Journal of Alloys and Compounds 509 (2011) 10207–10210

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Physical properties of syndiotactic polystyrene (sPS)/poly(2,6-dimethyl-1,4-phenylene oxide (PPO) alloys and their feasible estimation for reflective cups of light emitting diodes (LEDs)

Ming-Hua Chung[a,*], Jian-Shian Lin[b], Tsung-Eong Hsieh[a], Nien-Po Chen[b], Chen-Ming Chen[c], Chin-Hsiu Cheng[c], Lung-Chang Liu[c]

[a] *Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, 300, Taiwan, ROC*
[b] *Department of Electro-Optical Engineering, Yuanze University, Taoyuan, 320, Taiwan, ROC*
[c] *Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, 30011, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 11 February 2011
Received in revised form 10 August 2011
Accepted 14 August 2011
Available online 22 August 2011

Keywords:
Composite materials
Polymers
Elastomers
Plastics
Mechanical properties
Thermochemistry
Thermal analysis

ABSTRACT

In this paper, the effects of antioxidants and processing parameters on the thermal stability and processability of sPS have been investigated. Experimental results indicate that a long processing duration and mechanic shearing force accelerate the thermal oxidation and addition of antioxidants into sPS can effectively improve color contamination and thermal stability. Furthermore, feasible estimation of sPS/PPO alloys for reflective cups of light emitting diodes (LEDs) have also been made, demonstrating that sPS/PPO alloys are potential candidates by the appropriate prescription of impact modifiers, flame retardants, and titanium dioxide.

1. Introduction

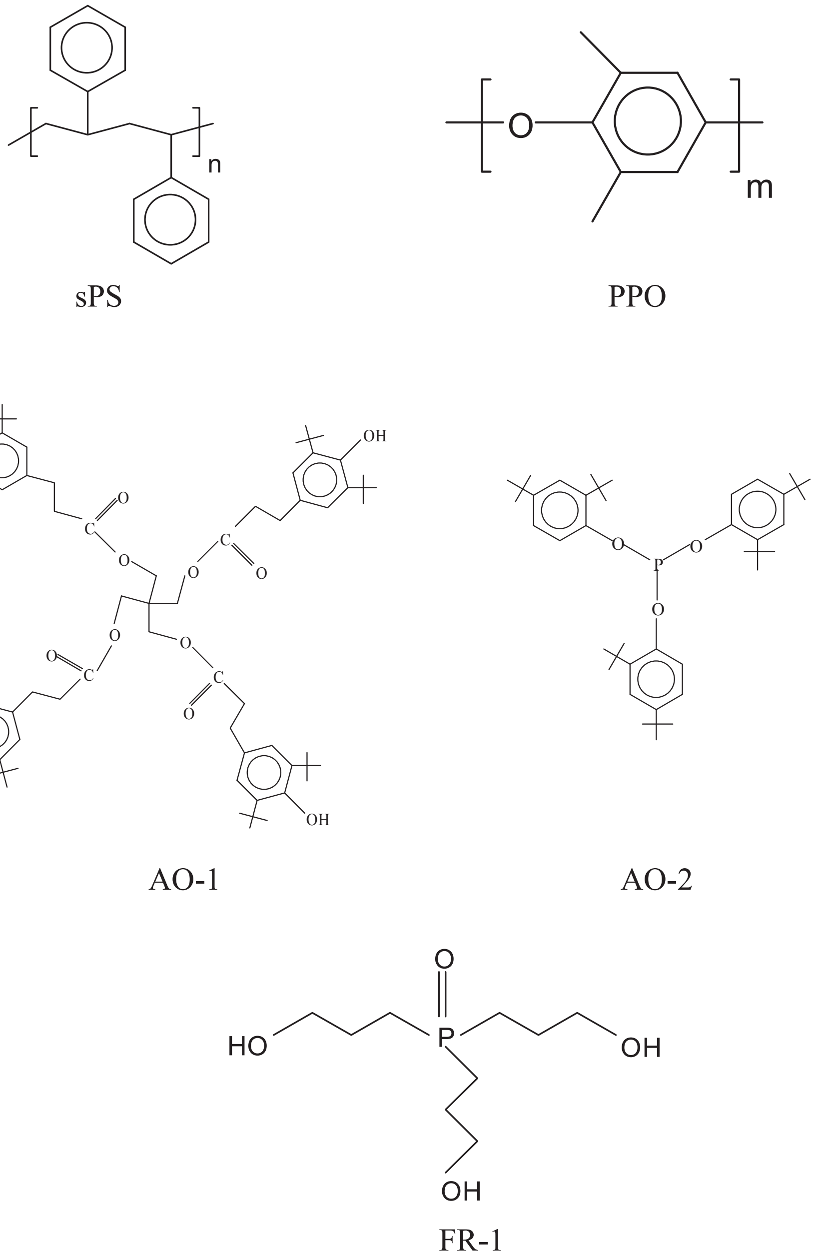
Syndiotactic polystyrene (sPS) was firstly synthesized by Idemitsu Kosan Co. of Japan with metallocenes as the catalysts in 1985 and has been known to be a semicrystalline polymer owing to its syndiotactic configuration. Recently, it has attracted much attention because of lower density, easier processibility, and better resistance to chemicals as well as heat compared with atactic polystyrene (aPS). Moreover, its dielectric properties are superior to those of other polymeric materials except for flouropolymers, rendering sPS the opportunity to be a potential material for electronic parts of surface mounting technology (SMT). sPS not only can be comparable to liqutid crystal polymers (LCPs) and polyphenylene sulfide (PPS) on the application of electronic parts but also possesses the advantage of low cost for its monomer. Besides electronic parts, sPS is also a candidate material for automobile parts, electrical housing, mechanical parts, etc.

The processing temperature of sPS is extremely high due to its high melting temperature (approximately 270 °C). The mechanical shearing force and the high temperature during operation drop the stability of sPS. The thermal oxidation of atactic polystyrene has been thoroughly reported [1], whereas that of sPS is less studied. According to Gacther and Muller's proposed degradation mechanism of polymers [2], addition of antioxidants prevents or inhibits thermal oxidation reactions. Therefore, we have introduced the antioxidants into sPS to decrease the discoloration, which resulted from the thermal oxidation. Furthermore, we have blended poly(2,6-dimethyl-1,4-phenylene oxide)(PPO) with sPS to increase the oxidative induction temperatures (OIT) and the time needed to induce thermal decomposition (TD). Although the literatures about properties of s-PS/PPO blends have been reported [3–5], their physical properties are not dissatisfactory. In order to further promote the physical properties of sPS/PPO alloys, some additives (i.e. titanium dioxide, impact modifiers, and flame retardants) have also been added into them. Finally, lab-made sPS/PPO alloys have been palletized and injection-molded to be reflective cups for light emitting diodes (LEDs), proving that they are potential reflective materials for optoelectronic applications.

---

* Corresponding author. Tel.: +886 3 5732475; fax: +886 3 5732347.
E-mail address: mhchung81@yahoo.com.tw (M.-H. Chung).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.08.061



sPS PPO

AO-1 AO-2

FR-1

Fig. 1. The structures of sPS, PPO, antioxidants, and flame retardant.

2. Experimental

2.1. Materials

sPS (Idemitsu Kosan Co.; M_w = 481,000; Fig. 1) was firstly washed with methyl ethyl ketone for purification and then dried in vacuum. Amorphous PPO (M_w = 60,000, T_g = 230 °C; Fig. 1) was purchased from Nippon Polyester Co. and utilized without further purification. The antioxidants (Fig. 1) used in this study were AO-1 (Irganox 1010; Ciba Co.) and AO-2 (Irgafos 168; Ciba Co.). The impact modifier, flame retardant (Fig. 1), and titanium dioxide used in this paper were IM-1 (Hytrel; DuPont Co.), FR-1 (FR-T; FMC Co.), and TiO_2 (ST-21; Ya Chung Co.; average diameter of particle: 20 nm; anatase), respectively.

2.2. Instruments

The purified sPS, PPO, antioxidants, impact modifier, and flame retardant were compounded and pelletized by an extruder (Brabender PL 2100) at 295 °C. The prescription and operational parameters of sPS and sPS/PPO alloys were listed in Table 1. The OIT, defined as the temperature at which the oxidation happens, were measured by a differential scanning calorimeter (DSC, PerkinElmer 7 series) with a heating rate of 10 °C/min and an air flow rate of 20 mL/min. TD was recorded by a thermogravimetric analyzer (TGA, PerkinElmer 7 series) at 300 °C under an air flow rate of 20 mL/min and defined as the duration to a weight loss of 1.5 wt%. The melt flow index (MFI) and the yellowness index (YI) were measured by a MI meter (Toyoseiki Seisakusho Ltd. Type 3056) following ASTM D1238 with a load of 2160 g and by a colorimeter (Juki JP7100F) following ASTM D1925, respectively. Furthermore, we measured the molecular weight, reflectivity, and hygroscopicity with a gel permeation chromatography (GPC; Waters GPC 150CV), a transmission and reflection rate measurement system (Ho-Ming Tech. Co.; MFS-TR; 250–800 nm), and a standard of ASTM D-570, respectively. The notched Izod impact strength and flammability were respectively examined by a standard of ASTM D-256 and UL-94 standard measurement. The data for physical properties of sPS and sPS/PPO alloys after compounding were tabulated in Table 2. Moreover, the reflective cups for LEDs were injection-molded at 310 °Cby an IS30FPA3-1A (Toshiba Co.).

3. Results and discussion

3.1. Improvement of discoloration

As shown in Fig. 2 and Tables 1 and 2, thermal oxidation occurs during compounding, resulting in color contamination. While prolonging the operational duration, as manifested in case of samples a

Table 1
The prescription and operational parameters of sPS and sPS/PPO alloys.

Sample	sPS (wt%)	PPO (wt%)	TiO_2 (wt%)	AO-1 (wt%)	AO-2 (wt%)	IM-1 (wt%)	FR-1 (wt%)	Screw speed (rpm)	Operational time (min)
a	100	–	10	–	–	–	–	30	4
b	100	–	10	–	–	–	–	30	12
c	100	–	10	–	–	–	–	60	4
d	100	–	10	–	–	–	–	90	4
e	100	–	10	1	0	–		30	4
f	100	–	10	0	1	–	–	30	4
g	100	–	10	1	1	–	–	30	4
i	100	10	10	1	1	–	–	30	4
j	100	20	10	1	1	–	–	30	4
k	100	30	10	1	1	–	–	30	4
l	100	30	10	1	1	1	–	30	4
m	100	30	10	1	1	2	–	30	4
n	100	30	10	1	1	2	10	30	4

Note: The processing temperature was fixed at 295 °C.

Table 2
The physical properies of sPS and sPS/PPO alloys after compounding.

Sample	Mn × 10^3	$M_w \times 10^3$	Poly dispersity	MFI (g/10 min)	YI	OIT (°C)	TD (min)	Reflectivity[a] (%)	Hygro-scopicity (%) @ 23 °C/24 h	Notched Izod impact strength (kg cm/cm)	Flammability (UL-94)
a	139	428	3.08	4.1	33.6	274	12.7	–	–	–	–
b	122	361	2.96	12.2	35.4	271	8.8	–	–	–	–
c	132	403	3.05	8.6	>50 (Gray)	272	9.6	–	–	–	–
d	129	398	3.09	10.5	>50 (Dark gray)	270	7.7	–	–	–	–
e	138	430	3.12	4.2	15.3	325	28	–	–	–	–
f	140	427	3.06	4.0	23.6	310	18.2	–	–	–	–
g	137	429	3.13	4.1	2.2	331	40	93	0.31	–	–
i	180	529	2.94	5.2	2.0	342	55	93	0.33	–	–
j	203	547	2.69	5.5	2.0	351	63	93	0.34	–	–
k	234	578	2.47	6.9	2.9	358	65	93	0.36	3.2	V1
l	235	577	2.46	7.0	2.0	360	68	93	0.36	4.7	V1
m	234	576	2.46	7.1	2.0	362	70	93	0.36	5.3	V1
n	236	578	2.45	7.5	2.2	359	66	93	0.39	5.1	V0

[a] Average values measured at 400–800 nm.

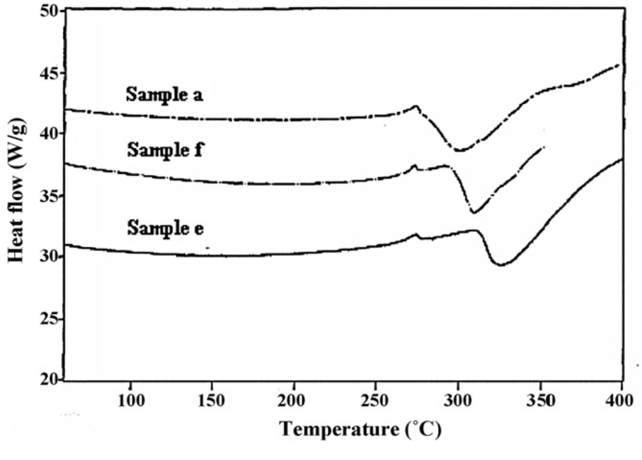


Fig. 2. The DSC results of samples a, e, and f.

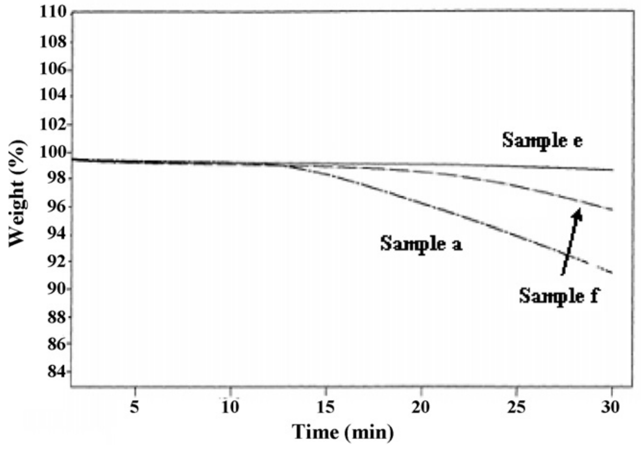


Fig. 3. The TGA results of samples a, e, and f.

and b, thermal oxidation deepens and molecular weight decreases, reducing TD and raising YI as well as MFI. Compared with the results of sample a, c, and d, furthermore, we find that the increase of mechanic shearing force can deteriorate the thermal oxidation and scissor the polymer chains so that sample c and d become highly color-stained and their MFI rise.

In order to avoid discoloration, we have tried to blend the primary antioxidants (i.e. AO-1) with sPS. As shown in Tables 1 and 2 and Figs. 2 and 3, addition of AO-1 is capable of decreasing the thermal oxidation by chelating the free radical, retarding free-radical-induced thermo-degradation [6]. Therefore, the increase of OIT and TD has also been observed. In addition, we have also found that AO-1 (primary antioxidant) is a more powerful antioxidant than AO-2 (secondary antioxidant). Thus, sample e exhibits lower YI and higher OIT as well as TD than sample f.

Although we have demonstrated that blend of primary antioxidants with sPS can improve the color contamination and thermal stability, the results for AO-1 are still dissatisfactory. In order to further reduce the color stain and thermal degradation, both primary antioxidant (AO-1) and secondary antioxidant (AO-2) have

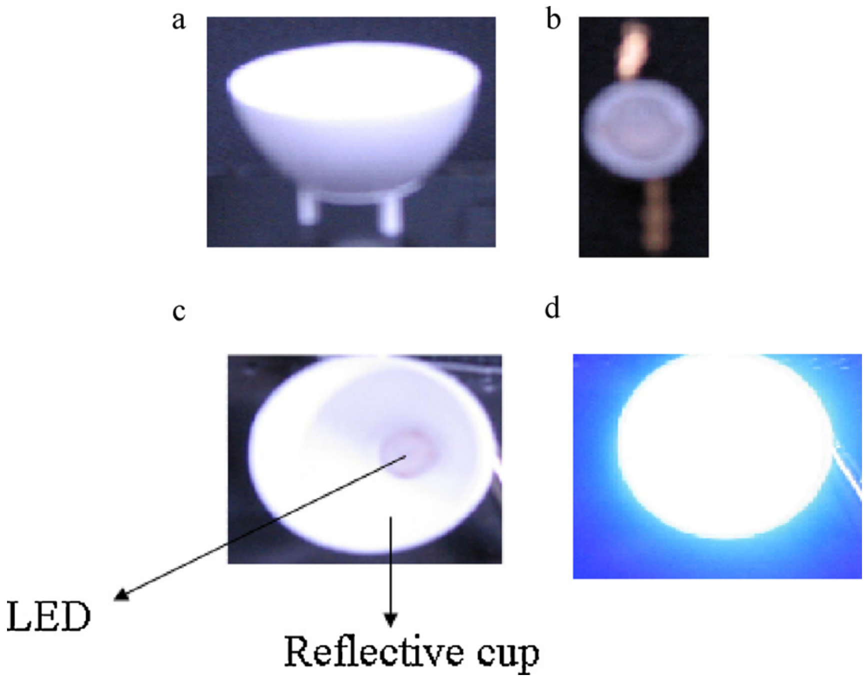


Fig. 4. The picture of (a) lab-made reflective cup (top diameter: 22 mm; bottom diameter: 6 mm; thinkness: 1 mm; height: 15 mm) for LEDs; (b) LED (1 W; Bright Led Electronics Co.); (c) combination of reflective cup and LED without actuation; (d) combination of reflective cup and LED with actuation.

been consequently added into sPS (i.e. sample g). The experimental results reveal that the synergy of primary and secondary antioxidants can further effectively diminish the discoloration and increase the OIT as well as TD because AO-2 decomposes the hydroperoxide generated during the operation, eventually further impeding the thermal oxidation and degradation [7].

3.2. Enhancement of physical properties

Although we have improved the problem of color-stains described above and sample g exhibits good reflectivity (93%) and hygroscopicity (0.31%), its OIT and TD are disqualified to fit the requirements of reflective cups for LEDs since the commercial materials (i.e. nylon 9T; GN2330; Kuraray Co.) have higher thermal resistance (OIT: 355 °C; TD: 64 min.) and other excellent physical properties (reflectivity: 91%; hygroscopicity: 0.42%; notched Izod impact strength: 5.0 kg cm/cm; flammability: UL-94 V0). Therefore, we have tried to blend different proportion of PPO with sample g to form sPS/PPO alloys (i.e. samples i, j, and k). As shown in Tables 1 and 2, incorporation of PPO can increase the thermal stability and slightly raise the hygroscopicity. In case of sample k, its OIT and TD can achieve 358 °C and 65 min, surpassing the specification of commercial nylon 9T. However, the impact strength and flammability of sample k are still lower than commercial nylon 9T. In order to heighten the impact strength, we have added IM-1into the sample k. As shown in Tables 1 and 2, the notched Izod impact strength increases with the amount of IM-1 and the impact strength of sample m is 5.3 kg cm/cm, exceeding that of commercial nylon 9T. The raise of impact strength results from that IM-1 is a thermoplastic polyester composed of soft polyether as well as hard polyester and can hence effectively cushion the shear stress [8]. Nevertheless, the flammability of sample m is merely UL-94 V1 and not good enough compared with commercial nylon 9T. Consequently, 1 wt% of FR-1 has then added into the sample m, successfully promoting its flammability to be UL-94 V0. The improvement of flammability comes from that FR-1 decomposes to phosphoric acid as well as phosphoric derivatives during the combustion conditions and they function as radical traps to assist the quenching of flame [9].

3.3. Feasible estimation for reflective cups of LEDs

Since sample n exhibits good physical properties, we have tried to apply it for the feasible estimation for reflective cups of LEDs with injection-molding technique as manifested in Fig. 4. The experimental results represent that the performance of lab-made reflective cup/LED is comparable to that of commercial nylon 9T and sPS/PPO alloys are potential reflective materials for photoelectric utilization. In the near future, further investigation such as electrical measurements, durable examination, optical characterization, etc. will be executed.

4. Conclusions

We conclude that thermal oxidation takes place during the compounding of sPS and the molecular weights as well as thermal characterization are highly dependent on the processing parameters. With appropriate antioxidants, the color stain and thermal stability can be dramatically improved. Furthermore, sPS/PPO alloys are potential materials for reflective cups of LEDs with proper recipes of TiO_2, antioxidants, impact modifiers, and flame retardants.

References

[1] V. Kovaceic, M. Bravar, D. Hace, Die Angewandte Makromolekulare Chemie 137 (1985) 175.
[2] R. Gacther, H. Muller, Plastic Additives Handbook, 2nd ed., Hanser, New Jersey, 1983, p. 63.
[3] G. Guerra, C. De Rosa, V.M. Vitagliano, V. Petraccone, P. Corradini, Journal of Polymer Science Part B: Polymer Physics 29 (1991) 265.
[4] E.M. Woo, Y.S. Sun, C.P. Yang, Progress in Polymer Science 26 (2001) 945.
[5] S.H. Hwang, Y.S. Kim, H.C. Cha, J.C. Jung, Polymer 40 (1999) 5957.
[6] H.R. Allcock, F.W. Lampe, Contemporary polymer chemistry, 2nd ed, Prentice Hall, New Jersey, 1990, p. 127.
[7] M.O. Liu, H.F. Lin, M.C. Yang, M.J. Lai, C.C. Chang, M.C. Feng, P.L. Shiao, I.M. Chen, Polymer Degradation and Stability 91 (2006) 1443.
[8] J.T. Lutz Jr., R.F. Grossman, Polymer modifiers and additives, Marcel Dekker, New York, 2001, p. 331.
[9] J.T. Lutz Jr., R.F. Grossman, Polymer modifiers and additives, Marcel Dekker, New York, 2001, p. 176.