Stabilization of polypropylene-based materials *via* molecular retention with hyperbranched polymer

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Akanksha Matta, Ikki Katada, Junji Kawazoe, Patchanee Chammingkwan, Minoru Terano, Toshiaki Taniike*

Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

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ABSTRACT

A novel approach for the stabilization of polypropylene (PP) has been proposed, which is based on the addition of a hyperbranched polymer (HBP) to reversibly trap stabilizer molecules in the dendritic interior and to prevent their volatilization. The lifetime of PP was at maximum 493% elongated by the addition of a small amount of HBP, which itself never suppressed the oxidative degradation, but effectively delayed the volatilization of stabilizers. The stabilization effect of HBP was further signified in the case of PP/SiO_2 nanocomposites: HBP was grafted to SiO_2 surfaces during melt mixing and was better dispersed through the nanoparticles in the matrix, providing 776% improvement in the lifetime. The versatility of the strategy was also confirmed for a variety of hindered phenols.

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1. Introduction

Significant advances have been made in the last few decades on the development of renewable feedstock-based polymers and recycle/reuse technologies of fossil-based polymers [1]. For the latter, a key issue is to suppress the degradation of polymeric materials during processing and service as much as possible [2]. In order to suppress the degradation, the mechanistic understanding is essential: It has been well documented in literature that the degradation of polymers can be initiated by oxygen, shear, heat, light, catalyst residues and *etc* [3—5]. Even a small extent of degradation has an enormous effect on their physical properties [6]. Controlling or inhibiting the reactions responsible for degradation has considerable advantages in terms of attaining practical stability [7]. This can be achieved by appropriately incorporating additives to the formulation of a polymeric material [8]. A large variety of stabilizers have been developed for each kind of polymers and they can be roughly categorized as anti-oxidants, UV absorbers and UV stabilizers [9], hindered amine light stabilizers (HALS) [10], anti-hydrolysis agents [11], and metal passivation agents [12]. The efficiency of stabilizers depends on many factors such as the chemical

activity of functional groups, the compatibility, and the diffusivity of stabilizers in polymer matrices, while the retention of a stabilizer is one of the most important factors for long-term stabilization, since a stabilizer can be gradually lost in the atmosphere through volatilization or elution [13,14]. High molecular-weight or polymer-grafted stabilizers [15] can suppress or even eliminate these physical losses, but at the same time sacrifice the mobility, which is crucial especially for low temperature, *e.g.* in the case of photo degradation [16]. A practical solution for this tradeoff problem between the retention and mobility involves combination of low molecular-weight and high molecular-weight stabilizers [17].

There have been massive synthetic developments in the field of hyperbranched polymers (HBP) in the last two decades [18]. The hyperbranched polymers have highly branched three-dimensional globular architecture consisting of a polyfunctional central core covalently linked to the layers of repeating units and a number of terminal groups [19]. The properties are in striking contrast with linear polymers [20]: The nature of the end groups [21,22] largely affects properties such as the solubility and chemical reactivity, while their three-dimensional structure results in low viscosity at a given molecular weight [23]. Moreover, the globular shape and the presence of internal cavities are responsible for encapsulating guest molecules or nanomaterials in the macromolecule interior [24], which leads to a wide range of potential applications including drug delivery [25—27], catalysis [28,29], and coatings or additives [30]

and so on. Drug molecules, genetic materials, targeting agents, catalytic entities, and dyes have been enclosed within the dendritic structure either by physical bonding (non-bonding interactions) or by chemical bonding (complexation or covalent conjugation) [31,32]. However, no report has been published to exploit the encapsulating ability of HBP for suppressing the physical loss of stabilizers and thus elongating the lifetime of polymers.

In this study, we have developed a new strategy to inhibit the physical loss of stabilizers with the aid of HBP. The concept is to reversely trap stabilizers in the dendritic structure of HBP to prevent the volatilization of stabilizers without penalizing their mobility. The methodology has been successfully proven for elongating the lifetime of polypropylene (PP) and PP/SiO$_2$ nanocomposites. It was found that a small amount of HBP, which itself does not stabilize PP, significantly enhanced the efficiency of hindered phenol anti-oxidants to stabilize PP-based materials.

2. Experimental section

2.1. Materials

Additive-free PP powder ($mmmm$ = 95 mol%, Mn = 57,000, Mw = 290,000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 5.0) was synthesized by bulk polymerization using a 4th-generation Ziegler-Natta catalyst. AO-20, AO-30, AO-40, AO-50, AO-80, Irganox 245, Irganox 259 and Irganox 1010 were donated from ADEKA Co., Ltd. and Toyotsu Chemical Co. SiO$_2$ nanoparticles (AEROSIL®300, average diameter of 7 nm, surface area of 300 m^2/g) were dried at 200 °C under vacuum prior to the usage. Hyperbranched bis-MPA polyester-16-hydroxyl, generation 2 (G2-HBP, MW = 1750) and hyperbranched bis-MPA polyester-64-hydroxyl, generation 4 (G4-HBP, MW = 7323) were purchased from Aldrich Co., Ltd.

2.2. Preparation

PP powder and 0.07 wt% of AO-50 were melt-mixed using a two-roll mixer at 185 °C and 20 rpm for 5 min, and then 1.0 wt% of G2- or G4-HBP was added. The mixture was kneaded at the same temperature for another 10 min. Thereafter, the melt-mixed sample was hot pressed into a 100 μm-thick film at 230 °C and 20 MPa for 10 min, followed by quenching at 100 °C for 5 min and subsequently at 0 °C for 5 min. Nanocomposite samples were similarly prepared, except the fact that 5.0 wt% of SiO$_2$ was added in the melt mixing. Thus prepared samples were designated as PP, PP/G2-HBP, PP/G4-HBP, PP/SiO$_2$, and PP/SiO$_2$/G4-HBP. Few other samples were additionally prepared using other anti-oxidants *viz.* BHT, AO-20, AO-30, AO-40, AO-80, Irganox 245, Irganox 259 and Irganox 1010, instead of AO-50.

2.3. Characterizations

Accelerated degradation at 150 °C and 180 °C was performed on a chemiluminescence analyzer (CLA, Tohoku Electronic Industrial Co., Ltd., CLA-ID2-HS) under dry air flow of 100 mL/min. The lifetime of samples was defined in terms of oxidative induction time (OIT), which indicates the initiation timing of auto-oxidation process and is straightforward derived from a chemiluminescence curve along the degradation time. A specimen was placed in an aluminium pan and loaded in a chamber of CLA, which was preliminary heated to a desired temperature.

Volatilization of anti-oxidants was examined by thermogravimetric analysis (TGA, Mettler Toledo TG50). Film samples containing 5.0 wt% of BHT with and without G4-HBP was subjected to isothermal heating at 100 °C under nitrogen atmosphere (50 mL/min). The dispersion of HBP in the matrix was studied through the

observation of freeze-fractured surfaces using scanning electron microscopy (SEM, HITACHI, S-4100) operated at an accelerating voltage of 20 kV. A fractured surface was obtained by freezing a sample in liquid nitrogen for 3 min and then breaking by bending. The fractured sample was placed in tetrahydrofuran (THF) to extract HBP droplets with the aid of sonication for 4 h. The sample was subjected to platinum sputtering for 100 s prior to the SEM measurement.

3. Results and discussion

Anti-oxidants have been recognized to protect polymers from oxidation by scavenging free radicals or decomposing hydroperoxide, thus interfering the auto-oxidation [33]. It is well known that oxidative degradation of many polymers is accompanied by very weak emission in visible light. The chemiluminescence method has been widely used for the detection of the initial stage of degradation due to its high sensitivity. Specifically in the case of polyolefins, a CL profile affords an induction time (OIT) before a sharp onset of oxidative degradation. The OIT offers a facile measure of the lifetime of a sample [34], where anti-oxidants suppress the oxidation to elongate the OIT. In other words, the OIT can also be considered as a measure of stabilization efficacy of the anti-oxidants. The chemiluminescence curves were first compared between PP films stabilized with AO-50 (0.07 wt%) in the absence and presence of G4-HBP (1.0 wt%) at 180 °C (Fig. 1). It can be seen that with the addition of G4-HBP, the OIT value increased to a noticeable extent from 0.4 to 1.2 h.

The effects of HBP on the stabilization of PP are summarized in Fig. 2, where the generation of HBP and the temperature of the degradation were varied. It is noted that the degradation at 150 °C and that at 180 °C presumed the solid and molten states of PP, respectively. The most important conclusion of Fig. 2 is that the addition of HBP always led to significant increments of OIT. The order of the OIT values followed PP/G4-HBP > PP/G2-HBP » PP irrespective of the degradation temperature. Moreover, the improvement over PP became more remarkable in the solid state than in the molten state.

It was presumed that HBP might interact with AO-50 in a way to improve its efficiency, while it was also suspected that the HBP itself possesses an anti-oxidant ability. In order to acquire complete information for the effect of HBP addition, it was necessary to investigate the stabilization of PP exclusively by HBP without the use of other anti-oxidants. This was done by Soxhlet extraction of AO-50 with hexane from the three samples *viz.* PP, PP/G2-HBP and PP/G4-HBP, which resulted in comparable OIT values (Fig. 3) at
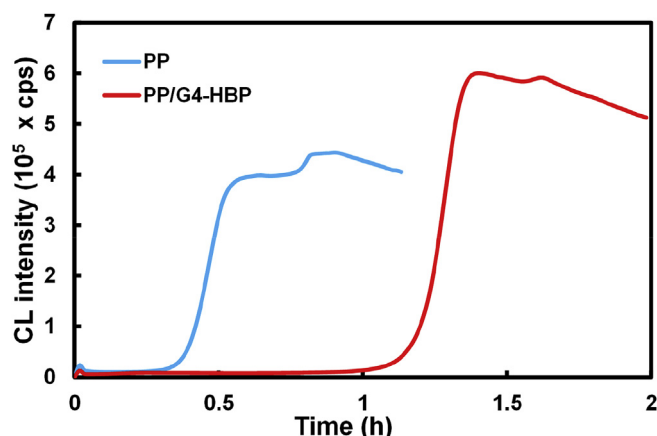

Fig. 1. CL curves for PP and PP/G4-HBP measured at 180 °C.