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Polymer degradation initiated via infectious behavior

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Abstract

Understanding polymer degradation phenomena is of critical importance for material reliability. A novel dual stage chemiluminescence detection system has been developed and applied to probe for material interaction effects during polymer degradation. Evidence is presented for the first time that in an oxidizing environment a degrading polymer A (in this case polypropylene, PP) is capable of infecting a different polymer B (in this case polybutadiene, HTPB) over a relatively large distance. In the presence of the degrading material A, the thermal degradation of polymer B is observed over a significantly shorter time period. Infectious intermediate volatiles from material A are able to initiate and shorten the degradation processes in material B. This observation documents infectious behavior that will have significant consequences for materials interactions, understanding material degradation processes and long-term aging effects in combined material exposures.

Keywords: Polymer degradation; Infectious processes; Material interaction

1. Introduction

Understanding polymer degradation phenomena is of critical importance for material selection, performance, optimization strategies and lifetime prediction [1–3]. All polymeric materials are subject to long-term degradation processes due to simple thermo-oxidative sensitivity or more complex hydrolytic and synergistic reactions leading to degradation. It was shown that some aging processes in polymers are of heterogeneous nature and can be initiated via impurities, catalysts or other chemical reagents [4–7]. It has also long been recognized that the thermal degradation of polymers under oxidative conditions can be described by the complex auto-oxidation scheme first established in the 1940–1950s [8–10] and involves the generation of peroxides and other oxidized species. It was also shown that for the degradation of a polypropylene (PP) sample composed of individual reactor particles, the initiation or induction time and thus degradation timing of the weakest particles would determine the lifetime of the collective sample of this material [5]. Such degradation processes were explained within a heterogeneous model [4,5] allowing for localized reactions, active intermediates and propagation of degradation reactions throughout the material [6,7]. Experimental evidence was obtained to support the notion that an infectious volatile could carry the degradation from particle to particle in the sample [5]. This is consistent with earlier speculation on adverse effects under combined oven aging conditions leading to complications for accelerated aging tests of polymers [11]. Some intriguing anecdotal evidence of possible infectious polymer degradation phenomena leading to 'real world' problems was reported in the Boston Globe newspaper, discussing the concern of diseased antique dolls potentially infecting other high value collectibles, and exhibitors insisting on quarantine precautions, to quote: 'two dolls were under quarantine at the Hudson show, which featured the prized possessions of some of New England's best known collectors. They had been banished from the hall-out of fear they would infect others' [12]. Similar infectious phenomena for materials in 'nature' have been described for the infectious ripening of fruit via ethylene transfer [13–15], or the tin disease (tin pest) leading to unexpected and sometimes infectious degradation of organ pipes and other tin items at cold conditions [16]. A suitable experimental method to study such degradation phenomena in polymers is the monitoring via

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chemiluminescence (CL) [4,17], with the overall suitability of CL studies in polyolefin degradation having recently been reviewed [18]. All thermal degradation reactions of hydrocarbon based polymers are accompanied by the emission of visible photons, with the intensity reflective of the relative activity of the degradation process [4,5,18]. CL monitoring hence allows for the determination of induction times, maximum oxidation times and intensity, and is an ideal tool to analyze in situ polymer degradation reactions [4,5]. It has also been applied via CL imaging [19–21] to evaluate the efficiency of antioxidants in polymers [22] or better explore the nature of some degradation mechanisms [18]. In this study a novel highly sensitive dual-stage CL instrument was developed, opening up a new direction in CL studies, and utilized to study the synergistic interaction of two different polymeric materials in a thermo-oxidative environment.

2. Experimental

The CL instrument was designed to incorporate two individually temperature-controlled hot stages (for two samples) and a highly sensitive single photon counting photomultiplier tube (PMT). A large diameter PMT is capable of collecting the combined CL signal from both stages. Fig. 1 shows the schematic setup with the left and right hot stage separated by approximately 25 mm. The initiating polymer was placed on the left stage with a carrier gas (oxygen flow ranging from 25 to 250 cm^3/min) directing any gaseous volatiles or infectious agents towards the right sample. To allow for infectious phenomena to be studied, the experiments required a fast and actively degrading polymer, and a receiving polymer with differing properties (i.e. longer degradation times at low temperatures). PP was chosen as the quickly degrading (short degradation peak at 150 °C), and thus particularly active, polymer and was obtained as an unstabilized reactor powder material with typical samples of 10 mg used in the CL experiments. Unstabilized HTPB (cured hydroxyl-terminated polybutadiene) [23] was selected as the receiving one and was utilized as a sliver of a 2×6 mm^2 strip sample of approximately, 5 mg. One complication in combined exposure experiments is the large dynamic range in CL intensity of different polymers, with PP at 150 °C of such intensity, that any signal originating from HTPB at lower temperatures would be swamped. The PP sample location was, therefore, covered with Al-foil, only allowing approximately 1% of the total signal to reach the PMT, but still sufficiently intense to clearly identify the PP degradation peak and its relative timing features.

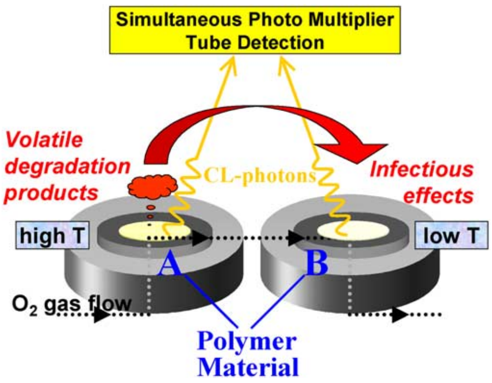

Fig. 1. Schematic of instrumental setup with photon emission and detection from two hot stages.

3. Results and discussion

The primary information from thermal degradation experiments is the CL signal versus time. At any specific degradation temperature the polymer will display a short induction time, an increase to maximum degradation intensity and a signal decrease when most of the material has degraded (see signal features in Fig. 2). The timing and magnitude of this process is temperature dependent and highly reproducible. As a representative example, Fig. 2 shows the signal of two individual samples, the PP at 150 °C displaying a peak intensity at ∼1 h and the HTPB at 60 °C showing a main peak at ∼38 h. Also included in Fig. 2 is the expected combined signal (simulated blue curve) obtained by simply adding the PP and HTPB signals. This is the signal that should result from a combined experiment where both materials would behave as individual samples with zero interaction. However, for a combined experiment where both samples are simultaneously placed on their respective hot stage at time zero, the combined signal (red curve) in Fig. 2 is observed. It is obvious that the ‘normally slower’ HTPB sample has degraded considerably faster in the presence of the initiating PP. In this case, the HTPB peak was observed after only ∼15 h, or ∼39% of its normal peak position. Another example is presented in Fig. 3,

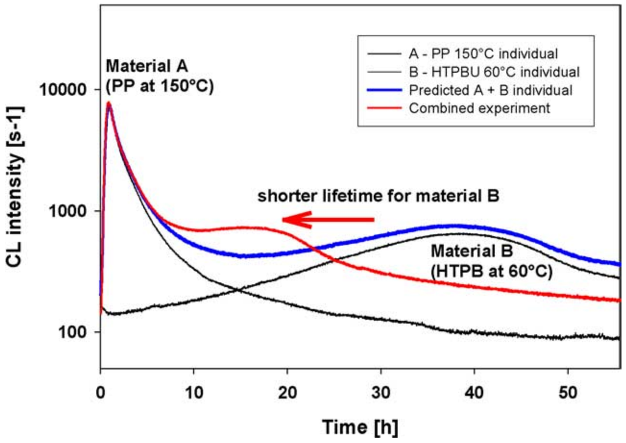

Fig. 2. Individual and combined degradation of PP (150 °C) and HTPB (60 °C) samples monitored by chemiluminescence.

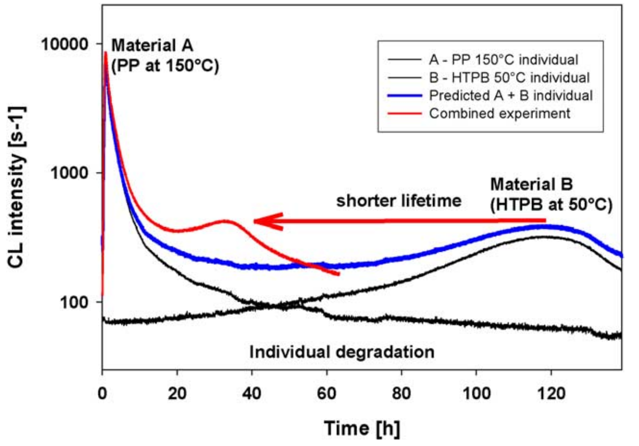

Fig. 3. Individual and combined degradation of PP (150 °C) and HTPB (50 °C) samples monitored by chemiluminescence.

showing the expected zero interaction signal of a simultaneous PP and HTPB experiment exposed at 150 and 50 °C, respectively, and the observed signal with again a considerably faster response of the HTPB material (∼33 h instead of ∼120 h). The shift in the HTPB's response is best presented in an Arrhenius diagram (Fig. 4) showing the HTPB peak position time versus inverse temperature. The longer aging times correspond to the individual material's behavior, whereas the shorter times relate to the peak position time in the presence of the initiating PP in the combined experiments. The shift towards shorter degradation times is significant and apparent for all temperatures investigated. For the HTPB at 40 °C a peak time of ∼300 h would be predicted, however, in the presence of the initiating PP the peak is observed after only 100 h. It is also noteworthy to mention that in a similar experiment conducted with the PP degrading at 130 °C the HTPB also showed its main degradation peak at ∼100 h, demonstrating that infectious volatiles were also produced from the lower temperature PP. The above experiments were conducted at an oxygen flow rate of 25 cm^3/min. Interestingly, the 'shortened degradation' of the HTPB can still be observed at a very high flow rate of 250 cm^3/min, but the time reduction is not as pronounced (only at 67% instead of 49% (25 cm^3/min) of the normal peak position of an HTPB at 70 °C). For very high flow rates one would assume that the infectious intermediates would be so diluted and quickly carried away that the initiating effect should eventually disappear. As a trend this is correct, but faster aging has been observed also at high flow rates, suggesting the extreme sensitivity of the receiving polymer to even traces of infectious volatiles.

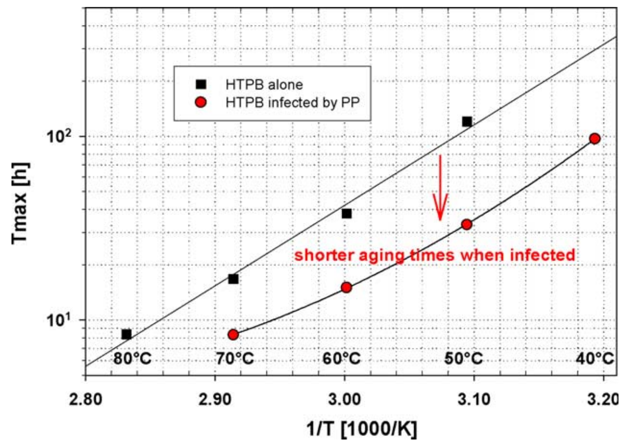

Fig. 4. Arrhenius plot of the maximum CL times for HTPB at different temperatures showing the significantly faster degradation when infected by the PP degrading at 150 °C.

4. Conclusion

A novel chemiluminescence technique was introduced and applied to the interaction processes of polymer materials when they degrade. Here we present for the first time evidence that in an oxidizing environment a degrading polymer A (in this case polypropylene, PP) is capable of infecting a different polymer B (in this case polybutadiene, HTPB) over a relatively large distance. This suggests that materials degradation of completely different polymers can also be subject to infectious processes, similar to initiation via infectious agents propagating in disease sensitive populations or previously discussed for the degradation of individual polymer samples. In the presence of the degrading material A, the thermal degradation of polymer B is observed over a significantly shorter time period. Infectious intermediate volatiles from material A are able to initiate and shorten the degradation processes in material B. Considering that the initiating polymer is a sample of only 10 mg, that the materials are separated by ∼25 mm, and that a significant carrier gas flow is applied, all imply that an extremely reactive infectious volatile must be transmitted and that the receiving polymer must be highly susceptible to traces of such species. The observed infectious behavior of 'communication between two polymeric materials' should be of significance similar to other infectious phenomena in nature. It is also interesting to note that polymers may not just interact on the macromolecular chain level, such as discussed for critical processes in the evolution of life [24], but also via gas phase processes involving low molecular weight degradation products, essentially making another polymer aware that something may be happening in its neighborhood and stimulating a response (degradation). This observation is perhaps not unexpected, but documents a novel infectious behavior and will have consequences for polymer materials interactions, understanding material degradation processes and long-term aging effects in combined material exposures. Efforts are currently under way to determine the nature of the infectious agents.

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