Preparation and properties of polystyrene composites modified by macromolecular antioxidant

Qi Chen1, Zhiwei Xie1, Xu Xu1, Wei Xu2, Yufan Huang1, Yingqiang Zhang1*

1. School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418, People’s Republic of China
2. Shanghai Institute of Quality Inspection and Technical Research, Shanghai, 201114, People’s Republic of China
sh_yqzhang@sina.com

Abstract. A macromolecular antioxidant was prepared by copolymerization with styrene and modified A1010-co-PS. Its chemical structure was confirmed by Fourier transform infrared (FTIR). It was added into the formula of PS composite material and the thermal and oxygen aging experiment was carried out on the material. The tensile strength is stable at about 27MPa, the bending strength is stable at about 33MPa, and the impact strength is stable at about 2.3kJ/m². The results show that it has a more significant effect than antioxidant 1010 and has higher performance stability.

1. Introduction
Polystyrene is one of the most widely used plastics in the world, with good dimensional stability and electrical insulation properties as well as excellent transparency, excellent mechanical properties, easy to process. Therefore, it has been widely used in the automotive and engineering industry, home appliances and other fields. However, easy aging limits its further applications in some areas. In order to improve the anti-aging performance, varieties of antioxidants have been applied and many related studies have been carried out.

Hindered phenolic antioxidants [1-3] are important antioxidants, compounds which have substituents on one or both sides of the hydroxyl group (-OH) on the benzene ring. Due to the space barrier of -OH, H atom is easy to fall off from the molecule, and the combination with peroxide free radical (ROOꞏ) and hydroxyl free radical (ꞏOH) makes it inactivated, thus terminating the chain reaction of thermal oxygen aging. At present, most methods are to add small molecule antioxidants directly to PS in the processing process. In order to obtain high antioxidant properties, it needs high load of these antioxidants, which will deteriorate the physical and mechanical properties of PS composites. In addition, differences in compatibility may cause some additives to be separated from the composites. One new strategy is to macromolecule antioxidants [4]. The increase of molecular weight of antioxidant can improve its thermal stability in processing. The increase of molecular weight means the increase of branched chains, the extension of carbon chains and the increase of carbon content, which make it more compatible with the polymer. Researchers put more efforts on antioxidant macromolecule in recent years. Yang Lin et al [5] studied the thermo-oxygen stability of HIPS by antioxidant GM mechanical properties of the high impact polystyrene resin with different content of the new antioxidant GM were measured.
In this study, antioxidant 1010 was selected, macromolecularized, synthesized into a new antioxidant monomer, and copolymerized with styrene to form characteristic antioxidant polystyrene, and its structure was characterized by FT-IR. The antioxidant polystyrene was added into the composite material formula for processing and forming, and the thermal and oxygen aging of the composite material was carried out by using the thermal and oxygen aging box, and then the mechanical properties were tested and studied.

2. Experimental

Materials
Isophorone diisocyanate (IPDI) was supplied by Wanhua polyurethane Co., LTD. (Yantai, China). [Pentaerythritol tetrakys 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate] (Antioxidant 1010) was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Hydroxyethyl acrylate (HEA), Dibutyltin dilaurate (DBTDL), ethyl acetate, styrene (St), benzoyl peroxide (BPO), acacia gum powder and sodium hydroxide were all supplied by Shanghai organic pharmaceutical chemical production co., LTD. Sodium chloride was purchased from Shanghai reagent No.1 factory. The processing formula is provided by Shanghai Yingke industrial co., LTD.

2.1. Preparation of macromolecular antioxidant monomer
IPDI (46g) was placed in a four-side flask equipped with a mechanical stirrer and thermometer, and fitted with a spherical condensing tube. DBTDL added into in a nitrogen environment, with stirring on and temperature at 38℃. 18.6g of HEA (HEA/IPDI=1/1, mol) was added into the flask by a constant pressure funnel at a constant speed, and the reaction lasted for 1.5 hours. 60g of antioxidant 1010 was dissolved in 120g of ethyl acetate, then poured into another four-way flask, and the reactant of the previous step were dropped into the 1010 solution under the condition of nitrogen, water bath temperature of 80℃ and stirring on. The reaction lasted for 16 hours, and the macromolecular antioxidant monomer was obtained.

2.2. Synthesis of polystyrene containing macromolecular antioxidant
Arabica gum powder (2.4g), sodium chloride (10g) and deionized water (135mL) were mixed into a four-necked flask equipped with a mechanical stirrer, thermometer and a spherical condenser tube. Stirring and control the water bath temperature at 80℃. Clean styrene (20mL) with 5% sodium hydroxide solution to remove the polymerization inhibitor, BPO (0.25g), macromolecular antioxidant (1010/St=1/2), stired well and pour into the flask. The temperature of the water bath was rose to 85℃, and the reaction lasted for 5 hours. Then the temperature rose to 90℃, and the reaction lasted for 1 hour. The antioxidant polystyrene (A1010-co-PS) was obtained.

2.3. Processing and molding of polystyrene composites
First, coal ash was mixed with aluminum-titanium coupling agent to improve its compatibility, and then coal ash and polystyrene were put into a drying oven to dry for 8h. The materials were weighed according to the formula and put into the high-speed mixing machine. The processing formula is shown in Table 1. Antioxidant 1010 and A1010-co-PS were added to the formula, respectively, in amounts of 0.1%, 0.2%, 0.3%, 0.4% and 0.5%. After mixing evenly, the materials were poured into the twin-screw extruder for extrusion and granulation. Processing parameters are shown in Table 2 and Table 3. The extruded and granulated polystyrene particles were put into a drying box and dried for 8h. Then they were added into an injection molding machine to melt and shoot glue. Experimental splines were prepared for performance testing.
### Table 1 Experimental formula of PS/coal ash composite

| Materials | coal ash | HIPS | PS | Foaming agent | MAPS |
|-----------|----------|------|----|--------------|------|
| weight/g  | 300.00   | 123.86 | 465.23 | 8.00 | 20.60 |

| Materials                        | weight/g |  |
|----------------------------------|----------|---|
| White oil                       | 23.23    |  |
| Nucleating agent                | 28.08    |  |
| Cross-linking agent             | 1.00     |  |
| Conditioning agent              | 40.00    |  |
| Antioxygen                       | variable |  |

**Total/g** 1000

### Table 2 Machining parameters of twin-screw extruder

| Name              | Set value     | Name              | Set value     |
|-------------------|---------------|-------------------|---------------|
| 1 zone            | 180℃          | 2 zone temperature control | 220℃          |
| 3 zone            | 220℃          | 4 zone temperature control | 220℃          |
| 5 zone            | 220℃          | 6 zone temperature control | 220℃          |
| Machine head      | 210℃          | Melt temperature  | 190℃          |
| Melt pressure     | 15MPa         | Rotary speed of screw feeder | 38r/min      |

### Table 3 Processing parameters of injection molding machine

| Name         | Temperature /℃ | Name         | Temperature /℃ |
|--------------|----------------|--------------|----------------|
| Nozzle       | 220            | 1 zone       | 220            |
| 2 zone       | 200            | 3 zone       | 180            |
| 4 zone       | 25             | 5 zone       | 25             |

3. Results and discussion

#### 3.1. FT-IR analysis

The structure of the A1010-co-PS was confirmed by FT-IR analysis. As shown in Figure 1, no absorption peaks for the free NCO groups were observed between 2205 and 2270 cm⁻¹, indicating completion of the reaction. The stretching vibration peaks of Benzene ring, C=O double bond, -CH₃ and phenolic hydroxyl groups were at 1535 cm⁻¹, 1731 cm⁻¹, 2950 cm⁻¹ and 3377 cm⁻¹ respectively which suggested that required A1010-co-PS was synthesized successfully.
3.2. Thermal deformation temperature analysis of PS composites

The thermal deformation temperature of PS composites was evaluated. Figure 2 shows the thermal deformation temperatures of PS composites with different formulations. The results showed that when the proportion of antioxidant 1010 was increased, the thermal deformation temperature of the composite decreased. When the proportion of A1010-co-PS added to the composite material increases, the thermal deformation temperature of the composite material increases. It can be seen from the figure that the thermal deformation temperature of A1010-co-PS contained in the formula is relatively stable, about 66.3℃.

The reason for this result is that after the addition of small-molecule antioxidant 1010, the compatibility between the materials becomes worse, and the deformation temperature of the materials with poor compatibility is lower when the deformation amount is the same. However, the molecular structure of A1010-co-PS contains PS fragments, which can have good compatibility with the PS matrix, so the deformation temperature is higher.

3.3. Testing of mechanical properties of PS composites

For the composite materials with different proportion of antioxidant addition, they were put into the thermal oxygen aging box and subjected to thermal oxygen aging at 40℃, 50℃ and 60℃, respectively. The aging time was 12 hours. The tensile strength, bending strength and impact strength of unaged and aged materials were measured.
Figure 3, 4 and 5 respectively show the tensile strength, bending strength and impact strength of PS composites with different formulations at different aging temperatures. It can be seen from the figure that the mechanical properties of composite materials show a similar trend with the increase of the addition ratio. With the increase of the proportion of antioxidant 1010, the tensile, bending and impact properties all declined significantly, while with the increase of the proportion of A1010-co-PS, the mechanical properties of the material changed little and were stable, and the antioxidant properties were improved. The tensile strength is stable at about 27MPa, the bending strength is stable at about 33MPa, and the impact strength is stable at about 2.3kJ/m². After aging at different temperatures for 12 hours, the stability of mechanical properties was still high when A1010-co-PS was used.

The reason for this result is that after the addition of small molecule antioxidant 1010, the internal compatibility of the material becomes worse, resulting in a decrease in the mechanical properties of the material. However, the molecular structure of A1010-co-PS contains PS chain segment, which can have a good compatibility with PS matrix. Therefore, the addition ratio of A1010-co-PS will not affect the mechanical properties of the composite material too much.

Fig. 3 Tensile properties of PS composites with different formulations
(a) unaged, (b) aged at 40°C, (c) aged at 50°C, (d) aged at 60°C
Fig. 4 Bending properties of PS composites with different formulations (a) unaged, (b) aged at 40℃, (c) aged at 50℃, (d) aged at 60℃
4. Conclusion

We prepared the macromolecular antioxidant, and via the polymerization of styrene, the modified polystyrene A1010-co-PS was successfully polymerized. The structure of the modified polystyrene A1010-co-PS was confirmed by FT-IR. In the thermal and oxygen aging experiment of materials, A1010-co-PS, as an additive, has the more significant effect than antioxidant 1010. The amount of addition could not have a notable impact on the mechanical properties of materials, for its higher performance stability. In a word, all the above results reveal the macromolecular antioxidant has extensive potential applications in flame retardant PS composite products.

References

[1] Ouyang C F. Improving the aging resistance of SBS tri-block copolymer modified asphalt by addition of antioxidants[J]. Polymer Degradation and Stability, 2006, 91(4): 795-804.
[2] Shehata A B. Effect of some polymeric phenolic antioxidants on the properties of SBR volatilizates[J]. Polymer Plastics Technology and Engineering, 2005, 44(7): 1281-1295.
[3] Lundback M, Hedenqvist M S, Mattozzi A. Migration of phenolic antioxidants from linear and branched polyethylene[J]. Polymer Degradation and Stability, 2006(91): 1571-1580.
[4] Wang Gang, Wang Jian. Advances in the mechanism of antioxidant action [J]. Aging and application of synthetic materials, 2006, 35(2): 38-42.
[5] Yang Lin. Effect of antioxidant GM on thermal oxygen stability of HIPS [J]. Aging and application of synthetic materials, 2012, 41(3): 1-5.