

Thermal Behavior of Blends Based on High-Molecular Polyoxyethylene and Salts from Seawater and Sea Lye

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Received 24 November 1997; accepted 30 March 1998

ABSTRACT: The purpose of this study was to increase the thermooxidative stability and flow of high-molecular polyoxyethylene (HMPOE) by introducing readily available, technologically convenient, and economical additives. Binary systems consisting of HMPOE with mean viscosity molar mass $\bar{M}_v = 3,2 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ and inorganic salts from both the seawater and sea lye and, also, MgCl_2 of concentration from 1 to 10 mass % with respect to HMPOE, were prepared. The thermal behavior of these systems was studied by using dynamic thermal analysis, dynamic viscometry, and melt index determination. The presence of salts of concentrations from 3 up to 10 mass % in HMPOE was found to increase the temperatures of initial thermooxidative decomposition of the polymer. At the same time, the degree of viscosity reduction ($-\Delta\eta$, %) corresponding to lowering the average molar mass after the heat treatment for 20 h at 150°C decreased. Another effect of the salts was found to be the increased melt flow of HMPOE above 250°C . The best stabilizing effect was obtained in the presence of salts in sea lye and, also, MgCl_2 . © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 995–999, 1998

Key words: polyoxyethylene blends; salts from seawater and sea lye; thermal stability; melt flow

INTRODUCTION

Polyoxyethylene (POE) is known to be easily subjected to thermooxidative destruction. Besides, the high molecular POE (HMPOE) does not practically flow in the molten state, even at relatively high temperatures. Consequently, the processing of HMPOE into manufactured products is rather difficult.

Data about a number of organic and inorganic additives improving POE thermal stability to a different degree have been published so far.^{1–6} Some metal salts of 30–40 mass % concentrations with respect to POE are known to form ionic complexes with POE, which have high ionic conductivity and thermooxidative stability.^{7–9} Most frequently, the investigations dealt with the morphology and ionic conductivity of these complexes.^{10–12}

We have found that significantly lower concentrations (from 2 to 5 mass %) of some alkaline salts result in high thermooxidative stability of POE and, also, increase HMPOE flow in a molten state.^{13–16}

The majority of the thermostabilizers used are chemically pure compounds, which are not always readily available and, also, are sometimes in convenient in both the technological and economical aspects.

The purpose of the present work was to study the influence of inorganic salts contained in seawater and sea lye on the thermal stability and flow characteristics of HMPOE.

EXPERIMENTAL

Materials

Binary systems based on HMPOE of mean viscosity molar mass $\bar{M}_v = 3,2 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ and inor-

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Journal of Applied Polymer Science, Vol. 70, 995–999 (1998)

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CCC 0021-8995/98/050995-05

Table I Content of the Basic Salts in Seawater and Sea Lye from the Coastal Zone of Bourgas (Black Sea)

Ionic Content g/L	Conc in Seawater g/L	Conc in Sea Lye g/kg
Na ⁺	5.40	10.00
K ⁺	0.17	17.30
Ca ²⁺	0.24	—
Mg ²⁺	0.64	91.80
Ba ²⁺	1.00	0.41
Cl ⁻	9.60	193.00
Br ⁻	0.04	4.60
SO ₄ ²⁻	1.30	—
HCO ₂ ⁻	0.20	—
SO ₃ ²⁻	—	41.15
Total mineralization	18.6	437.9 ^a

^a The value of the total mineralization is higher than the sum of the ionic content given in Table I because no complete data concerning the content of the various ions are available.

ganic salts from seawater and sea lye were studied. The content of salts in the blends varied from 1 to 10 mass %.¹⁷ Blends of HMPOE with MgCl₂ of the same inorganic salt content were also studied. Enclosed are the results obtained for the blend containing 3 mass % of MgCl₂ for comparison.

HMPOE employed was a commercial product of Chimko, Bulgaria. Seawater was provided from the coastal zone of Bourgas, and sea lye with density of 1.286 represented the liquid fraction obtained after concentrating the seawater followed by separation of NaCl. The content of salts in seawater and sea lye is shown in Table I.

Blends of HMPOE and inorganic salts were prepared by mixing HMPOE with seawater, sea lye, or with aqueous solution of MgCl₂, and the subsequent vacuum evaporation of water at 50°C.

Methods

The thermal behavior of blends was studied by the method of the combined dynamic thermal analysis (TG, DTG, DTA), using Derivatograph MOM (Budapest, Hungary) at the temperature interval of 20–600°C and heating rate of 6°C/min. The sample of 0.1 ± 0.00005 g mass was placed in a metallo-ceramic crucible, and a static atmosphere of air was employed. The initial temperatures of thermooxidative decomposition (T_o) and of intensive decomposition (T_i) were evaluated by using the methods of the tangent and half-angle method, respectively (Fig. 1). The mass loss val-

ues at 250°C ($-\Delta M_{250^\circ}$) were obtained from the corresponding TG curves. The initial temperatures of oxidizing (T_{ox}) were obtained from DTA curves.

The dynamic viscosity (η) and the degree of its reduction ($-\Delta\eta$, %) for both HMPOE and the corresponding blends were determined on Reotest-2 rotation viscosimeter (Germany) in 0.5% aqueous solution at 30°C. These measurements were conducted before and after the thermal treatment of samples for 20 h at 150°C, respectively.

The melt indexes (MI) of HMPOE and its blends were determined by using an extrusion plastometer according to ASTM-D-1238-65 T at 200, 250, and 280°C and under the load of 21.6 kg.

RESULTS AND DISCUSSION

Thermal analysis data show that the increase in the content of salts resulted in both the higher initial temperature of thermooxidative decompo-

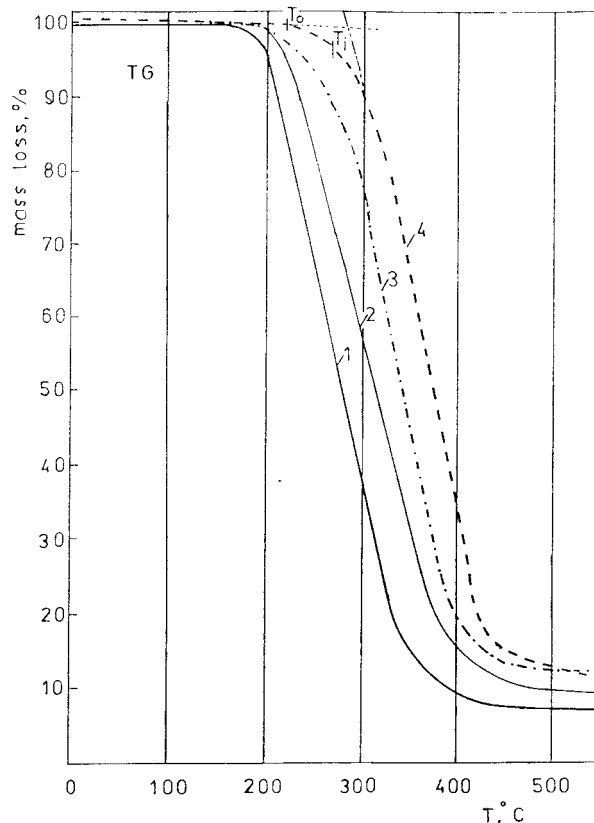


Figure 1 TG curves of HMPOE and its blends with inorganic salts from seawater and blends with MgCl₂: (1) - HMPOE; (2) - HMPOE blended with 1 mass % of salts; (3) - HMPOE blended with 5 mass % of salts; (4) - HMPOE blended with 3 mass % of MgCl₂.

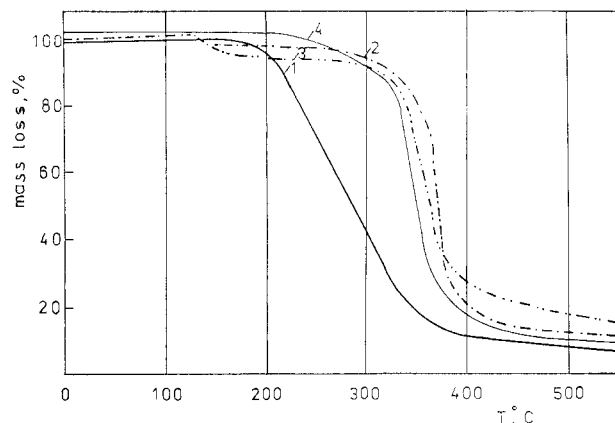


Figure 2 TG curves of HMPOE and its blends with inorganic salts from sea lye (without NaCl) and blends with MgCl_2 : (1) - HMPOE; (2) - HMPOE blended with 1 mass % of salts; (3) - HMPOE blended with 5 mass % of salts; (4) - HMPOE blended with 3 mass % of MgCl_2 .

sition (T_o) and temperature of strong decomposition (T_i) of the blends, as compared to HMPOE without additives (Figs. 1 and 2; Table II). The highest increase was observed for blends containing from 3 to 10 mass % of the salts in sea lye ($T_o = 280\text{--}300^\circ\text{C}$ and $T_i = 320\text{--}340^\circ\text{C}$), respectively (Fig. 2, curves 2 and 3). A somewhat slighter effect was observed with blends containing 3 mass % MgCl_2 ($T_o = 240^\circ\text{C}$ and $T_i = 260^\circ\text{C}$; Fig. 1, curve 4; Fig. 2, curve 4). The corresponding effect was even less pronounced for blends with salts from seawater ($T_o = 200^\circ\text{C}$; $T_i = 230^\circ\text{C}$) (Fig. 1, curve 3).

The mass loss at 250°C determined from the TG curves (Table II) decreased significantly from 28 mass % for HMPOE down to 0–3 mass % for blends, containing sea lye salts and MgCl_2 .

At the same time, the initial temperatures of oxidation determined from DTA curves in air

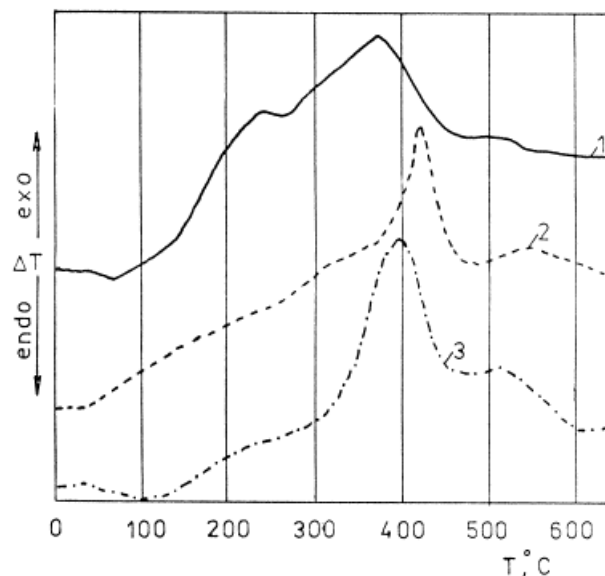


Figure 3 DTA curves of HMPOE and its blends with inorganic salts from sea lye: (1) - HMPOE; (2) - HMPOE blended with 1 mass % of salts; (3) - HMPOE blended with 5 mass % of salts.

medium (Fig. 3) indicated a sharp increase, even at low concentrations of inorganic salts (from 1 to 5 mass %) in comparison with those for the HMPOE (from 150 to 300°C). Besides the considerable shift towards higher temperatures, there was also a certain reduction in the initial exothermal effect of HMPOE oxidation.

Therefore, these blends are quite stable at a temperature of $260\text{--}300^\circ\text{C}$, and no significant mass loss can be expected under the operation conditions.

This thermostabilizing effect was revealed in air (that is, the oxidizing medium) only, which confirmed its antioxidative nature.

Retaining the total mass of HMPOE under the conditions of dynamic heating does not nec-

Table II Thermal Characteristics of HMPOE and Its Blends with Inorganic Salts from Seawater and Sea Lye and Blends with MgCl_2

System	Salt Content Mass (%)	T_o ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	$-\Delta M_{250^\circ}$ Mass (%)	T_{ox} ($^\circ\text{C}$)
HMPOE	0	180	195	28	150
HMPOE + salts from seawater	1	180	210	15	170
	5	200	230	7.5	200
	1	260	310	0	260
HMPOE + salts from sea lye	3	300	335	1	300
	5	280	340	0	300
	10	300	320	0	300
HMPOE + MgCl_2	3	240	260	3	230

Table III Dynamic Viscosity (η) and Degree of its Reduction ($-\Delta\eta$, %) after Heating HMPOE and Its Blends with Salts from Seawater and Sea Lye and Blends with MgCl_2

System	Salts Content, Mass (%)	η Before Heating, Pa · s ($f = 0.686 \text{ s}^{-1}$)	η After Heating, Pa · s ($f = 0.686 \text{ s}^{-1}$)	$-\Delta\eta$ (%)
HMPOE	0	18,5	5,78	68,8
HMPOE + salts from seawater	1	12,0	6,2	48,3
	3	11,6	6,6	43,1
	5	12,0	5,8	51,4
	1	11,6	6,2	46,6
	3	11,6	10,2	13,4
HMPOE + salts from sea lye	10	10,5	10,0	5,0
	10	10,0	9,3	7,0 ^a
	10	9,1	8,9	2,2 ^b
	10	8,1	8,0	1,3 ^c
	1	15,8	5,8	63,3
	5	10,4	8,1	22,1
HMPOE + MgCl_2	10	8,9	8,1	9,0
	10	7,7	7,2	6,5 ^b
	10	7,0	6,7	4,3 ^c
	10	6,2	6,0	3,2 ^d

^a At rate $f = 0,4115 \text{ s}^{-1}$.^b At rate $f = 0,2286 \text{ s}^{-1}$.^c At rate $f = 0,1372 \text{ s}^{-1}$.^d At rate $f = 0,0762 \text{ s}^{-1}$.

essarily mean that the average molar mass of polymer remains unchanged. To check the degree of thermostability of these systems under

isothermal conditions, a prolonged procedure of treatment (20 h at 150°C) was employed, and the dynamic viscosities of both the initial and

Table IV Melt Indexes (MI) of HMPOE and its Blends with Salts from Sea Lye and Blends with MgCl_2

System	Salts Content Mass (%)	Temperature (°C)	MI g/10 min
HMPOE	0	200	0.8
	0	250	2.0
	0	280	17.3
	1	200	0.3
HMPOE + salts from sea lye	1	250	0.6
	1	280	3.8
	3	200	0.5
HMPOE + salts from sea lye	3	250	4.0
	3	280	18.5
	5	200	0.7
HMPOE + salts from sea lye	5	250	12.1
	5	280	58.0
	10	200	5.1
HMPOE + salts from sea lye	10	250	32.6
	10	280	56.0
	3	200	0.1
HMPOE + MgCl_2	3	250	2.5
	3	280	15.4

thermally treated blends were evaluated. The results showed (Table III) that the viscosity reduction ($-\Delta\eta$, %) of thermally treated blends containing salts of 5 mass % concentration was significantly lower as compared to thermally treated pure HMPOE. Therefore, these results confirmed the essential thermostabilizing effect of the salts on HMPOE under the conditions of heating in air. The most favorable stabilizing effect was observed with the inorganic salts in sea lye and/or $MgCl_2$ of concentrations from 3 to 10 mass %.

These salts are known to form ionic complexes with POE, which is believed to be the probable explanation of the thermostabilizing effect observed. Salts in seawater have a weaker effect, which is believed to result from the significant NaCl content. The latter does not form ionic complexes with POE.

The results obtained at this stage of investigation showed also that the sea salts from sea lye of 5 to 10 mass % content increased the melt flow of HMPOE at 250°C and improved its processability (Table IV).

CONCLUSIONS

1. Blends consisting of HMPOE and inorganic salts contained in seawater and sea lye and, also, $MgCl_2$ of 1 to 10 mass % content can be prepared by employing a simple and readily available method.
2. By using both the thermal analysis and viscometry methods, it is proven that the inorganic salts introduced in concentration of 3 to 10 mass % significantly increase the initial temperatures of thermooxidative destruction. At the same time, the viscosity, as an indication of the average molar mass, remains almost unchanged even after the thermal treatment of blends for 20 h at 150°C.
3. The salts derived from sea lye of 5 to 10

mass % concentration in the blends increase the melt flow of HMPOE at 250°C.

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