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44. Polymeric Polyolefin Antioxidants

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SUMMARY

Polymeric antioxidants prepared from 2,6-di-tertiary-butyl-4-vinyl (4-isopropenyl)phenol and butadiene or isoprene, and their hydrogenated products (6-8 mol % of phenolic AO in the polymer) were tested by oxygen-uptake studies for their effectiveness as antioxidants for polyolefins and polydienes. The polymeric antioxidants seem to be slightly less effective in short-term protection against oxidation at 150° C as compared to low molecular weight antioxidants, but more effective in long-term protection of the polymer samples at a level of 0.1 weight percent.

INTRODUCTION

An antioxidant must be compatible in a polymer matrix in order to be effective (1) and preclude exudation, and must be present at the site where attack of oxygen on the polymer chain is occurring (oxygen has a high permeability in most polymers (2-4).

It is well established also that extraction or leaching of stabilized polymer samples over prolonged periods with common solvents is capable of removing essentially all of the stabilizer (5).

Volatility is also an important factor for antioxidant activity; an increase in additive molecular weight results in an increase of functional effectiveness (5,6).

In view of these facts, polymeric and polymer-bound antioxidants offer several advantages over conventional antioxidants, and while some of these are obvious, some are more subtle. No losses of stabilizer due to volatilization are expected for high molecular weight antioxidants. Leaching of the stabilizer from the polymer matrix is also negligible. One frequently overlooked advantage of stabilization with a polymer system is that uniform molecular dispersion of the functional moieties can be readily accomplished (7) provided the percentage of stabilizer units in any copolymer or graft is insufficient to cause incompatibility and phase separation.

There are some potential drawbacks for polymeric stabilizers; it seems difficult to create one general-purpose (6) polymeric antioxidant which would be compatible with several important classes of polymers. The decreased mobility of the polymeric additive may hamper the ability of the stabilizer to reach sites of attack by oxygen (6,8), decreasing the antioxidant activity.

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It has been suggested (6) that a molecular weight of 3,000 to 20,000 would be optimum for polymeric antioxidants, striking a balance between volatility, compatibility, and mobility.

We have recently prepared polymeric antioxidants by copolymerizing 2,6-di-tertiary-butyl-4-vinyl(4-isopropenyl)phenol with styrene, methyl methacrylate (9), 1,3-butadiene, and isoprene (10). We have hydrogenated the latter two copolymers to modified polyethylene and ethylene/propylene alternating copolymers (10,11).

Oxygen-uptake experiments provide direct volumetric determination (12, 13) of the amount of oxygen reacting with a degrading virgin or stabilized polymer, and are especially useful for measuring the induction period of oxidation. The results of these experiments correlate relatively well with polymer lifetimes in actual use (14).

It was the objective of this work to blend selected polymers containing the antioxidant function, study their oxygen uptake as a means of investigating their effectiveness as antioxidants, and compare the results with those obtained with low molecular weight antioxidants.

EXPERIMENTAL

Solution Blending of Copolymers

Diene copolymers of 2,6-di-tertiary-butyl-4-vinylphenol and 2,6-di-tertiary-butyl-4-isopropenylphenol were blended with homopolymers of 1,3-butadiene and isoprene, and styrene-butadiene rubber (see Tables 1 and 2). The blends were made by mixing a cyclohexane solution of the appropriate diene polymer (30 mL of a 2 g/60 mL solution) with a cyclohexane solution of the polymeric stabilizer (0.6 mL of a 0.015 g/2 mL solution of butadiene copolymers; 1.0 mL of a 0.016 g/2 mL solution of isoprene copolymers). The blend, containing 0.001 g of phenolic stabilizer per gram or 0.1 weight % antioxidant units, was precipitated in methanol (250 mL), dried at 60° C and 0.005 mm for two days, and stored in the cold.

Hydrogenated diene copolymers of 2,6-di-tertiary-butyl-4-vinylphenol or 2,6-di-tertiary-butyl-4-isopropenylphenol were blended with polyolefins similarly. The blends were made by mixing a hot <u>o</u>-xylene solution of the appropriate polyolefin (50 mL of a 4 g/200 mL solution) with an <u>o</u>-xylene solution of the hydrogenated polymeric stabilizer (0.5 mL of a 0.02 g/2 mL solution for hydrogenated butadiene copolymers, 0.5 mL of a 0.03 g/2 mL solution for hydrogenated isoprene copolymers). The blend, containing 0.001 g of phenolic stabilizer per gram or 0.1 weight % antioxidant units, was precipitated in methanol (250 mL), dried at 60° C and 0.005 mm for two days, and stored in the cold.

The following blends were made with diene polymers for oxygen-uptake experiments (all blends contained 0.1 weight % phenolic units): Poly(2,6-di-tertiary-butyl-4-vinyl(or 4-isopropenyl)phenol-co-butadiene with <u>cis</u>-polybutadiene; random <u>cis</u>-, <u>trans</u>-polybutadiene and styrene/butadiene rubber and poly(2,6-di-tertiary-butyl-4-vinyl(4-isopropenyl)phenol-co-isoprene with <u>cis</u>-polyisoprene or <u>trans</u>-polyisoprene; and hydrogenated poly(2,6-di-tertiary-butyl-4-vinyl(4-isopropenyl)phenol-co-butadiene and hydrogenated poly(2,6-di-tertiary-butyl-4-vinyl(4-isopropenyl)phenol-co-isoprene with HDPE, LDPE, LLDPE, and atactic polypropylene.

Measurements

Oxygen-uptake experiments were performed at 150° C and one atmosphere oxygen pressure using a volumetric apparatus (14). Fifty mg of the blend to be tested were placed in a glass tube which was closed at one end, or a round-bottom flask, followed by a plug of glass wool, 2 g of calcium oxide,

TABLE 1. Solutions of Phenol-Diene Copolymers Prepared for Blending with Polydienes

Polymer	Antioxidant (mol %)	Polymer (g)	Volume of Solution* (mL)
Poly(2,6-di-tertiary-butyl-4-vinylphenol-co-butadiene)	6	0.015	2.0
Poly(2,6-di-tertiary-butyl-4-isopropenylphenol-co-butadiene)	6	0.015	2.0
Poly(2,6-di-tertiary-butyl-4-vinylphenol-co-isoprene)	8	0.016	2.0
Poly(2,6-di-tertiary-butyl-4-isopropenylphenol-co-isoprene)	6	0.016	2.0
cis-Polybutadiene	–	2.0	60.0
Random *cis*-, *trans*-Polybutadiene	–	2.0	60.0
cis-Polyisoprene	–	2.0	60.0
trans-Polyisoprene	–	2.0	60.0
Styrene-butadiene copolymer (SBR), 25% styrene	–	2.0	60.0

*All solutions in cyclohexane, 99^+%.

TABLE 2. Solutions of Hydrogenated Phenol-Diene Copolymers Prepared for Blending with Polyolefins

Polymer	Antioxidant (mol %)	Polymer (g)	Volume of solution (mL)
Hydrogenated poly(2,6-di-tertiary-butyl-4-vinylphenol-co-butadiene)	6	0.02	2.0
Hydrogenated poly(2,6-di-tertiary-butyl-4-isopropenylphenol-co-butadiene)	6	0.02	2.0
Hydrogenated poly(2,6-di-tertiary-butyl-4-vinylphenol-co-isoprene)	8	0.12	2.0
Hydrogenated poly(2,6-di-tertiary-butyl-4-isopropenylphenol-co-isoprene)	6	0.03	2.0
High-density polyethylene (HDPE)	–	4.0	200
Low-density polyethylene (LDPE)	–	4.0	200
Linear low-density polyethylene (LLDPE); poly(ethylene-co-1-butene)	–	4.0	200
Atactic polypropylene	–	4.0	200

*All solutions in *o*-xylene, 97%.

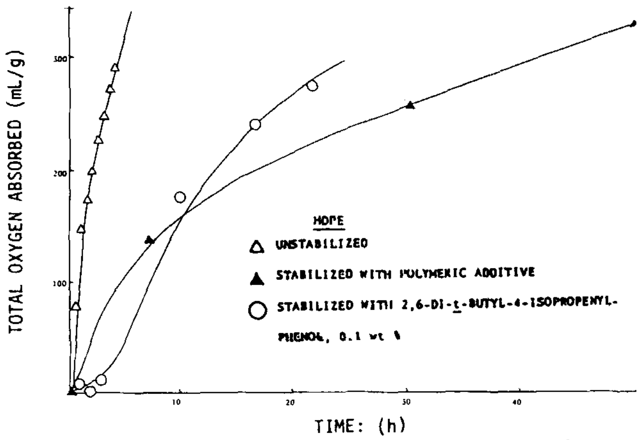

Figure 1. Oxygen-uptake curves for unstabilized and stabilized HDPE.

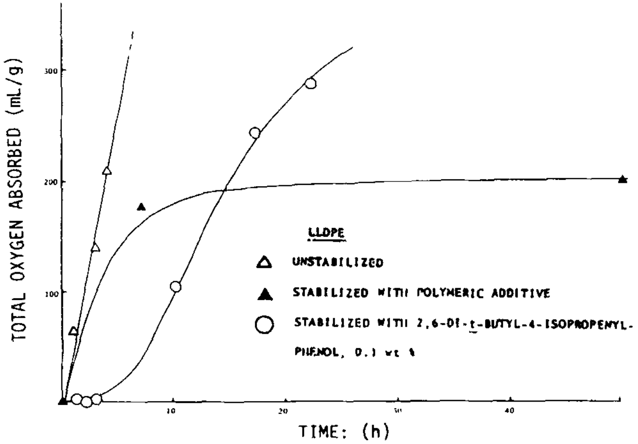

Figure 2. Oxygen-uptake curves for unstabilized and stabilized LLDPE.

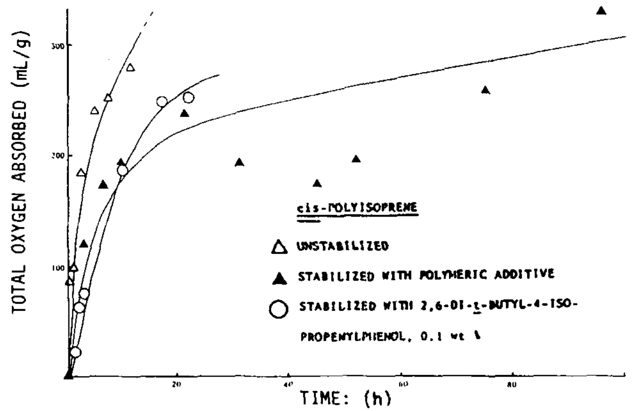

Figure 3. Oxygen-uptake curves for unstabilized and stabilized cis- polyisoprene.

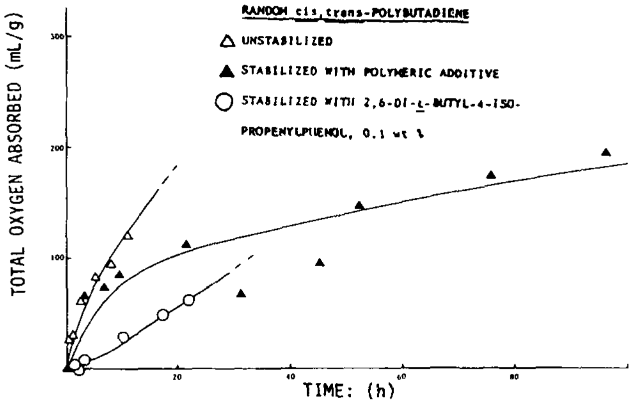

Figure 4. Oxygen-uptake curves for unstabilized and stabilized random cis-, trans-poly butadiene.

and another plug of glass wool. The glass tube was then attached to the measurement apparatus by a short length of tygon tubing. The apparatus was alternately evacuated and filled with oxygen three times. After the final filling, the pressure in the apparatus was adjusted to one atmosphere with the aid of a Firestone valve and by raising or lowering the mercury reservoir until the level in the reservoir was the same height as that in the buret of the apparatus. The sample tube was kept in a 150°C silicone-oil bath throughout the experiment, and oxygen uptake was determined volumetrically by direct reading of the buret.

Oxygen-Uptake Studies of Blends

Preliminary results from oxygen-uptake experiments appear in Figures 1 through 4. Data are shown for unstabilized polydienes and polyolefin samples (controls) and selected polydienes and polyolefins stabilized with 0.1 weight % antioxidant moieties. Oxygen absorbed is expressed in terms of mL of oxygen absorbed per gram of polymer. Sample size was 50 ± 1 mg.

No induction period was observed in the case of control samples. Periods of reduced oxygen uptake are seen for the stabilized samples. Thus, results from preliminary oxygen-uptake testing of samples stabilized with the polymeric antioxidants prepared earlier showed that the polymeric antioxidants are effective antioxidants, based on this kind of experiment. In short-term exposure, they seem to be slightly less effective than the low molecular weight stabilizers, but at long-term exposure they are superior. The scatter in some of the graphs is due to inadequate control of temperature, with as much as ±5°C variation.

The specific blends tested at 150°C were: HDPE stabilized with hydrogenated poly(2,6-di-tertiary-butyl-4-vinylphenol-co-butadiene) (Figure 1); LLDPE stabilized with hydrogenated poly(2,6-di-tertiary-butyl-4-vinylphenol-co-butadiene) (Figure 2); *cis*-polyisoprene stabilized with poly(2,6-di-tertiary-butyl-4-isopropenylphenol-co-isoprene) (Figure 3); and random *cis*-, *trans*-polybutadiene stabilized with poly(2,6-di-tertiary-butyl-4-vinylphenol-co-butadiene) (Figure 4). All blends contained 0.1 weight % phenolic monomer units. Unstabilized controls and samples with 0.1 weight % monomeric stabilizer are also plotted (15,16).

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