Reaction model describing antioxidant depletion in polyethylene–clay nanocomposites under thermal aging

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ABSTRACT

Antioxidants are typically added to polyethylene to extend its durability, and recently clay nanoparticles have been blended into polyethylene to improve mechanical properties. However, the clay nanoparticles also accelerate the rate of antioxidant depletion in polyethylene. This paper uses a mathematical model to describe the underlying mechanisms of antioxidant (hindered-phenol) depletion and to predict experimentally-measured antioxidant profiles in polyethylene–clay nanocomposites. The mathematical model uses a reaction kinetic scheme that includes free radical initiation and propagation reactions, antioxidant stabilization reactions and free radical termination reactions. In the model, alkyl free radicals oxidize rapidly. The role of antioxidants is to stabilize the oxidized free radicals to hydroperoxides, and interrupt propagation reactions. However, in nanocomposites, continuous depletion of antioxidant is caused by the clay acting as a catalyst to decompose hydroperoxides and regenerate alkyl free radicals. This cyclic hydroperoxide generation and decomposition leads to much faster antioxidant depletion in polyethylene nanocomposites. Phenoxyl radicals of antioxidants generated by stabilization reactions contribute to terminate polymeric free radicals and limit their accumulation. Predictions of antioxidant depletion are compared to experimental results for accelerated aging of polyethylene and nanocomposite samples.

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1. Introduction

The global production of polyethylene (PE) is about 100 million tons per year and is growing almost 5% annually due to its wide variety of applications. Several advantages of PE over other plastics/metals include low cost, good processability, non-toxicity and good recycling performance. However, PE is inferior to other plastics/metals in mechanical properties. Many properties of PE, such as modulus [1–5], barrier properties [6–9], and even strength [10] are improved by adding clay and carefully processing it to form nanocomposites. Despite a large amount of research on material properties and processing techniques of PE nanocomposites, the long-term performance is still poorly understood. Long-term degradation of PE properties is primarily due to environmental

oxidative degradation which is inhibited by antioxidants (AO). However in nanocomposites, a high amount of AO is required to inhibit the degradation because the clay catalyzes the degradation of polyethylene. This accelerated depletion of AO has challenged the commercialization of PE-clay nanocomposites. In this paper a model of AO depletion is used to explore mechanisms by which the presence of clay leads to accelerated AO depletion.

PE-clay nanocomposites contain several components that may contribute to generation of additional free radicals and faster AO depletion. The type of clay widely used with PE is montmorillonite, which is a layered alumino-silicate of roughly 1 nm thick negatively-charged silica layers separated by metal cations. The cations are partially exchanged with organic modifiers and compatibilizers to enhance dispersion within PE [11]. During processing, the layers can exfoliate to disperse nanometer-thick clay platelets throughout the polymer thus forming a "nanocomposite". The organic modifiers (alkyl ammonium ions) and compatibilizers enhance interaction between clay and PE, but they also have a negative effect on processing and durability [12,13] of PE products. During PE melt processing, thermal decomposition of the organic modifier is known to be enhanced by the so-called Hoffman

elimination [14]. Also, the presence of transition metal ions as impurities in the clay can catalyze the degradation reactions [15]. Oxidative polymer degradation of nanocomposites is reported to be about 4 times faster than pure polymer [16]. AO stabilizes oxidized free radicals and generates hydroperoxides which can degrade to regenerate free radicals, a cycle that leads to depletion of AO and is accelerated in nanocomposites.

The degradation of PE mainly occurs due to fast oxidation of the free-radicals when exposed to atmospheric oxygen followed by propagation. Therefore, AO is incorporated in polymeric materials to interrupt propagation of the oxidized free radicals and enhance durability. During aging, AO reacts preferentially to PE and stabilizes the oxidized free radicals. After the AO is depleted, the PE material is no longer protected from environmental oxygen. Therefore, degradation of PE can be divided into two broad phases: (Phase-I) AO-rich phase when AO protects PE from degradation, and (Phase-II) PE-degradation phase when AO no longer protects PE, and chain reactions lead to increases in free radical concentrations. The model in this paper applies to Phase-I degradation during which the PE product retains its designed properties.

Our prior experimental study of AO depletion in neat PE and nanocomposites [17] has guided development of the model in this paper. Here 'neat PE' refers to PE with 2wt% maleic-anhydride grafted PE (MA-g-PE). Consumption of AO in neat PE and its nanocomposite under normal atmospheric conditions may take several decades; therefore, accelerated thermal aging was used in the experimental study. Samples were held at 85 °C in a circulated air atmosphere, and AO concentrations in aged samples were determined by measuring 'oxidation induction times' (OIT). Although OIT is an indirect measure of active AO concentration present in a polymeric sample, OIT and AO concentration are linearly proportional for the AOs (Irganox-1010, and Irganox-1076) discussed in this paper [18–20]. Although there might exist some deviation from this linear relationship for aged PE and PE-clay nanocomposites as discussed by Richaud [21] it can still be considered to be linear in all samples for simplicity. The results showed that in the PE-clay nanocomposite samples, AO depleted at a much faster rate than neat PE. This could be due to higher rate of decomposition of hydroperoxides in presence of clay leading to formation of more free radicals [22,23].

Depletion of AO in PE and PE degradation has been modeled by several researchers. Smith et al. [24] created a diffusion-reaction model to describe depletion of AO in MDPE pipe incubated in hot-water at 80 °C, 95 °C and 105 °C. They considered an overall zero order reaction parameter which depended on AO concentration and position with a diffusion coefficient that varied linearly with position. Zero order kinetics was chosen because AO depletion was linear for short time data, but the long-time data invalidates this assumption. The model in this paper predicts an initial linear decrease in AO concentration without zero order assumption followed by asymptotic approach to zero to predict long term data. Smith et al. also considered variation in the AO diffusion coefficient with position to predict the skewedness in AO profiles due to water exposure in inner side of the pipe and air exposure in the outer side. But this skewedness of the AO profile was not found in water/water or air/air exposures. A non-uniform initial AO distribution was also used in the model. Although the justifications for these assumptions were not well developed, the model agreed with the AO depletion behaviors in PE pipes. Richaud et al. [25] also modeled AO depletion in PE at high temperatures. Their study focused on sulfide AO which stabilizes hydroperoxides from further decomposition. Unlike Smith, they used chemical reaction schemes together with physical loss of AO by diffusion of AO into the environment to describe experimental results. They found that simple kinetic models, where physical loss is either independent of or

proportional to AO concentration, fail to predict experimental results of concentration versus time at 110 °C and 120 °C. Therefore, they proposed a new model which considers an excess AO relative to its saturation threshold in the polymer, which provides a reservoir for PE stabilization. This modification produced good agreement between the model and experimental results.

Recently, Gutiérrez et al. [16] studied the influence of clay on oxidation kinetics of unstabilized PP-clay nanocomposites at temperatures of 60 °C, 80 °C and 100 °C. They measured a 40% reduction in oxygen permeability due to clay addition. Diffusion limitations caused carbonyl groups to concentrate in a degraded superficial layer close to the sample surface. The depth of this layer was 17 μm for PP and 10 μm for the nanocomposites aged at 100 °C; this difference was attributed to decrease in O_2 diffusivity by adding clay. The mathematical model they proposed matched experimental features when the O_2 diffusivity in nanocomposites was 40% less than PP. Their study based on onset of carbonyl group also shows the induction period of nanocomposites to be about 30% less than PP. The model considered a cyclic hydroperoxide decomposition route for generation of newer free radicals. β-scissions of alkoxy radicals were considered to be instantaneous. To effectively agree with the experimental carbonyl buildup data, the initial hydroperoxide concentration in the nanocomposite was considered to be double that of PP. In unstabilized polymers, the rate of oxygen consumption by free radicals is much higher than in polymers containing antioxidants. Our models have shown that in thin samples (a few millimeters) of neat PE stabilized with AO, oxygen consumption is slow enough compared to diffusion that the oxygen quickly saturates and becomes uniform throughout the sample.

Although there is some prior work in the literature on modeling AO diffusion and depletion in PE & PP, there are not any published models of AO depletion in PE-clay nanocomposites. This paper presents the first model of AO depletion in PE that includes both AO and the effects of nano-clay. The reaction kinetic schemes for AO depletion in neat PE as well as its nanocomposites are discussed first in this paper emphasizing which of the reactions can be accelerated in nanocomposites and lead to faster depletion of AO. The next section describes the development of mathematical model to predict concentration of AO and other polymeric reactive groups at different aging times. Diffusion and physical loss of AO and other reactive species are ignored, so that concentrations of all species depend on chemical reactions only; the effect of diffusion of both AO and oxygen will be treated in another paper. The results section discusses a Base-Case result obtained by the model to understand different features of the model. This is followed by comparison of experimental results with model predictions to explain the key mechanisms of AO depletion. Some of the key parameters in the model were adjusted to agree with experimental OIT profiles.

The model in this paper does not consider diffusion of O_2 and AO, which can significantly affect the distribution of different species throughout the depth of the samples. Another paper will present a model of AO depletion that includes both reactions and diffusion mass transfer. The model in this paper, therefore, does not consider any physical interaction of AO with clay such as adsorption onto clay surface. Therefore, this model serves the purpose of understanding the contribution of chemical reactions on AO depletion. A homogeneous degradation process is assumed with global concentrations of AO and other reactive species, which gives average values of PE oxidation behavior. It is known that phenolic AOs and O_2 diffuse only into amorphous phase of PE, therefore, the oxidative degradation reactions and stabilization takes place in amorphous phase only. However the assumption of global concentration for all species is justified because the phenolic results are relatively insensitive to the phenolic concentration (shown in Supplementary Document). Different polymeric reactive species