

Synthesis of (3-*tert*-butyl-4-hydroxy-5-methylphenyl) Propionate Derivatives and Their Thermal Antioxidation Behavior for POM

Dongkyung Park,^{1,2} Daisuke Kobayashi,³ Hongsuk Suh,¹ Youngki Cho,² Areum Lee²

¹Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, Korea

²R&D Center, Songwon Industrial Co., Ltd. 737-2, Yochon-Dong, Nam-Gu, Ulsan, Korea

³Mitsubishi Gas Chemical Company, Inc., Yokkaichi Plant, 2-4-16 Hinaga Higashi, Yokkaichi, Mie, Japan

Received 2 April 2011; accepted 1 July 2011

DOI 10.1002/app.35186

Published online 21 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polyoxymethylene (POM) has been widely utilized in industry due to its light weight properties in engineering plastics. At present, POM applications are expanding into the car industry, especially in fuel tanks. Hindered alkyl phenol derivatives have been used as antioxidants for POM; however, these compounds are easily extracted by solvents. Two antioxidants with new structures (*N,N'*-triethylenedioxy-bis(3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamamide) and *N,N',N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-3-oxapentyl]melamine) were synthesized and characterized, and their perform-

ance as antioxidants for POM was investigated in the present study. The results revealed that *N,N'*-triethylenedioxy-bis(3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamamide) has good heat aging resistance compared to existing antioxidants for POM, and *N,N',N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-3-oxa-pentyl]melamine has good extraction resistance against solvents. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1731–1736, 2012

Key words: additives; antioxidants; compatibility; plastics; resists

INTRODUCTION

Polyoxymethylene (POM) is one of the most popular engineering plastic materials for the replacement of metals due to its desirable properties such as low weight, corrosion resistance, resistance to fatigue, ease of fabrication, and low coefficient of friction.

Regardless of these superior properties, specific physicochemical properties such as heat stability and extraction resistance are required for POM applications. Generally, the structure and properties of polymeric materials are altered due to degradation initiated by temperature, shear stress, or UV-light during processing, use, and recycling. Degradation leads to dissociation and can cause component failure. POM homopolymers are inherently unstable because they can be degraded via depolymerization at the chain end due to the presence of thermally unstable hydroxyl groups. This process is accompanied by the formation of formic acid, which causes acidolysis of the polymer and accelerates degradation. For this reason, POMs are often transformed into thermodynamically stable polymers through the addition of suitable terminal groups (end capping)

or copolymerization.¹ Kern and Chedron investigated the degradation behavior of POM in the early 1960s.² To reduce the degradation sensitivity of POM, copolymers have been investigated by several groups.^{3–5} Moreover, changes in the properties of POM due to processing, aging, and recycling have been studied by Archodoulaki.^{6,7} To prevent degradation, many stabilizers including hindered alkyl phenols have been used to reduce initial chain scission.^{8,9} In particular, 2,2'-methylenebis-(4-methyl-6-*tert*-butyl phenol) and 4,4'-butylidene bis(3-methyl-6-*tert*-butyl phenol) have been used as thermal stabilizers.¹⁰ Nowadays, triethylene glycol-bis-3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl) propionate and *N,N'*-hexamethylene-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate are preferred stabilizers because they provide good heat stability.¹¹ To improve the physical and chemical properties of polymers, copolymerization has been conducted to reduce the rate of depolymerization; however, the initiation of depolymerization is not completely prevented. Thus, a more specific stabilizer must be developed.

EXPERIMENTAL

Materials

Two commercial antioxidants were used to acquire comparative data for POM, and many chemicals

Correspondence to: D. Park (dkpark@songwonind.com).

were used for the preparation of hindered alkyl phenol antioxidants. POM used in this study was a commercial grade powder without any additives and supplied by Mitsubishi Gas Chemical Co., Inc., which was a copolymer type. Ethyl acetate was purchased from SK Chemicals, and petroleum ether, hexane, and (ethylenedioxy)diethylamine were obtained from Aldrich. Methyl-3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate, *N,N'*-hexamethylenebis(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (**AO-1**), and triethylene glycol-bis-3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionate (**AO-2**) were provided by Songwon industrial Co., Ltd., and were used without further purification.

Synthesis

Synthesis of *N,N'*-triethylenedioxy-bis(3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamamide) (**AO-3**)

Methyl 3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate (177 g, 0.707 mol) and (ethylenedioxy) diethylamine (50 g, 0.337 mol) were added into a 1-L four-neck flask equipped with a methanol separator, condenser, thermometer, and mechanical stirrer and were heated to 170°C. The reaction mixture was sustained at 170°C for 9 h under nitrogen, and the progress of the reaction was monitored by HPLC. Upon completion, the reactants were cooled to 50°C, and ethyl acetate and hexane were added into the reactor to form a clear solution. After cooling the solution to 5°C with an ice bath, precipitated **AO-3** was purified by crystallization and was washed with petroleum ether. Yield: 177 g, 89%. **AO-3**, white crystal, m.p. 135–138°C. ¹H NMR (CDCl₃, 300 MHz, δ ppm): 1.36 (s, 18H, *t*-Butyl), 2.17 (s, 6H, Ar—CH₃), 2.36 (t, 4H, *J* = 7.8 Hz, Ar—CH₂—), 2.80 (t, 4H, *J* = 7.8 Hz, CO—CH₂—), 3.35–3.50 (m, 12H, —CH₂CH₂—), 4.93 (s, 2H, —OH), 5.84 (s, 2H, —NH), 6.78, 6.91 (s, 4H, Ar—H). IR (KBr): ν_{max} 3356 (—OH), 3224 (—NH), 1632 (amide C=O).

Synthesis of tri(5-hydroxy-3-oxa-pentyl)melamine

Cyanuric chloride (53.7 g, 0.291 mol), potassium carbonate (77.9 g, 0.534 mol), and 1,4-dioxane (565 g) were added to a four-neck flask equipped with a condenser, thermometer, and mechanical stirrer and stirred at room temperature for 10 min. Diglycolamine (102.3 g, 0.973 mol) was added dropwise over 1 h at 45°C, and the reaction mixture was heated to 96°C for 5 h under nitrogen atmosphere. Upon completion, the reaction mixture was cooled to 90°C and filtered. 1,4-Dioxane and diglycolamine were removed by steam distillation at 140°C and 50 mbar. Subsequently, 99.3 g of tri(5-hydroxy-3-oxa-pentyl)-melamine was acquired in 87% yield.

Synthesis of *N,N',N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-3-oxa-pentyl]melamine (**AO-4**)

Tri-(5-hydroxy-3-oxa-pentyl)melamine (99.3 g, 0.254 mol), xylene (59.6 g), and tetraisopropyl titanate (0.4 g) were added to a 1-L four-neck flask equipped with a condenser, thermometer, and mechanical stirrer. The reactants were heated to 120°C and were treated with methyl 3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate (286.5 g, 1.145 mol) over 2 h. Subsequently, the reaction mixture was heated to 150°C and aged for 10 h. Upon completion, toluene (300 g) and water (120 g) were added, and the reaction was refluxed for 1 h. Water was separated, and toluene was removed by distillation at 110°C and 50 mbar. The residue was treated with methanol (540 g) and celite (10 g), and the mixture was filtered at 60°C. Methanol was removed by distillation, and excess methyl 3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate was removed by thin film distillation at 190°C and 1 mbar. Subsequently, 212.6 g of *N,N',N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-3-oxa-pentyl]melamine was acquired in 80% yield. **AO-4**, yellowish powder, m.p. 41–43°C. ¹H NMR (CDCl₃, 300, δ ppm): 1.36 (s, 27H, *t*-butyl), 2.17 (s, 9H, Ar—CH₃), 2.59 (t, 6H, *J* = 7.6 Hz, Ar—CH₂—), 2.82 (t, 6H, *J* = 7.6 Hz, CO—CH₂—), 3.47–3.58 (m, 24H, —CH₂CH₂—), 4.2 (s, 3H, —OH), 5.2 (s, 3H, —NH), 6.79, 6.91 (s, 6H, Ar—H). IR (KBr): ν_{max} 3420 (*N*—H, OH), 1732 (amide C=O).

Characterization and methods

Instrumental analysis methods

¹H-NMR: ¹H-NMR spectra data were obtained on a Gemini-300 MHz NMR spectrometer. IR: Infrared spectra data were recorded on a FTS-40A Fourier transform infrared spectrometer. (Conditions: mass and thickness of KBr tablets, 0.05 g × 0.5 mm; 10% antioxidant concentration.) The purity of the samples was determined by HPLC (Waters 2690). Conditions: column: Symmetry C18, 5 μm, 3.9 × 150 mm, mobile phase: 1.0 mL/min (acetonitrile: water; ethylacetate), detectors: UV detector (280 nm).

Extrusion test

Extrusion tests were performed under the following conditions: PCM30 Extruder (IKEGAI Ltd./Japan)/cylinder temp: 180°C – 240°C – 240°C – 230°C; screw speed: 100 rpm; vacuum: –600 mmHg; output: 3 kg/h.

Heat aging test

The specimens were stored at 140°C in a 41-S5 Drying machine (Satake Chemical Equipment Mfg, Ltd.,

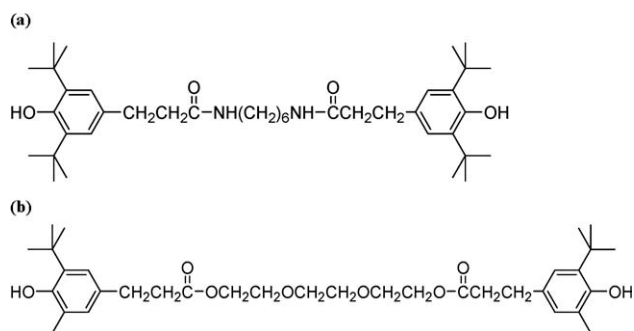


Figure 1 Chemical structure of hindered phenol antioxidants. (a) *N,N'*-Hexamethylenebis(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (AO-1) and (b) triethylene glycol-bis-3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionate (AO-2).

Japan), and were taken out every 250 h. The specimens were controlled humidity at 23°C, 50%RH for 48 h. The tensile strength and elongation of the specimens were determined with a STROGRAPH ApII Tensile tester (Toyo Seiki Seisaku-syo, Ltd./Japan) according to ISO527/1-1993(E). Discoloration was evaluated on a SE2000 Colorimeter (Nippon Densyoku Industries Co., Ltd., Japan), and the weight change was determined with a BP210S Weighing machine (Sartorius Mechatronics Japan, Japan).

Extraction test

The degree of extraction was judged by the weight loss of samples before and after extraction treatment. The weight loss becomes larger if the antioxidant in POM is extracted.

Extraction: Using liquid nitrogen, POM sample pellets were crushed, and the crushed sample was passed through 60 mesh sieve and caught on 200 mesh sieve. Their sieves have 75 and 250 μm opening size, respectively; 10 g of the resulting material was extracted with 50 mL of CHCl_3 via a Soxhlet extractor.

Weight loss: 2 g of sample was added to test tube, and then was treated at 220°C for 2 h under vacuum at 10 mmHg. The weight loss (W) can be calculated with the following equation.

$$W [\%] = (W_0 - W_t) / W_0 \times 100.$$

where W_0 is the weight of sample before extraction treatment and W_t is the weight of sample after extraction treatment.

Melt index test

The melt index (MI) was measured with melt Indexer L241 (Takara Thermistor Co., Ltd./Japan). The measurement temperature was 190°C, and the load was 2.16 kg.

RESULTS AND DISCUSSION

Synthesis and characterization of the antioxidants

Two commercial antioxidants (AO-1, AO-2) that are widely used in POM applications are shown in Figure 1.

To develop a specific stabilizer with high extraction resistance against solvent and reinforced toughness, two new alkyl phenol antioxidants (AO-3, AO-4) were designed by recombining the basic templates of two currently used antioxidants (AO-1 and AO-2) (see Fig. 2).

As shown in Scheme 1, AO-3 was synthesized by amidating methyl 3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate with (ethylenedioxy)diethylamine and removing methanol by distillation. AO-4 was synthesized by the transesterification of methyl 3-*tert*-butyl-4-hydroxy-5-methylphenylpropionate with tri(5-hydroxy-3-oxa-pentyl)melamine.

Structural properties

The structural properties of the newly developed antioxidants are shown in Figure 3. In AO-3, the C6 linkage of AO-1 was modified with an oxyalkylene fragment; however, the amide groups that stabilize POM by decreasing the acidity of the material and providing a hydrogen bond between the $N-H$ of the amide and the $O-H$ in POM were maintained to improve the extraction resistance to solvent. The oxyalkylene group in AO-3 enhances the solubility of POM, improves the antioxidant activity, and induces good heat stability. In addition, AO-3 has a 3-*tert*-butyl-4-hydroxy-5-methylphenyl group, which is more effective in discoloration than 3,5-di-*tert*-butyl-4-hydroxyphenyl. The core structure of AO-4 was based on melamine, which is a well known auxiliary additive that induces high heat stability in POM. The introduction of melamine into AO-4 has two positive effects on POM. As described above, melamine enhances the heat stability of POM. Secondly, the amine functional groups can react with the carbonyl and hydroxyl groups of POM. The addition of

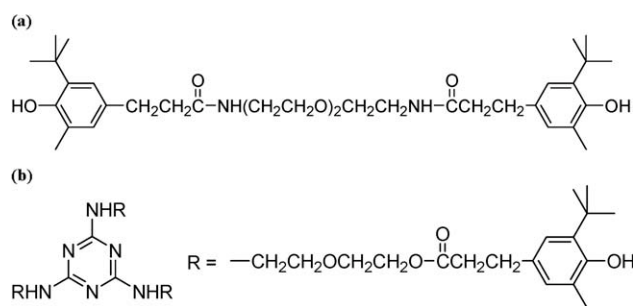
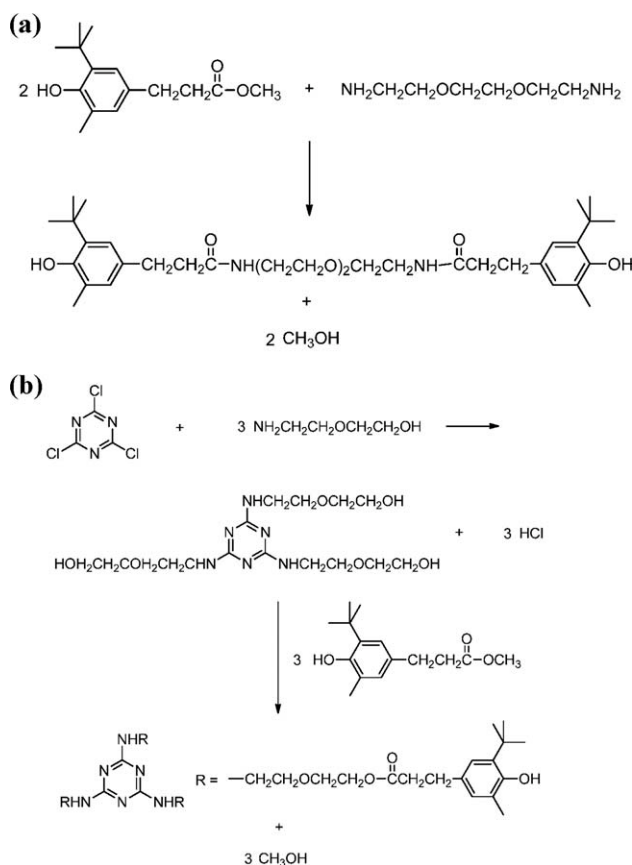


Figure 2 Chemical structure of newly developed hindered phenol antioxidants. (a) *N,N'*-Triethylenedioxy-bis(3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamamide) (AO-3) and (b) *N,N,N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-3-oxa-pentyl]melamine (AO-4).



Scheme 1 Reaction scheme of **AO-3** and **AO-4**. (a) *N,N'*-triethylenedioxy-bis(3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamamide) (**AO-3**) and (b) *N,N',N'*-tris[(3-*tert*-butyl-4-hydroxy-5-methylphenyl)-propionyl-3-oxa-pentyl] melamine (**AO-4**).

TABLE I
Stabilized POM Prepared with a $\phi 30$ Twin Extruder

1	O	9.7
2	O	9.5
3	O	10.0
4	O	12.7

Crude polymer = 100 phr; antioxidant = 0.3 phr; melamine = 0.1 phr.

O: Good performance during extrusion (smooth surface and no vent up).

oxyalkylene and 3-*tert*-butyl-4-hydroxy-5-methylphenyl groups on melamine increases the compatibility and protects the material from discoloration.

Thermal stability

Extrusion performance

POM powder (0.3 phr of antioxidant and 0.1 phr of melamine) were compounded with a mixer, then were extruded by a twin extruder. The polymer including antioxidants did not vent-up during the extrusion process, and the strands possessed a smooth surface. As shown in Table I, **AO-4** presented a marginally higher MI value than **AO-1~3**.

Heat aging test

The weight loss and tensile strength results showed that POM with **AO-1~3** displayed similar thermal properties; however, POM with **AO-4** was inferior to the other antioxidants (see Figs. 4 and 5). The

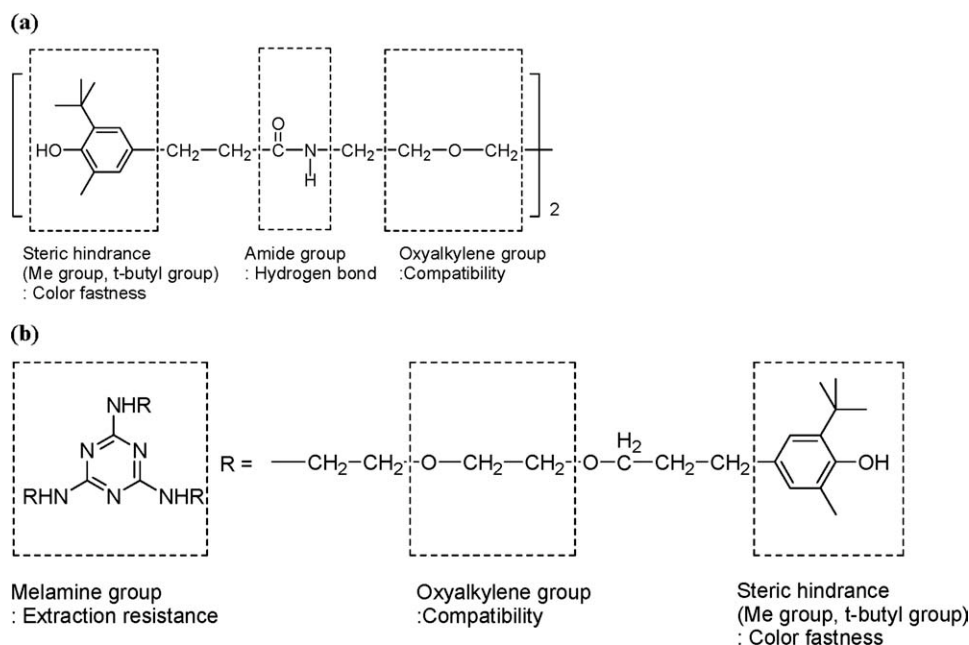


Figure 3 Structural properties of newly developed hindered phenol antioxidants for POM: (a) **AO-3** and (b) **AO-4**.

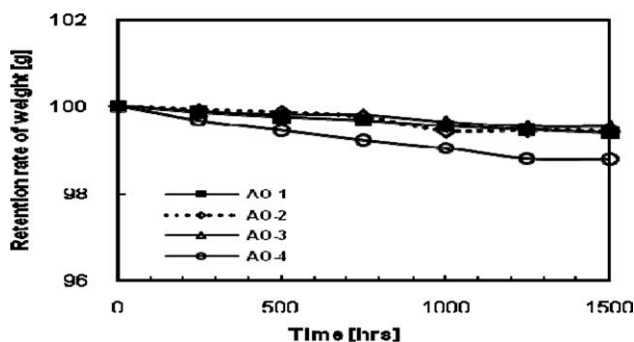


Figure 4 Weight change of POM at 140°C under isothermal condition for 1500 h.

characteristics of **AO-4** were relatively poor because **AO-4** has a reactive site in its molecular structure, and further reactions occurred during the heat aging test at 140°C. Moreover, **AO-4** was unstable in the resin, and its properties were altered at high temperatures.

As shown in Figure 6, the tensile elongation tests showed that **AO-3** was superior to the other materials due to the structural modifications and introduction of functional groups with positive aspects into **AO-1** and **AO-2**. The following order of stability was observed: (best) **AO-3** > **AO-1** > **AO-2** > **AO-4** (worst). The results suggested that amide groups are the most important factor affecting tensile elongation. The substitution of C6 with oxyalkylene groups also had a positive effect on the tensile elongation.

Discoloration

AO-2 > **AO-3** > **AO-4** > **AO-1**

Figure 7 shows the change in discoloration in the POM resin as a function of the structural properties and functional groups of the antioxidants. Generally, two factors affected the discoloration of POM. During the storage and processing of polymer resins and the end use of the plastic, hindered phenols act as radical scavengers by donating hydrogen atoms to radicals. Once the hydrogen atom is transferred, the stability of

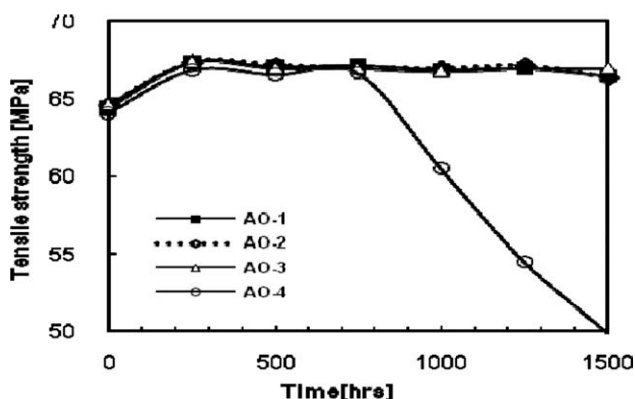


Figure 5 Tensile strength of POM at 140°C under isothermal condition for 1500 h.

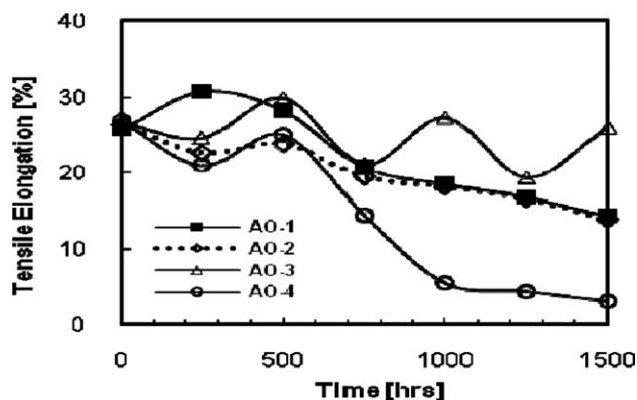


Figure 6 Elongation at 140°C for 1500 h.

the radical increases, and stilbenequinone derivatives are formed. Stilbenequinones are yellow and red in color and affect the color of the polymer.¹² In turn, the color of stilbenequinones is determined by the size of the alkyl groups on the phenol. With less-hindered alkyl groups, the color is less intense, and the stability of the compound is lower. Also, the regioselectivity of the alkyl groups on the phenol affects discoloration. For instance, when the *tert*-butyl group is in a 2,6-orientation, the formation of colored stilbenequinones in the resin is accelerated. When the alkyl group is changed from *tert*-butyl to methyl, less discoloration is observed in the resin. Alternatively, when amine and amide groups are present in the antioxidant structure, lower color stability is observed due to the oxidation of the amine during processing at high temperatures.

AO-2 > **AO-3** > **AO-4** > **AO-1**

According to the discoloration results, substituted phenols have a stronger effect on color stability than amines.

Extraction test

AO-4 > **AO-3** ≥ **AO-1** > **AO-2**

AO-4 displayed outstanding performance in the solvent extraction test, as shown in Figure 8. The

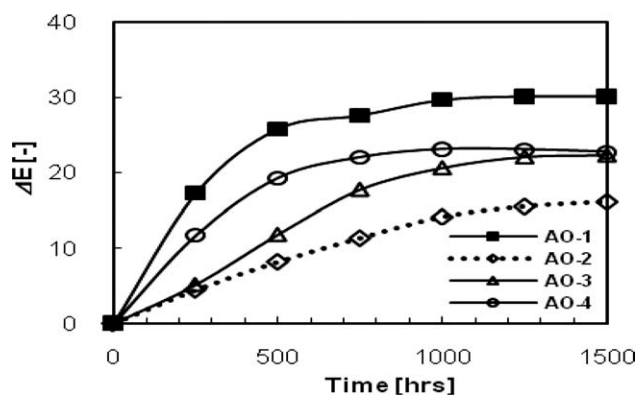


Figure 7 Discoloration after aging at 140°C for 1500 h.

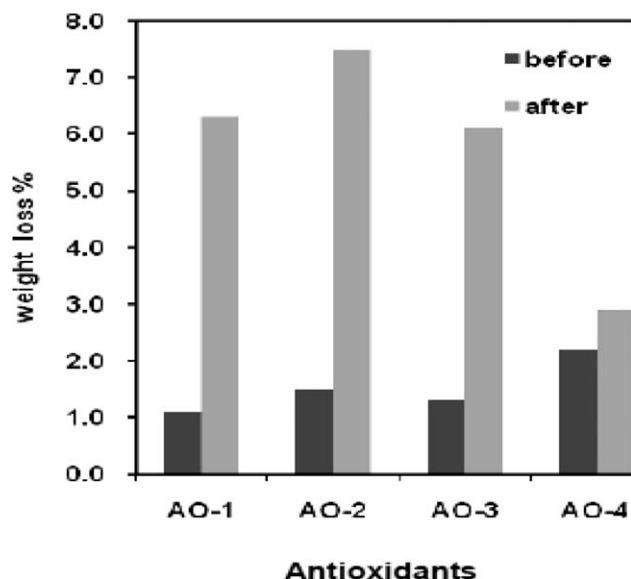


Figure 8 Extraction of crushed pellets by CHCl_3 at 90°C for 6 h.

superior properties of this material were attributed to the three possible reactions between POM and **AO-4**. First, the amine groups on the melamine core can react with carbonyl groups to form an enamine. Secondly, a substitution reaction between the hydroxyl group and the amine of the melamine core can occur. The third possible reaction is the formation of hydrogen bonds between the hydroxyl groups on POM and the amine groups on the antioxidants. **AO-1** and **AO-3** have better solvent extraction resistance than **AO-2** due to the fact that **AO-1** and **AO-3** are capable of forming a hydrogen bond with POM.

CONCLUSIONS

In the present study, two new antioxidants with hindered alkyl phenol groups were developed by

combining the good features of existing antioxidants. The physicochemical properties and antioxidative performance of POM resins were examined, and **AO-3** showed superior tensile elongation compared to **AO-1** and **AO-2** and excellent extraction resistance compared to **AO-2**. Moreover, **AO-4** showed outstanding extraction resistance as a reactive antioxidant for POM. Despite its resistance performance, **AO-4** displayed inferior overall results in heat aging tests due to the presence of reactive functional groups. Specifically, **AO-4** has a positive and negative side and is a reactive antioxidant. The results obtained from **AO-4** indicate that the amine in melamine can react with POM and that the resin degrades at high temperatures. Thus, the elongation of **AO-3** and extraction resistance of **AO-4** should be further improved to develop next generation commercial products for POM.

References

1. Grassie, N.; Roche, R. S. *Makromol Chem* 1968, 112, 16.
2. Kern, W.; Cherdron, H. *Markromol Chem* 1960, 40, 101.
3. Hermann, H. D.; Weissermel, K. *Makromol Chem* 1966, 94, 91.
4. Inoue, M. *J Appl Polym Sci* 1964, 8, 2225.
5. Luftl, S.; Archodoulaki, V.-M.; Seidler, S. *Polym Degrad Stab* 2006, 91, 464.
6. Archodoulaki, V.-M.; Luftl, S.; Koch, T.; Seidler, S. *Polym Degrad Stab* 2007, 92, 2181.
7. Archodoulaki, V.-M.; Luftl, S. L.; Seidler, S. *Polym Degrad Stab* 2004, 86, 75.
8. Zweifel, H. Ed. *Plastic Additives Handbook*, 5th ed.; München: Hanser Verlag, 2000.
9. Sable, H. D.; Schlaf, H.; Unger, P.; Ziegler, U. In: Botterbruch, L., Ed. *Technische Thermoplaste: Polymercarbonate, Polyacetale, Polyester, Cellulosester*; München: Carl Hanser Verlag, 1992; pp 300–395.
10. Brydson, J. A., Ed. *Plastics Materials*, 5th ed.; Butterworths: London, 1989; pp 497–516.
11. Takatoshi, M.; Chiharu, N.; Hiroshi, M.; Hiroshi, Y.; Kazuo, K. U.S. Pat. 2001, 6, 2001, 211, 268.
12. Rabek, J. F., Ed. *Photostabilization of Polymers: Principles and Application*. London: Elsevier Applied Science, 1990; pp 80–166.