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Polymer Degradation and Stability 91 (2006) 1156–1165

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

The efficacy of photostabilizers on the color change of wood filled plastic composites

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Received 4 January 2005; received in revised form 18 May 2005; accepted 28 June 2005

Abstract

In this study, we compared the performance of different hindered amine light stabilizers and ultraviolet absorbers as photostabilizers of wood plastic composites (WPC). We showed how their functional groups and molecular weights influence the photostabilization of WPC subjected to natural weathering for 2000 h. The changes were followed using color measurements and FTIR spectroscopy which provided insight into the photodegradation mechanism of weathered WPC.

The results indicate that weathering causes color fading and changes in yellowing. We propose that WPC undergo two competing redox reactions upon UV exposure. The first is the oxidation of lignin which leads to the formation of paraquinone chromophoric structures which is dominant in the first 250 h of exposure. The second is the reduction of the paraquinone structures to hydroquinones which leads to photobleaching.

High molecular weight diester HALS were found to be the most effective in controlling long term fading and yellowing changes. Furthermore, the addition of a benzotriazole ultraviolet absorber shows great synergism in controlling fading when added to a diester HALS.

Keywords: Wood plastic composites; Photodegradation; Photostabilization; HALS; UV absorbers; Lignin; Photobleaching; Photoyellowing; Chromophores

1. Introduction

The use of lignocellulostic fibers as reinforcing fillers in the thermoplastic industry has gained much acceptance in recent years and is expected to keep growing. Wood fibers are desirable fillers because of their low density and cost, abundant availability, biodegradability and their high specific strength and modulus [1].

In North America, building products particularly decking, account for 75% of the wood plastic composite (WPC) market. In fact, 500,000 tons of WPC are expected to be in use for building products in 2006 [2]. In this way, as the outdoor applications of WPC become more widespread, the durability of these products against weathering, particularly ultraviolet (UV) light becomes a concern. UV exposure can cause changes in the surface chemistry of the composite – also known as photodegradation – which may lead to discoloration [3–8] making the products aesthetically unappealing. Furthermore, prolonged UV exposure may ultimately lead to loss in mechanical integrity [3–6,8].

The photodegradation mechanisms of wood and plastic separately are well documented in literature. Many researchers have proposed that carbonyl groups are the main UV light absorbing species responsible for

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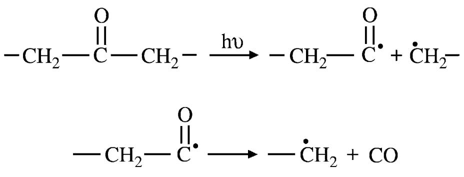
doi:10.1016/j.polymdegradstab.2005.06.024

the photo-initiation reactions in polyethylene [9–11]. The degradation of the carbonyl group may proceed according to Norrish Type I or Norrish Type II reactions. Norrish Type I reaction proceeds in the presence of UV light which allows for the formation of free radicals. In turn, these free radicals attack the polymer as seen in Scheme 1 [10]. This may lead to termination via cross linking or chain scission [10]. If the degradation occurs according to Norrish Type II, then both carbonyl and vinyl groups are produced, as seen in Scheme 2, and chain scission occurs [9,10]. In this way, during the exposure of polyethylene to UV light, both chain scission and cross linking reactions are competing. Chain scission lowers the molecular weight of the polyolefin [9,10]. Kaci et al. has suggested that the weathering of polyethylene results in an increase in crystallinity which indicates that chain scission has occurred [11]. Chain scission causes short chains to form which are more mobile and crystallize easily resulting in embrittlement. Cross linking, on the other hand, does not affect polymer crystallinity [10,23].

The photodegradation of wood is attributed to the degradation of its components namely cellulose, hemicellulose, lignin and extractives [16]. However, research has shown that the breakdown of lignin to water soluble products – which eventually leads to the formation of chromophoric functional groups such as carboxylic acids, quinones and hydroperoxy radicals – is the main cause for discoloration, mainly yellowing in wood [17–19]. Lignin undergoes photodegradation via many different pathways. Ultimately, they all lead to the formation of chromophoric groups which have a characteristic yellow color [33]. One of the most noted reaction pathways is the Phenoxy Quinone Redox Cycle [29–33] as seen in Scheme 3 [33]. This reaction suggests that the hydroquinones and paraquinones are a redox couple [32]. Under irradiation, the process begins with the oxidation of the hydroquinones to form paraquinones (chromophoric structures) which are further reduced to hydroquinones as the cycle repeats itself.

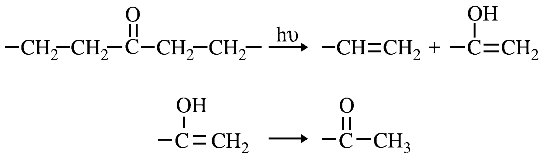
The development of hindered amine light stabilizers (HALS) three decades ago led to an increase in the outdoor use of polyolefins [12]. HALS have been extensively examined for polyolefins protection as free radical scavengers. They have been reported to photostabilize unfilled high density polyethylene (HDPE) and polypropylenes (PP) [13,14]. In addition to HALS, UV absorbers (UVA) are commonly used photostabilizers in polyolefins. Their protection mechanism is based on the absorption of harmful UV radiation and its dissipation as heat [15]. Furthermore, Gugumus has reported that the behavior of UV absorbers in combination with HALS may lead to synergistic effect in the UV protection of PE-LD films [15].



$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}- \xrightarrow{h\upsilon} -\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{\bullet} + \dot{\mathrm{C}}\mathrm{H_2}-$$

$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{\bullet} \longrightarrow -\dot{\mathrm{C}}\mathrm{H_2} + \mathrm{CO}$$

Scheme 1. Norrish Type I reaction for the photodegradation of HDPE.



$$-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}- \xrightarrow{h\upsilon} -\mathrm{CH{=}CH_2} + -\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}{=}\mathrm{CH_2}$$

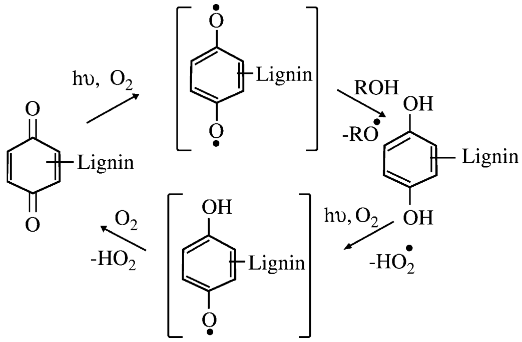
$$-\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}{=}\mathrm{CH_2} \longrightarrow -\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3}$$

Scheme 2. Norrish Type II reaction for the photodegradation of HDPE.

Based on the UV degradation mechanism of polyolefins and the mechanism of action of HALS, the WPC industry has adopted the use of HALS as part of its UV stabilizing additives [20]. However, the photodegradation mechanism of WPC is complicated because each component, namely wood and plastic, may degrade via a different mechanism.

Stark et al. [21] investigated the effectiveness of various photostabilizers including two different HALS, one UV absorbers (UVA) and one colorant on the UV stability of HDPE filled wood flour. After accelerated weathering using a xenon arc type lamp, their results indicated that both colorants and UVA were more effective photostabilizers than HALS [6].

However, it is important to note that the chemical structure and molecular weight of the HALS drive the stabilization mechanism and are important factors in their effectiveness against photodegradation in polyolefins [13,14]. In this way, a comparative analysis of the various HALS structures and their respective photostabilizing effect on WPC has not been reported. In addition, the changes in surface chemistry of the various HALS stabilized composites as well as a detailed analysis of color change may provide insight into the mechanism of action of HALS in WPC. The results from the study will aid in the development of a UV



Scheme 3. Phenoxy Quinone Redox Cycle involved in photoyellowing and photobleaching.