl acetate, chloroform, ethanol, petroleum ether, acetone and methanol separately and extracted continuously for 1 h at reflux conditions. Rao was produced from the collected extract evaporated at 40 °C under reduced pressure.

The antioxidant composition dissolved in trichloromethane was poured into a beaker containing polymer powder. The solvent was removed through evaporation. Double-roll blending machine was used for blending polymers with antioxidants. The mixed powders were compressed into films, 0.5 mm thick. The machining temperatures were 180 °C. The weight ratios of antioxidants were 0.2%, 0.4%, 0.6%, 0.8% and 1.0% for PP. Also, pure PP samples were prepared for the purpose of comparison.

Thermooxidative stability of the PP samples was evaluated by DSC. Non-isothermal conditions were chosen to estimate the effectiveness of antioxidants in polymer plaques. OIT* is determined as the point in the thermogram where the onset of the decomposition signal result. The oxidation was observed as an increase in heat flow. The samples of 5~8 mg were placed in perforated aluminum pans with an oxygen flow of 20 mL/min. Heating rates were 10 °C/min. All the samples were analyzed.

3. Results and discussion
From the non-isothermal DSC measurements, the DSC curves of non-stabilized PP and PP stabilized by natural antioxidant Rao extracted by different solvents and synthesized antioxidant Irganox B215 in various concentrations are plotted in Fig.1, and the values of OIT* for the samples are plotted in Fig.2. These 8 kinds of antioxidants all increased OIT* of PP obviously. OIT* increased with the content of antioxidants when the additive content of antioxidants was between 0 and 1.0%.
Figure 1. The DSC curves of PP stabilized with RAO and Irganox B215 in various concentrations
The antioxidant effect of rosemary antioxidant extracted with different solvents in PP is different. The order of oxidation resistance was chloroform > petroleum ether > ethyl acetate > acetone > ethanol > ether > methanol. With the increase of Rao dosage, the difference gradually decreased. After adding more than 0.6%, OIT* of PP with Rao remained stable. As showed in Fig.2, PP containing Rao, except the methanol extract, had higher OIT*-values than Irganox B215 at the same content below 0.6%. With the increase of antioxidants dosage, the OIT* of PP added with Irganox B215 was higher than that of PP added with Rao, which implies that Rao exhibits greater efficiency than Irganox B215 as a thermal antioxidant for PP in low temperature environment, however, the thermal stability of Rao is not as good as Irganox B215. When the OIT* of PP is not too high, Rao can play its antioxidant effect. When the amount of addition increases, the OIT* of PP is higher, and Rao is not stable, which led to a reduction in antioxidant properties. It is precisely because of this reason that with the increase of the addition of Rao, the antioxidant properties of PP, which are stable by Rao extracted by various solvents, gradually decrease.

The reason for the antioxidant activity of Rao is its ability to scavenge free radicals, chelate metal cations, and donate hydrogen atoms or electrons. The main components of Rao are rosmanol, carnosic acid and carnosol identified by LC-MS in our previous research (Figure 3), which are terpenoids with adjacent hydroxide groups. Many investigations have proved that rosmanol, carnosic acid and carnosol possess antioxidant properties. The key factor for the antioxidative function is the distinctive chemical structure, which is referred to as structure-activity relationships [12]. In the practical application, there is no need to separate and purify each component in Rao, which showed an improved performance in antioxidant capacity when they were used together for the synergistic effect [13].
4. Conclusion
Thermooxidative stability of PP stabilized by Rao has been investigated preliminarily. Rao is a more efficient thermal antioxidant for polymers compared to Irganox B215 in low concentration which implies that Rao can be used as a natural antioxidant in place of synthetic antioxidants for polymers. Rao has the characters to be a good natural antioxidant as vitamin E.

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