Effects of Phenolic Antioxidants on Ultrahigh Molecular Weight Polyethylene/Decalin Solution

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ABSTRACT: The degradation of ultrahigh molecular weight polyethylene (UHMW-PE) during its dissolution into decalin is discussed. The stabilization of the solution by three phenolic antioxidants, octadecyl β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (1076), tetrakis[methylene-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane (1010), and 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane (CA), and an auxiliary antioxidant, dilaurylthiodipropionate (DLTP) is also discussed. Among the three phenolic antioxidants, 1076 had the greatest effect. The auxiliary antioxidant was effective in stabilizing the solution when combined with one of the three phenolic antioxidants. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2877–2881, 2000

Key words: ultrahigh molecular weight polyethylene solution; decomposition; phenolic antioxidants

INTRODUCTION

Gel deformation is known to be an excellent method to produce high-modulus and high-strength polyethylene fibers or films. This method was first proposed by Smith et al.[1] and was mainly developed by Smith et al.[2–5] The average molecular weight of the polyethylene used to produce high-modulus and high-strength fibers and films or other engineering materials is usually above 1×10^6 and it is very important to maintain the molecular weight of ultrahigh molecular weight polyethylene (UHMW-PE) as high as possible in the finished fiber. The process, called gel fiber drawing, was first put into effect on an industrial scale. In general, when a UHMW-PE gel spinning solution is prepared by dissolving UHMW-PE (2–10%, w/w) into a proper solvent at a relatively high temperature, usually above 140°C, themooxidative degradation inevitably occurs, which will deteriorate the properties of the finished fiber. To prepare UHMW-PE fibers with high modulus and high strength, adding a proper amount of an antioxidant or thermostability agent into the solution is a common way to resist the degradation of UHMW-PE during its dissolution. To date, systematic studies on the degradation and antidegradation of a UHMW-PE/decalin solution have not been seen. It is known that polyolefins are sensitive to heat- and light-induced oxidative degradation. Studies in the past on the thermal oxidative stability of high-density polyethylene (HDPE) generated information on how HDPE is oxidized under thermal stress.[5,6] Alkyl and peroxyradicals, hydroperoxides, β-scission after hydroperoxide decomposition to carbonyl, and an alkyl radical end group are recognized as the major elements in the general oxidation. Effective stabilizer systems are largely developed through interrupting the degradation cycle, which results in the wide application of this polymer. Unstabilized and stabilized HDPEs were evaluated by oxygen uptake at 140, 100, and 40°C.[7] This article presents the degradation and

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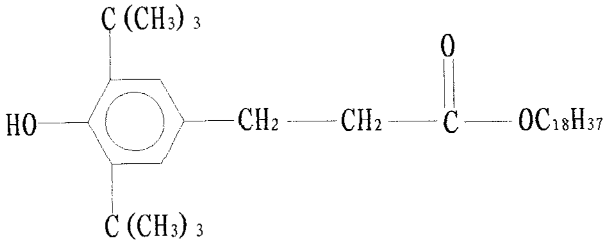
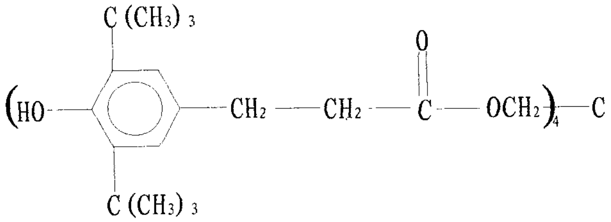
stabilization of a UHMW-PE/decalin solution with three penolic antioxidants, octadecyl β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (1076), tetrakis[methylene-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane (1010), and 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)-butane (CA), and an auxiliary antioxidant, dilaurylthiodipropionate (DLTP), as well.

EXPERIMENTAL

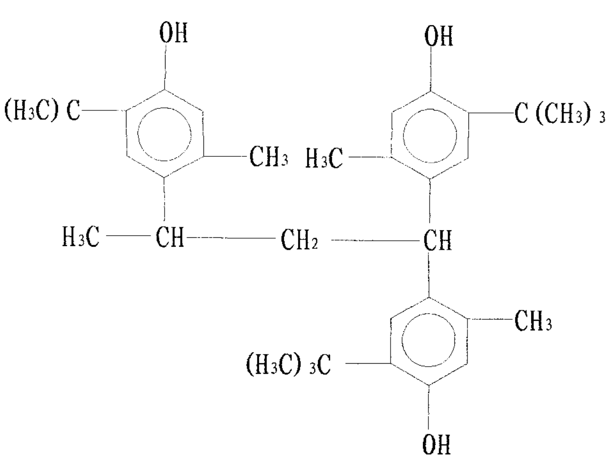
In this study, UHMW-PE, supplied by Beijing Auxilliaries Plant No. 2 (Beijing, China), with viscosity-average molecular weights, M_v's, of 2.0 × 10^6, 3.5 × 10^6, and 5.0 × 10^6 was used. The three phenolic antioxidants, 1076,



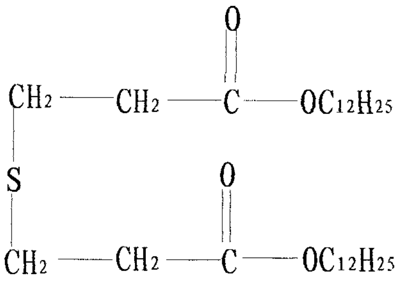
1010,



CA,



and an auxiliary antioxidant, DLTP,



were supplied by the Liaoning Organic Chemical Factory (Shengyang, China). Solutions were prepared by precisely weighing the polymer (1.0 wt %) and antioxidants (0.2 wt % to the UHMW-PE), putting them into conical flasks with a certain amount of decalin in them, heating the conical flasks to 140°C at a rate of 2°C/min, and then keeping them at this temperature for 120 s. The flow times (t') of the solutions were measured using an Ubbelohde viscosimeter according to the method of determination of the molecular weight by the viscosity.[8] Percentages of the contents of the antioxidants are all by mass.

RESULTS AND DISCUSSION

Polymer usually degrades according to the mechanism of an oxidative free-radical reaction. Initiation usually arises from the homolysis of —O—O— containing molecules, present at low concentrations in polyolefins. The hydroperoxides and peroxides in polyolefins, which can be determined by analysis, usually arise from manufacturing, processing, and storage. Alkoxy and hydroxy free radicals, from the homolysis of hydroperoxides and hydroperoxides, abstract hydrogen from the macromolecules to yield carbon-centered free radicals. The carbon-centered radicals react readily with oxygen to form alkyl peroxy radicals, which abstract hydrogen from the macromolecules to form hydroperoxides and propagate the chain reaction. Alkoxy radicals from the homolysis of hydroperoxides lead to chain scissioning, to molecular weight decrease, and, eventually, to deterioration of the quality of polymeric materials. The radical chain reaction is according to the following scheme[9,10]:

chain initiation

$$RH \rightarrow R\bullet + H\bullet$$

$$RH + O_2 \rightarrow R\bullet + HOO\bullet$$

$$\text{catalyzer survived} \rightarrow \text{radical}$$

chain propagation

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet$$

chain branching

$$ROOH \rightarrow RO\bullet + HO\bullet$$

$$ROOH + RH \rightarrow RO\bullet + R\bullet + H_2O$$

$$2ROOH \rightarrow RO\bullet + ROO\bullet + H_2O$$

$$RO\bullet + RH \rightarrow ROH + R\bullet$$

chain termination

$$HO\bullet + RH \rightarrow H_2O + R\bullet$$

$$2ROO\bullet \rightarrow ROOR + O_2$$

$$2ROO\bullet \rightarrow RO\bullet + O_2$$

$$R\bullet + ROO\bullet \rightarrow ROOR$$

$$2R\bullet \rightarrow R—R$$

The effects are more pronounced for UHMW polymers. According to the principle of their effects, antioxidants are usually classified into free-radical-resistant agents, that is, primary antioxidants (AH) which can combine with radicals to form stable compounds:

$$ROO\bullet + AH \rightarrow ROOH + A\bullet$$

$$ROO\bullet + A\bullet \rightarrow ROO\text{-}A$$

and peroxide decomposing agents, that is, auxiliary antioxidants which are usually effective when combined with primary antioxidants. The mechanisms of auxiliary antioxidants containing sulfur combined with phenolic antioxidants is not yet clear, but they are effective in reducing the rate of initiation in the chain decomposition of macromolecules and the rate of the branching reaction by decomposition of hydroperoxide.[11,12]

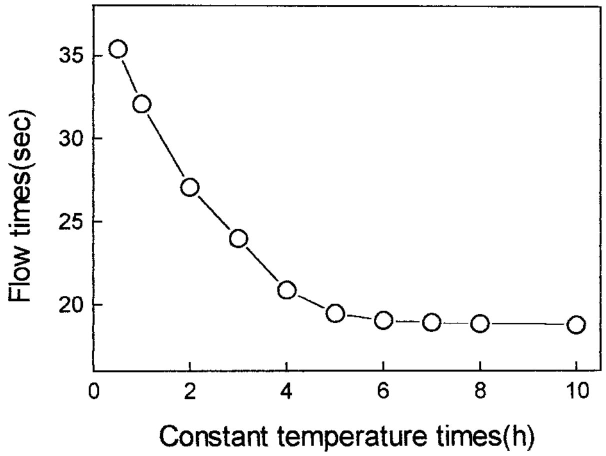


Figure 1 Flow times as a function of the time for UHMW-PE (M_v = 3.5 × 10^6)/decalin solutions at 140°C.

Figure 1 shows the changes of the flow time of the UHMW-PE solution, having no additive at 140°C. It is observed that the flow time almost decreases linearly with time in the initial 4–5 h, which indicates that the thermooxidative degradation of the polymer occurred under the condition of a constant high temperature. The molecular weight of UHMW-PE or the viscosity of the solution has therefore decreased severely. In about 7 h, the flow time decreases to an almost constant value.

Flow times of solutions containing various primary antioxidants were also measured as shown in Figure 2. The flow times of the three antioxidant-containing solutions varied with the identify and amount of the antioxidant included. According to the result of Figure 2, it can be concluded that the effects of the three antioxidants show the following: 1076 > 1010 > CA, which may be attributed to their different molecular structures.

According to their molecular structure, we know that 1076, 1010, and CA are phenolic antioxidants whose properties largely depend on the three substitutents on the benzene ring. In the 1076 or 1010 molecules, there are two *tert*-butyls, at both of the *ortho*-positions of the hydroxyl substitutents. Because *tert*-butyls are electron-donating substituents, the activities of 1076 and 1010 are greater than that of CA. Due to the relatively smaller steric effect than that in 1010, the hydroxyl in the 1076 molecules can donate hydrogen

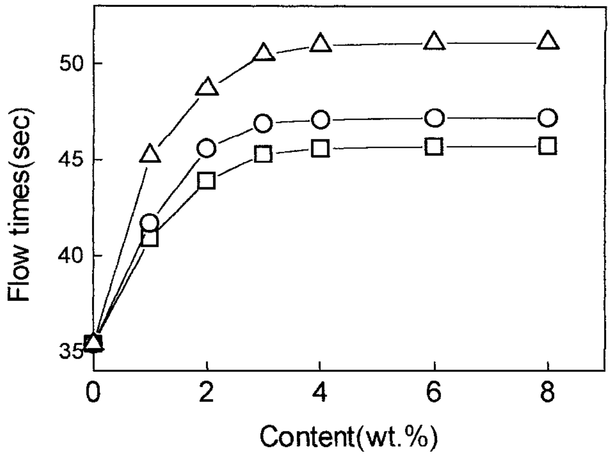


Figure 2 Change in flow time with increasing contents of antioxidants (UHMW-PE with $M_v = 3.5 \times 10^6$). (—□—) CA; (—○—) 1010; (—△—) 1076.

to capture active radicals more easily, and, so, 1076 has a stronger effect than has 1010 in antioxidation. In addition, Figure 2 shows that the effect of the additive increases rapidly with its content when below about 4% or so, but increases very slowly in the range of 4–6% and hardly increases any more when beyond 6%. Excessive use of additives may also deteriorate the quality of ultimate polymer products, so the content of antioxidants should be as low as possible.

Figure 3 shows the relationship between the molecular weight of UHMW-PE and flow time for the three antioxidants. It is evident that for PE of varying M_v the effects of the three antioxidants are still in order of 1076 > 1010 > CA.

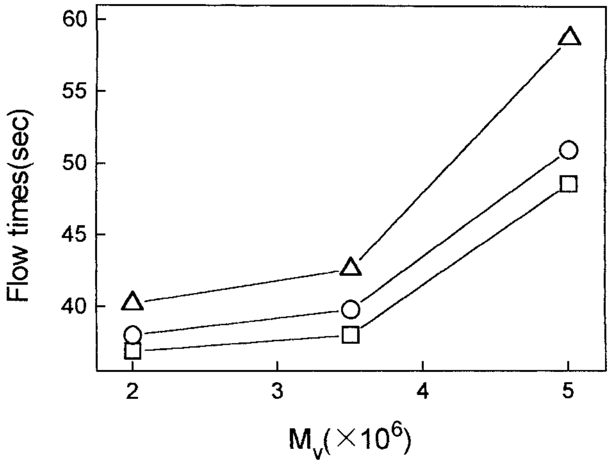


Figure 3 Change in flow times with increasing molecular weight of PE (antioxidant with 0.5%). (—□—) CA; (—○—) 1010; (—△—) 1076.

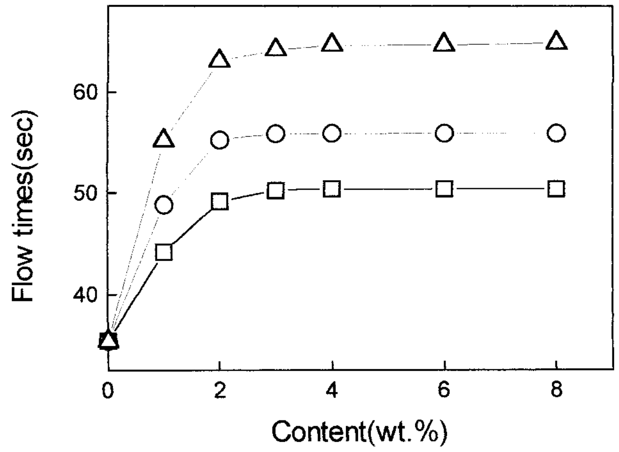


Figure 4 Change in flow times with increasing the contents of antioxidant/auxiliary antioxidant (UHMW-PE with $M_v = 3.5 \times 10^6$). (—□—) CA; (—○—) 1010; (—△—) 1076.

The use of peroxide-decomposing agents (auxiliary antioxidant) together with a free-radical terminating agent (primary antioxidant) can enhance the effect of antioxidative degradation. Figure 4 shows that DLTP is effective in the stabilizing the solution when combined with one of the three phenolic antioxidants. In Figure 4, the ratio of the primary antioxidants to the auxiliary antioxidant is 0.5.

CONCLUSIONS

The degradation of UHMW-PE during its dissolution into decalin was discussed. The stabilization of the solution by three phenolic antioxidants, 1076, 1010, and CA, and an auxiliary antioxidant, DLTP, was also studied. From the analysis of the data obtained in this study, it is concluded that the effect of 1076 is the greatest among the three phenolic antioxidants, and the auxiliary antioxidant is also effective in stabilizing the solution of UHMW-PE/decalin when combined with one of the three phenolic antioxidants. Although the effects of antioxidants increase with increase of the absolute contents of the antioxidants, the enhancement becomes very limited when the contents increase beyond 6%. The optimum content of the antioxidants is 4%.

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