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Remote inhibition of polymer degradation

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Abstract

Polymer degradation has been explored on the basis of synergistic infectious and inhibitive interaction between separate materials. A dual stage chemiluminescence detection system with individually controlled hot stages was applied to probe for interaction effects during polymer degradation in an oxidizing environment. Experimental confirmation was obtained that volatile antioxidants can be transferred over a relatively large distance. The thermal degradation of a polypropylene (PP) sample receiving traces of inhibitive antioxidants from a remote source is delayed. Similarly, volatiles from two stabilized elastomers were also capable of retarding a degradation process remotely. This observation demonstrates inhibitive cross-talk as a novel interactive phenomenon between different polymers and is consequential for understanding general polymer interactions, fundamental degradation processes and long-term aging effects of multiple materials in a single environment.

Keywords: Thermal polymer degradation; Material interaction; Antioxidants and Oxidation inhibition

1. Introduction

Understanding the fundamental nature of degradation mechanisms and aging phenomena in polymers is critical for material selection, performance assessment, optimization strategies and lifetime prediction of polymeric materials [1–3]. Examining the current trends in developing techniques and methods to study polymer degradation behavior, it is important to recognize that most polymer aging studies are being conducted on individual and often ideal materials. A pure polymer may be subjected to thermal, hydrolytic or other environments and the observed degradation features used for lifetime prediction. The limitations of such idealized aging studies should be obvious. There is no feedback available that would suggest how various materials might interact, or be affected by synergistic and inhibitive effects in environments where multiple materials may degrade simultaneously. This, however, should be a key goal for the study of many industrial components, or in situations where various materials would be confined to one aging environment. Very few studies have addressed the complexity of aging phenomena where infectious or other cross-talk phenomena between materials could be an important feature.

In order to better understand the basis of possible interaction between materials one has to briefly re-visit our current understanding of polymer degradation. For instance, for thermal degradation, it is well established that the degradation mechanism for polymeric materials can be described mechanistically by the complex auto-oxidation scheme first established in the 1940–1950's which involves the generation and activity of peroxides and other reactive intermediates [4–6]. More recently there have been ongoing discussions about the physical nature of polymer degradation showing evidence for heterogeneous processes [7–9]. In particular, chemiluminescene (CL) was used as a technique to demonstrate the highly localized nature in the degradation of polypropylene (PP), where the initiation or induction time of the least stable powder particle would determine the lifetime of a collective sample [10]. A heterogeneous model [10,11] was suggested allowing for localized reactions, active intermediates and propagation of degradation reactions throughout the material [12,13]. An infectious volatile was seen as transferring the degradation from particle to particle within a sample [10], consistent with some earlier speculations that combined oven aging conditions could lead to complications for accelerated aging tests of polymers [14,15].

Chemiluminescence is an experimental method that has been used widely to study in situ degradation phenomena in polymers [11,16,17]. There are ongoing discussions on the

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exact mechanistic nature of CL emission reactions [18], but most importantly thermal degradation reactions of hydrocarbon based polymers are accompanied by the emission of visible photons [16], with the intensity related to the activity of the degradation process [10,11,17]. CL measurements allow for the determination of induction times, maximum oxidation times and time-dependent degradation rates. The technique is an ideal tool to analyze in situ polymer degradation reactions as shown for polypropylene (PP) [10,11] and other materials [17]. Similarly, it has been applied via CL imaging [19–21] to evaluate antioxidant efficiencies [22], or support research of mechanistic issues [17]. The technique offers a great opportunity to probe real-time interactive effects between different materials.

Utilizing an innovative dual stage CL detection system we have recently shown for the first time that polymer degradation processes can be initiated by a degrading polymer A infecting a different polymer B in its vicinity [23]. This remote infectious process and synergistic cross-talk between materials was discussed as being similar to fruit ripening via ethylene transfer [24], or the tin disease (tin pest) leading to unexpected and sometimes infectious degradation of tin metal items [25]. Applying the same equipment it was also shown that traces of thermally labile peroxides can initiate polymer degradation remotely, thereby demonstrating that reactive intermediates of peroxidic nature could be easily transferred between materials and are sufficiently strong as remote initiators [26]. In the current study, first evidence of the opposite effect will be provided, where a polymer gives off traces of its antioxidants leading to remote inhibition in a neighboring polymer. This observation will demonstrate an example for inhibitive cross-talk as part of the degradation processes between different polymers.

2. Experimental

A novel CL system as reported earlier [23,26] was developed based on two individually temperature-controlled hot stages and a large diameter cooled photomultiplier tube (PMT) capable of collecting the combined CL signal from both stages. The tube is operated on plateau level sensitivity and the CL signal is collected via signal discriminator, amplifiers and commercial PC data acquisition software. Fig. 1 shows a schematic with the left and right sample stage separated by approximately 25 mm. The instrument enables one to investigate the effect of any volatile material (i.e. antioxidants) that may be given off from the left sample stage and interacting with a sample on the right stage. Using polymer samples in standard DSC sample pans (∼7 mm diameter), experiments were conducted under oxygen with a carrier gas flow of 25 cm^3/min transferring any volatiles towards the right sample. PP was selected as a polymer sensitive to the stabilizing effects of antioxidants and was obtained as an unstabilized reactor powder material. Stabilized polymers were HTPB (cured hydroxy-terminated polybutadiene) [27] and PBAN (polybutadiene–acrylonitrile–acrylic acid terpolymer). Both were utilized as thin slivers of approximately 5 mg taken from a 2× 6 mm strip sample. The HTPB contains 1% Vanox MBPC antioxidant (2,2′-methylene-bis-(4-methyl-6-*t*-butylphenol)) and the PBAN has 1.1% Agerite Stalite (mixture of alkylated diphenylamines) as an antioxidant. For the experiments requiring pure antioxidant (AO) samples, solutions of Vanox MBPC were deposited onto sample pans.

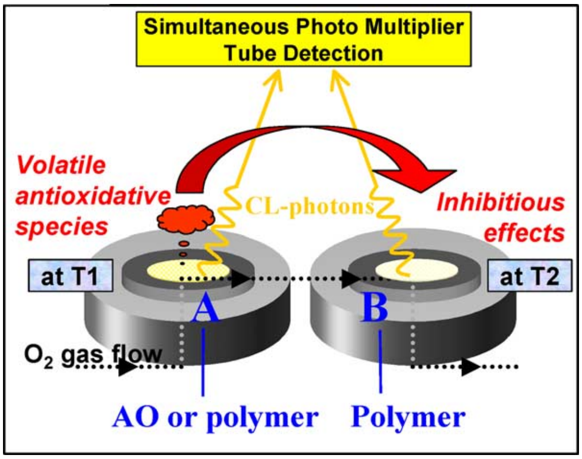

Fig. 1. Schematic of instrumental setup with potential for photon emission and detection from two hot stages.

3. Results and discussion

Typical CL signal traces collected during the thermal oxidation of polymers (isothermal experiments) involve an induction time, an increase to a maximum intensity and a subsequent signal decrease when most of the material has degraded [10,11,23,26]. The timing and relative magnitude of this process depends on temperature and is very reproducible. Different polymers have varying times to their maximum intensity ($t_{\max}$). Measuring their time responses at various temperatures serves as simple evidence for the progress and relative sensitivity of their degradation process. Any shifts in the $t_{\max}$ (CL peak time) reflects on accelerative or inhibitive reactions affecting the degradation reaction. For example, infectious phenomena (shorter $t_{\max}$) due to a degrading polymer or reactive peroxide in the vicinity of a sample were easily demonstrated [23,26]. Of interest in the current study was to identify if a common antioxidant would be volatile enough to affect the degradation of unstabilized PP. A small amount (50 µg) of Vanox MBPC, an antioxidant with a molecular weight of 340.5 g/mol and melting point of 125 °C, was deposited via a suitable toluene solution onto a DSC sample pan. Fig. 2 shows the CL monitored degradation of an individual PP sample at 130 °C (10 mg) and the corresponding CL signal when the PP sample is placed on the right stage in the presence of 50 µg AO on the left stage (also at 130 °C). The PP degradation is clearly retarded by traces of the AO or possibly any decomposition products that would have been transferred onto the PP sample. This is intriguing since the AO due to its high melting point and molecular weight would not be regarded as a particularly volatile substance. Furthermore, the PP consists of powder particles with large surface areas, which would make it

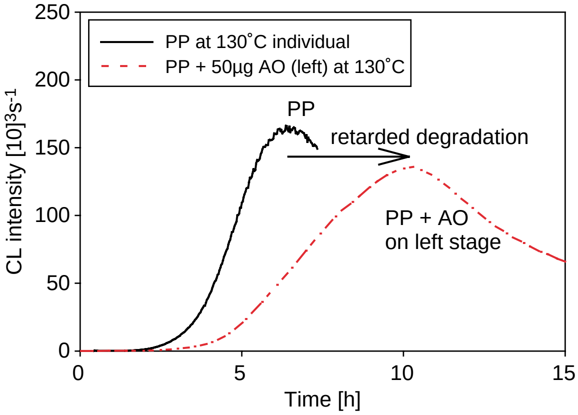

Fig. 2. CL monitored degradation of PP (130 °C) and inhibited by volatile antioxidant transferred from the left sample stage (50 µg Vanox MBPC).

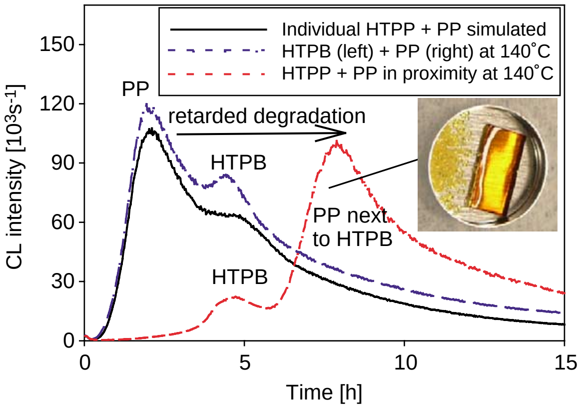

Fig. 4. Simulated degradation of individual 4.6 mg HTPB and 2.5 mg PP samples, a combined experiment (left and right sample stage) and a single sample pan experiment showing the retarded peak of PP when in the vicinity of HTPB (all experiments conducted at 140 °C).

difficult for traces of antioxidant to uniformly inhibit any degradation process. However, even traces (i.e. 1 µg) of AO deposited on the 10 mg of PP would result in a low-level stabilization effect (i.e. 0.01%), which would certainly support the observation. Since volatility and transfer of the AO is critical, a similar experiment was repeated at 110 °C, where AO volatility is lower. Interestingly, as shown in Fig. 3 the transfer of antioxidative species occurs as well and leads to successful inhibition in the PP sample, even at the lower temperature.

It was further explored if a stabilized polymer sample with dissolved AO in the matrix could give off antioxidant in sufficient quantities to measurably inhibit the degradation of the PP. A 5 mg sample of stabilized HTPB (1% AO, Vanox MBPC) was placed on the left stage and a 2.5 mg PP sample on the right stage. For such an experiment no significant effect on the PP was observed, which suggests that insufficient quantities of the AO were transferred across. Fig. 4 shows the result of the experiment with simultaneous samples of HTPB and PP at 140 °C (located on left and right stage, respectively) and also the simulated CL curve that would result from the concurrent degradation of individual samples (2.5 mg PP and 4.6 mg HTPB). There is no difference in the relative timing of the two polymers. A 5 mg sample of HTPB contains ∼50 µg of antioxidant, but the available quantities for desorption and transfer will be considerably lower. The antioxidant will be retained in the polymer matrix and limited volatilization will lead to overall lower quantities in the gas phase, which might be too dilute when approaching the right sample location in the current experimental setup. To explore if cross-inhibitive effects could nevertheless occur between different polymers, the two polymer samples were positioned closer together (see Fig. 4) by placing them in one sample pan (∼7 mm diameter) physically separated and thereby increasing the relative concentration of volatile AO traces in the vicinity of the PP. Fig. 4 includes the results for such a combined experiment of PP and HTPB at 140 °C (see picture insert in Fig. 4). It is obvious that the degradation of the PP material in this experiment is now considerably inhibited due to sufficient volatile antioxidative species being transferred from the HTPB. The $t_{\max}$ of the PP is shifted from about 2.1 to 7.9 h, and as the PP degradation is sufficiently inhibited no infectious effect of the PP on the HTPB is apparent (identical peak position of the HTPB). A similar experiment was repeated using stabilized PBAN containing a different type of antioxidant. Fig. 5 shows the CL trace of an individual PP sample at 140 °C, and the PP in the same pan as the PBAN (see picture insert for sample configuration in Fig. 5), where the $t_{\max}$ is shifted from approximately 2.1 to 8.1 h. The

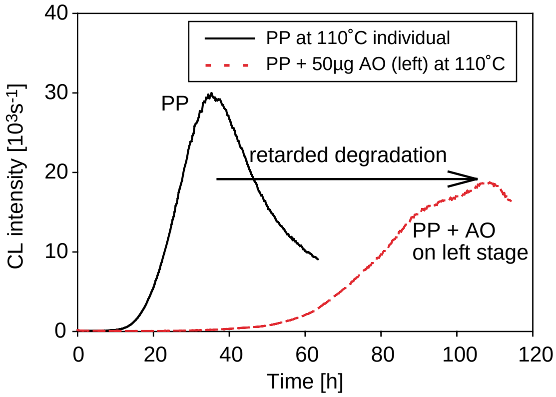

Fig. 3. CL monitored degradation of PP (110 °C) and inhibited by volatile antioxidant transferred from the left sample stage (50 µg Vanox MBPC).

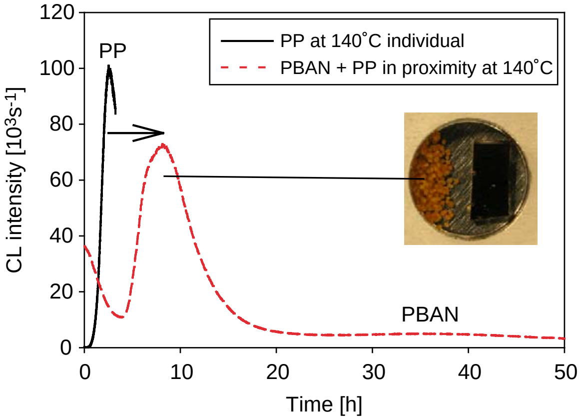

Fig. 5. Degradation of an individual 2.7 mg PP sample, and CL trace for a 2.7 mg PP and 4.7 mg PBAN sample in a single pan at 140 °C showing the retarded peak of PP when in the vicinity of the PBAN.

PBAN is a material that commonly displays higher initial activity (signal decay within the first 3 h) and a weak maximum at 35 h for this temperature. The inhibition effect in the PP is similar as observed for the HTPB experiment demonstrating again that sufficient quantities of AO causing inhibition were transferred.

These experiments demonstrate that antioxidants or their decomposition products with antioxidative properties can be successfully transferred from a stabilized polymer and result in remote inhibitive effects in a neighboring polymer. Obviously, relative volatility and concentration in the gas phase will be the controlling factors for such phenomena to exist, or to result in complications for combined accelerated polymer aging experiments. Likewise, variations in stability due to such remote interaction may be observed in closed environments where polymers age jointly. Larger amounts of stabilized polymer samples as commonly encountered in aging ovens (and perhaps with insufficient air purge) are expected to give off large enough quantities of antioxidants that could easily interfere with the intrinsic stability of less stable polymers in proximity.

4. Conclusion

These experiments have demonstrated that the novel dual stage CL instrumentation can be successfully applied to study infectious [23,26] and inhibitive cross-talk phenomena in combined thermal polymer degradation experiments. Traces of antioxidants or their decomposition products are sufficiently volatile to be carried between polymer samples and can lead to remote inhibition. The limits of this effect were shown for individual milligram quantity samples, when the amounts of transferred AO from a stabilized elastomer were too low to result in significant retardation of the degradation in the receiving polymer. This is in contrast with the very low amounts of peroxidic species (micrograms) found capable of inducing remote initiation [26]. However, when the separation is reduced between the polymers, remote inhibition indicative of cross talk between the materials could be observed. This demonstrates that the antioxidants investigated (or their degradation products) are sufficiently volatile to be transferred, but that critical concentrations are required to inhibit degradation in the receiving polymer. While the results presented are phenomenological in nature, they are important to understand the general aging phenomena of multiple materials in a single environment. These experiments demonstrate for the first time that remote inhibitive behavior between materials that age jointly is a distinct possibility.

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