Effect of Metallic Oxides on Thermal Stability of Ethylene–Propylene Terpolymer

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ABSTRACT: Thermal stability of ethylene–propylene terpolymer (EPDM) loaded with various metallic oxides (PbO, CuO, NiO, Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2) was assessed by the oxygen uptake method. The effects of 5 phr oxide of thermal aging of elastomer were investigated under isothermal (180°C) and isobaric (air at normal pressure) conditions. The influence of this was pointed out. Some mechanistic considerations on the oxidative degradation of EPDM are presented. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2155–2158, 2001

Key words: ethylene–propylene terpolymer; thermal degradation; metallic oxides; EPDM

INTRODUCTION

Although considerable research efforts have been devoted to the assessment of polymers[1–3] relatively few reports on thermal stability of polymers containing metallic oxides have been reported.[6,7]

A large variety of polymer materials, especially the electrical insulators, contain oxides to exhibit certain properties. Into this type of compounds such as dielectrics, products colored with inorganic pigments, shielding products, etc., can be included. Their stability depends on the behavior of oxides because of the differences in oxygen affinity and the interaction between the additive and the host matrix. The most important factors that influence the magnitude of changes in material properties are: chemistry of added oxides, size of particles, the vulcanization state of elastomers, and environmental conditions. The simultaneous presence of molecular oxygen and significant traces of water during the degradation stage of polymers can affect the rate of aging.

Hydroperoxides are the key products of the radical auto-oxidation of most of the polymers. Thus, oxidation can involve loaded oxide as a consequence of possible reactions occurring between hydroperoxides and metallic compounds. The nature of the metal will determine certain oxidation characteristics: induction time and aging rate.

RESULTS AND DISCUSSION

Ethylene–propylene–diene terpolymer containing 3.5% ethylidene–norbornene was supplied by Arpechim Piteşti (Romania). Some main structural characteristics have been presented in an earlier article.[8] It must be mentioned that this copolymer contains 29% propylene and 3.5% ethylidene norbornene. Oxide materials: PbO, CuO, NiO, Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2 (Merck®) were of analytical grade.

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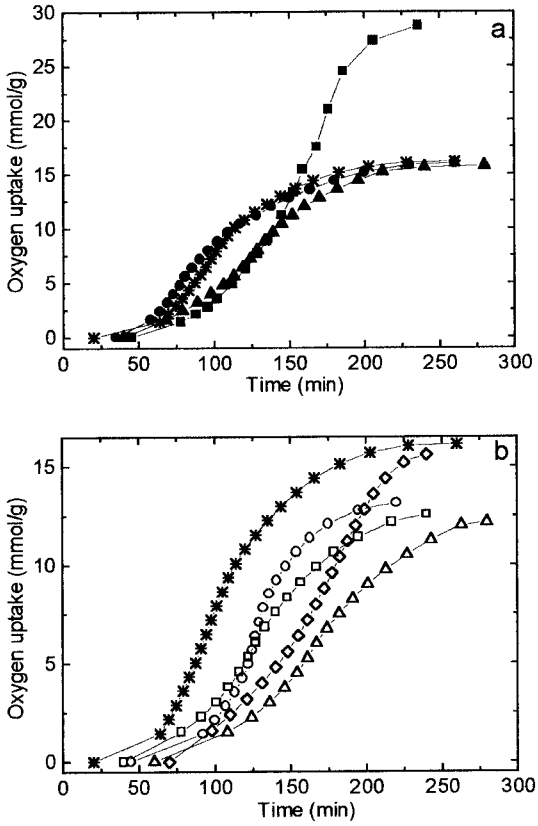

Figure 1 Oxygen-uptake diagrams for ethylene–propylene terpolymer loaded with metallic oxides. (a) (*) uncompounded; (■) PbO; (●) Cr_2O_3; (▲) NiO; (b) (□) CuO; (○) Fe_2O_3; (△) TiO_2; (◇) ZrO_2.

Samples were prepared by mixing EPDM solution in $CHCl_3$ with a fine powder of each oxide. Oxides were ground in a stainless ball mill until fine powder was obtained (particle size: 50–70 μm). They were individually added to the polymer solution in suitable amounts to achieve a concentration of 5%. These suspensions were poured on round aluminum trays. After solvent removal thin films (~50 μm) were obtained. The oxygen-uptake measurements were carried out under isothermal and isobaric conditions. Laboratory equipment was used to determine the amount of consumed oxygen.[9] The normal air pressure and the temperature of 180°C were chosen to obtain a significant oxidation rate.

Polymers can be characterized using several methods. A reliable alternative for the assessment of thermal degradation is oxygen uptake whose data reveal differences in chemical structures or formulations of various materials.

Figure 1(a) and (b) presents the oxygen-uptake diagrams for EPDM/oxide compounds. These graphs reveal the thermal stability of studied systems. It may be noticed that all compounded samples except the specimens containing Cr_2O_3 start oxidation after that process begins in the unloaded elastomer. The longest induction periods are shown by the samples consisting of ethylene–propylene terpolymer and TiO_2 or ZrO_2 (Table I).

The mechanism of thermal degradation of polyolefins presented by Bolland and Gee[10] assumes scission of C—H and C—C bonds and generation of free hydrocarbon radicals and hydrogen atoms. The oxidation rate will achieve maximum value when free radicals including hydrogen atoms attain the highest concentration. Thus, the shoulders on the oxidation rate curves [Fig. 2(a) and (b)] correspond to the inflection point when the formation rate of peroxy radicals becomes equal with the their depletion rate.

Table I The Main Kinetic Parameters of Thermal Degradation for EPDM Loaded with Various Metallic Oxides

Oxide	Oxidation Induction Time, t_i (min)	Maximum Oxidation Rate, V_{ox}^{max} (mol $O_2 \cdot g^{-1} \cdot s^{-1}) \cdot 10^7$	Damage Time, $t_{inf\,lex}$[a] (min)
free	61	36.9	77
PbO	78	72.9	183
NiO	75	29.6	128
CuO	61	25.3	138
Cr_2O_3	50	23.7	84
Fe_2O_3	87	59.1	139
TiO_2	100	20.8	180
ZrO_2	102	26.6	199

[a] Damage time is defined as the longest time of integrity maintenance.

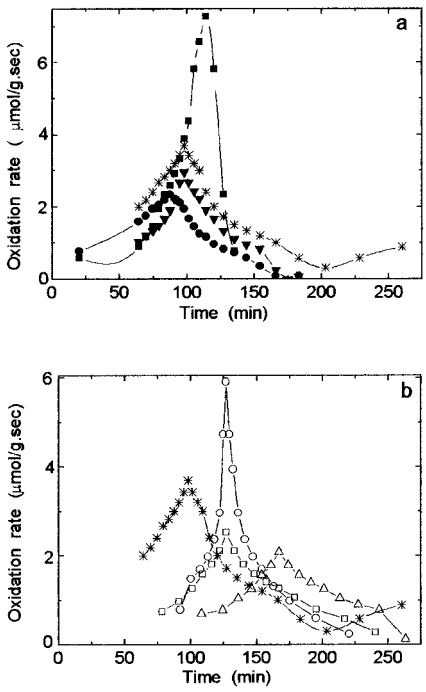

Figure 2 Oxidation rate vs. degradation time for ethylene–propylene terpolymer loaded with metallic oxides. (a) (*) uncompounded; (■) PbO; (●) Cr_2O_3; (▲) NiO; (b) (□) CuO; (○) Fe_2O_3; (△) TiO_2; (◇) ZrO_2.

The most stable compounds were the ethylene–propylene terpolymer containing zirconia and titania. They show the longest oxidation rates, the lowest oxidation rates, and the most extended damage times. This means that these oxides offer the longest durability of EPDM. A similar situation could be found when PbO was included in the elastomer matrix. In the contrast with TiO_2 and ZrO_2, a prolonged oxidation proceeds with a high oxidation rate after 183 min of inflection point; the probability of somewhat safety operation with this kind of material is very low.

During thermal degradation significant amounts of oxygen are consumed to produce water. This would suggest that oxides could be partially transformed into other chemical states, namely hydroxyoxides (possible in the case of CuO or Fe_2O_3) or acids (the most relevant example would be Cr_2O_3). It can be assumed that these intermediates react with hydroperoxides, the most abundant primary compound in oxidized poliolefins.[11]

The chemistry of studied oxides allows us to presume that the metal atoms with different valence states can be further oxidized by the abstraction of molecular oxygen simultaneously occurring with the oxidation degradation of polymeric substrate. This behavior was proven in the case of selenium, whose antioxidant activity was found for elementary selenium and SeO.[12]

CONCLUSIONS

On the basis of previous considerations some remarks can be made on the thermal stability of EPDM loaded with metallic oxides:

1. synthetic elastomers like ethylene–propylene terpolymer present a slight improvement of oxidation parameters except Cr_2O_3;
2. Cr_2O_3 proves the oxidative character over the whole duration of thermal oxidation. It determines the shortest life of ethylene–propylene elastomer samples;
3. the values of oxidation induction time places the studied oxides in the following order of increasing stability:
   $Cr_2O_3 < CuO < NiO < PbO < Fe_2O_3 < TiO_2 < ZrO_2$
4. the decreasing oxidation rate arranges oxides on the next sequence:
   $PbO > Fe_2O_3 > NiO > ZrO_2 > CuO > TiO_2$
   Cr_2O_3 was omitted because it displays clear oxidative properties.
5. inorganic pigments containing titania are the most recommended coloring matter.

The low content of metallic oxides in ethylene–propylene terpolymer slightly modifies the kinetic parameters (oxidation induction time and process rate) of thermal oxidation. It was assumed weak interaction between oxides and hydroperoxide intermediates. It can be postulate that the lifetime of elastomer products is not affected by the diffusion of several metallic oxides into the polymer bulk.

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