

Evolution of Peroxide Species During the Photooxidation of Poly(vinyl butyral)

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ABSTRACT: Photooxidizing films of poly(vinyl butyral) were investigated for the generation of solid-state and volatile peroxide species, acids, and changes in mass in order to gain insight into the factors that influence the levels of these peroxides during oxidation. Both the concentration of solid-state peroxides and the emission rate of volatile peroxides increased and subsequently declined, while acidic groups in the polymer accumulated without decreasing. After an initial increase, the mass of the films fell as volatile degradation products were released. It is suggested that the decline in the peroxide species, both in the polymer and volatiles, may be due to their reactions with other products of the polymer's oxidation, including aldehydes and acids. These results indicate that reactions besides the often-invoked homolytic cleavage of hydroperoxides may remove these species from the poly(vinyl butyral) and similar materials during advanced stages of photooxidation. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39753.

KEYWORDS: ageing; degradation; irradiation

Received 18 January 2013; accepted 10 July 2013

DOI: 10.1002/app.39753

INTRODUCTION

The oxidative degradation of polymeric materials generally proceeds through a series of radical reactions propagated by the homolysis of hydroperoxide intermediates.^{1,2} These chemistries ultimately lead to the formation of oxidized groups, such as alcohols, ketones, aldehydes, and carboxylic acids, while concurrent chain-breaking reactions eventually form molecules small enough to be released from the polymer as volatiles. Based on this understanding, much work studying the course of polymer oxidation has focused on measuring peroxides and oxidized groups in polymers,^{3–5} as well as the oxidized volatile degradation products they emit.^{6–8}

The oxidation of poly(vinyl butyral), a polymer used to make laminated glass in the automobile, photovoltaic, and building industries, and as a consolidant in the conservation of materials used in cultural property, can be mostly understood within this traditional framework.^{9–11} Upon exposure to ultraviolet radiation, hydroperoxides are formed in the polymer, and ring opening and chain scission reactions occur. An increase in carbonyl content and carbon–carbon double bonds is observed, along with a decrease in the molecular weight, as volatiles such as butyraldehyde and butyric acid are released. These chemical changes lead to the deterioration of the polymer's optical and mechanical properties, with yellowing, brittleness, and a decrease in tensile strength arising during the course of oxidation.

Another feature of the photooxidative degradation of poly(vinyl butyral) is the marked buildup and subsequent decline of the hydroperoxide concentration in the polymer. Remarkably, oxidation in this polymer seems to continue steadily despite these changes in the hydroperoxide concentration, with chain-breaking chemistries continuing at a constant rate even after the maximum peroxide concentration has been reached.¹¹

Similar trends in the concentration of solid-state hydroperoxides have been observed during the oxidation of films of dried oils¹² and of polypropylene¹³ and polyethylene.^{14,15} Kinetic models of polymer oxidation that take substrate consumption into account are able to generate curves in which hydroperoxides rise and fall.¹⁶ In the case of poly(vinyl butyral), however, over 90% of the initial mass of the polymer film still remains after the decline in the hydroperoxide concentration, suggesting that the peak may have additional origins.

Notably, the decrease in hydroperoxides in poly(vinyl butyral) roughly coincides with the onset of the net decrease in the mass of the polymer sample.¹¹ In light of the recent measurement of volatile peroxides from photooxidizing polypropylene,¹⁷ it seems plausible that some of the hydroperoxides lost in solid poly(vinyl butyral) may be accounted for among the volatile degradation products. The goal of this work was to investigate this and other possible causes for the decrease in hydroperoxides during the photooxidation of poly(vinyl butyral).

EXPERIMENTAL

Sample Preparation

Polymer films used for all analyses except UV transmission were prepared by depositing 2 mL of a 10% solution of unstabilized poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (average M_w 50,000–80,000 g mol⁻¹; 80% butyral, 18.5% alcohol, 1.5% acetate substitution; Aldrich) in ethanol (200 proof, CS/USP grade, Pharmco-Aaper) into preweighed low-form aluminum pans. Polymer films used to measure UV transmission were prepared by depositing 2 mL of the 10% polymer solution onto quartz plates. The films were allowed to dry at room temperature for 14 to 48 h and then at 70°C for 10 to 24 h. The dried films averaged ~80 μm in thickness.

Conditions of Exposure

Dried film samples were exposed to ultraviolet (UVB) radiation from a bank of fluorescent lamps (280–340 nm, $\lambda_{\text{max}} = 313$ nm; Q-Lab) situated in a climate-controlled room maintained at 23°C. Samples investigated for UV transmission, change in mass, and acid number were photooxidized in open air; those measured for solid-state and volatile peroxides were photooxidized while enclosed within a PTFE box sealed with a UV-transparent FEP film as its lid. The humidity for the open-air condition was maintained at 50% RH, while the PTFE box was filled with air that had been dried with Drierite and purified with Purafil and activated carbon. The irradiance at the samples, measured with a Model 1700 International Light Research radiometer, averaged 1.0 and 1.1 mW cm⁻² for those exposed in open air and in the box, respectively.

UV Transmission

Optical spectra of three polymer films prepared on quartz plates were measured in the transmission mode of a Perkin-Elmer Lambda 800 UV-vis spectrophotometer with a clean quartz plate as background. The average transmittance values from these triplicate samples are presented below, with error bars representing one standard deviation from this average.

Determination of Change in Mass

A Mettler H51AR analytical balance was used to measure the masses of the polymer films to 0.01 mg. The changes in the masses of the films after various periods of exposure to ultraviolet radiation were calculated as percentages, based on their initial masses after drying, before exposure. The data shown represent an average calculated from triplicate samples, with error bars reflecting one standard deviation.

Determination of Solid-State Peroxides

Iodometric titration^{18,19} was used to determine the concentration of hydrogen peroxide, hydroperoxides, and peroxyacids in the polymer films; the data has been presented below as “peroxide equivalents” so as to encompass all of these species. Poly(vinyl butyral) films were dissolved in ethanol, and, under a constant flow of nitrogen, 5 mL of glacial acetic acid (99.8%, Acros) were added to the solution, followed by 1 mL of saturated aqueous potassium iodide (99+, Acros). The mixture was allowed to stir for ~20 min; the yellow solution was then titrated with a standardized solution of sodium thiosulfate (99%, Sigma-Aldrich) until it was colorless. Blank determinations were always made, and the data presented below represent

the average from measurement of triplicate samples. Error bars reflect one standard deviation from this average value.

Determination of Volatile Peroxides

The fluorometric technique used to measure peroxide species in the volatile degradation products of photooxidizing poly(vinyl butyral) was adapted from a procedure traditionally used for measuring atmospheric hydrogen peroxide and hydroperoxides^{20,21} and has been described previously.¹⁷ Although this method is able to detect hydrogen peroxide and small hydroperoxides, peroxides, and peroxyacids simultaneously, it is not able to distinguish these peroxides from one another; each of these species produces the same fluorescent product during measurement. Thus, the “peroxides” and “peroxide equivalents” discussed below refer to the total hydrogen peroxide and organic hydroperoxides, peroxides, and peroxyacids measured.

Briefly, the PTFE box containing a polymer film was removed from the light bank periodically. The box was connected through PFA valves to the source of dried, purified air. The headspace gases were transferred through a glass frit into a scrubber solution containing 10 mM tris(hydroxymethyl)aminomethane (≥99%, Aldrich), 3 mM para-hydroxyphenylacetic acid (98%, Aldrich), and 0.1 μg mL⁻¹ horseradish peroxidase enzyme (320 U mg⁻¹, ThermoScientific). The fluorescence emission (ex. 320 nm, em. 410 nm) of this solution was then measured on a Varian Cary Eclipse fluorescence spectrophotometer. A calibration curve, prepared by measuring the fluorescence emission of a series of scrubber solutions spiked with hydrogen peroxide (35% in water, analysis grade, Acros) solution of known concentration, was used to determine the amount of peroxide from the measured fluorescence. Peroxide emission rates were then calculated by dividing the amount of peroxide by the period of UVB exposure that had elapsed since the previous measurement. Because removing the film samples from the boxes during the experiment would have caused volatile peroxides to be lost without being measured, the changes in the masses of the films used for these measurements could not be determined, and the rate is reported per polymer film rather than per unit mass of polymer. The data and error bars presented below represent the average and standard deviation, respectively, of two measurements, taken from separate film samples that were photooxidized in separate boxes.

The determination of the collection efficiency in the transfer of the headspace peroxides into the scrubber solution was beyond the scope of this work, and some losses may have occurred in the glass frit used to introduce the headspace to the scrubber and in photochemical reactions during the time between sampling. Thus, this method must be considered semiquantitative in nature, with some expectation that the measured values represent an undercounting of the generated peroxide species. Interpretation of the findings has thus been mainly confined to the time evolution of the peroxides, rather than the quantitative amounts measured.

Determination of Acid Number

The acidity of the polymer films during oxidation was measured by titration with alcoholic potassium hydroxide.²² Poly(vinyl butyral) films were dissolved in a 100 : 1 : 99 mixture of

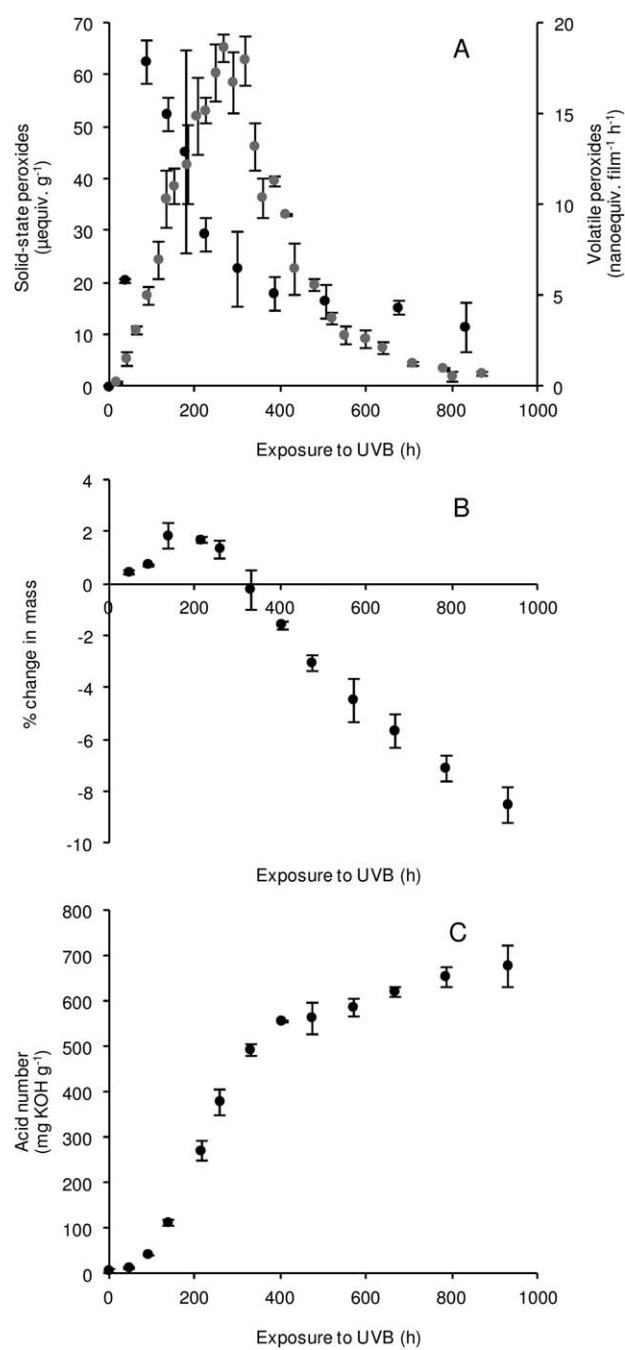


Figure 1. Effects of photooxidation of poly(vinyl butyral) films following exposure to UVB radiation on (A) the concentration of peroxides (●) and the emission rate of volatile peroxides (○), (B) the change in weight, and (C) the acid number.

toluene (HPLC grade, Fisher) : water (deionized) : isopropyl alcohol (99%, USP, Pharmco-Aaper). The solutions were allowed to stir for ~ 30 min, after which 0.5 mL *p*-naphtholbenzene indicator (1% w/v in isopropyl alcohol; Ricca) was added. The orange solution was then titrated with standardized potassium hydroxide (NF/FCC grade, Fisher) in isopropyl alcohol until it turned green. Blank titrations were always performed, and the average value of triplicate measurements is presented

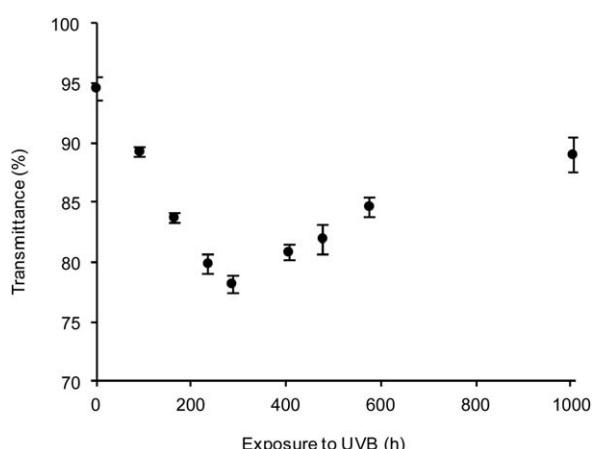


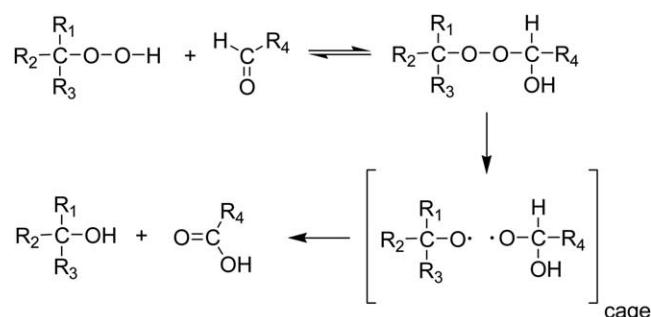
Figure 2. Transmission of poly(vinyl butyral) films at 313 nm during photooxidation.

below, with error bars reflecting one standard deviation from the average.

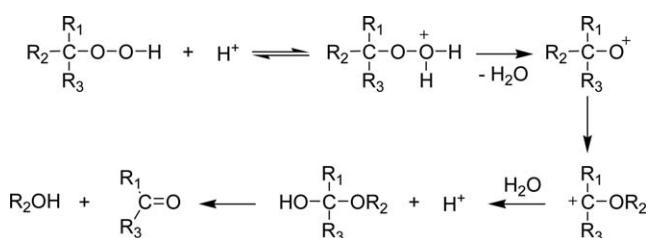
RESULTS AND DISCUSSION

The concentration of solid-state peroxides and the emission rate of volatile peroxides generated during the photooxidation of poly(vinyl butyral) films are shown in Figure 1(A). The formation of peroxides in the solid polymer occurs rapidly, and a maximum concentration is reached within 100 h of exposure to UVB radiation. After ~ 400 h, the peroxide concentration in the films has decreased and stabilizes at values between 10 and 20 microequivalents g^{-1} . The emission rate of volatile peroxides exhibits a similar trend, reaching a maximum at a later time, around 300 h of exposure, then decreasing to nearly zero after about 800 h.

It can be readily seen from Figure 1(A) that the rate of emission of volatile peroxides is increasing as the concentration of solid-state peroxides is decreasing, suggesting that these emissions may account, at least in part, for the peak observed in the concentration of peroxides residing in the polymer. While solid-state hydroperoxides are thought to form in the polymer by hydrogen abstraction after the addition of molecular oxygen to alkyl radicals, the chemical route to volatile peroxides has not been established. However, a few possibilities can be envisioned—volatile peroxides could be formed by scission reactions in hydroperoxide-containing segments near the ends of polymer



Scheme 1. Reaction of tertiary hydroperoxides with aldehydes.



Scheme 2. Acid-catalyzed decomposition of hydroperoxides.

chains, for example, or by recombination of hydroxyl and small alkoxy radicals formed by the homolysis of solid-state hydroperoxides. The former route would remove peroxides directly from the polymer; in the latter, the removal of hydroxyl and/or alkoxy radicals from the polymer as volatile peroxides would prevent the formation of new solid-state hydroperoxides, as these radicals are thought to generate alkyl radicals via hydrogen abstraction.

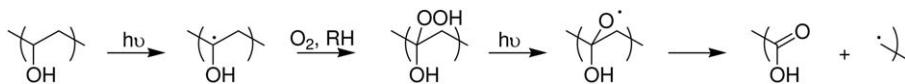
As mentioned in the introduction, a decrease in the creation of hydroperoxides during polymer oxidation due to substrate consumption has also been invoked to account for peaks observed in solid-state peroxides. Oxidized samples of poly(vinyl butyral), however, do not exhibit mass losses that would be expected to significantly diminish the amount of material in which peroxide groups could form, even after long exposures to UVB radiation. This is indicated by the data in Figure 1(B), which show the percent change in mass of the polymer films during photooxidation in open air; similar results were observed for samples photooxidized while enclosed within a PTFE box. Initially, the mass of the films increases, due to the incorporation of oxygen into the polymer as solid-state hydroperoxides are formed. After about 200 h of exposure, the oxidation chemistry has progressed to chain-breaking reactions that cause small molecules to be emitted from the polymer, and the mass of the films begins to fall. Even after 1000 h of exposure, well past the period when peroxides in the polymer were at a maximum, the film samples remain at over 90% of their original mass. While some of the mass is due to the oxygen that has been incorporated into the polymer, the amount of remaining material suggests that processes besides substrate consumption may contribute to the observed decrease in the concentration of peroxides in the polymer.

Other factors that would affect the formation of hydroperoxides in the polymer also seem to remain uninhibited during the course of photooxidation. Oxygen diffusion into the samples is expected to occur throughout their depth,²³ and, as shown in Figure 2, the films remain transparent to UV radiation, with transmission at 313 nm always above 75%. The initial decrease in transmission at this wavelength may be due to $n \rightarrow \pi^*$ transitions of carbonyl groups that formed upon oxidation. The return to higher transmittance after about 300 h may be due to the release of carbonyl-containing fragments as volatiles.

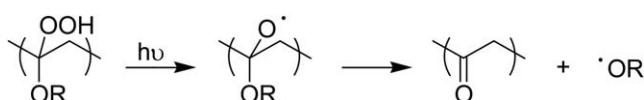
Thus, the decrease in peroxides in the polymer may derive from an increase in the rate of their removal, rather than a decline in their production. As mentioned above, schemes of polymer oxidation often focus on reactions involving hydroperoxides and the radicals formed upon their homolysis. Although the quantum yield of this reaction is not expected to change during the course of oxidation, other chemistries that remove peroxides may become possible at the later stages, when various other moieties have also accumulated in the polymer. Reactions between aldehydes and primary or secondary hydroperoxides have been observed under conditions of thermal oxidation, for example, and yield carboxylic acid and aldehyde or ketone, respectively. While these reactions are thought to proceed through a concerted mechanism that may not be occurring under the room temperature conditions being considered here,²⁴ the cage reaction proposed for tertiary hydroperoxides and aldehydes to form carboxylic acids and tertiary alcohols, shown in Scheme 1, may serve to remove peroxides from the polymer at later stages of photooxidation.²⁵

The acid-catalyzed decomposition of peroxides is another reaction that may remove peroxides from the solid polymer after prolonged photooxidation.^{25–27} The reaction involves protonation of the hydroperoxide followed by rearrangement to yield a ketone and either alcohol or water, as shown in the generalized mechanism in Scheme 2. Migration of hydride (i.e., R₂ = H in Scheme 2), which would lead to the formation of water, occurs more readily than alkyl shifts that would generate alcohol. Thus, this reaction is expected to occur mainly with primary or secondary hydroperoxides in the polymer, species that may be formed by reactions following those of initially produced tertiary hydroperoxides, or with volatile peroxides that have been generated but not yet migrated out of the polymer. Carboxylic acids that could catalyze the decomposition of these peroxides are among the products generated in highly oxidized polymers. Butyric acid is a known product of the photooxidation of poly(vinyl butyral),^{10,11} and chain-end acids could easily be formed at the polymer's alcohol group by the pathway shown in Scheme 3.

Figure 1(C) shows the evolution of acidic groups in poly(vinyl butyral) films during photooxidation. The concentration of acids grows with an increasing rate for the first 400 h of exposure to UVB radiation. After this time, further accumulation in the polymer occurs slowly, though this measure does not account for small molecule acids released by the polymer. By comparison with Figure 1(A), it can be seen that the decrease in solid-state and volatile peroxides coincides with the period when acids are accumulating in the polymer, an observation consistent with the involvement of acids in the removal of these peroxide species. Additionally, an inverse correlation has been observed between the concentration of peroxides that accumulate in poly(vinyl butyral) films and their potential to generate acids according to Scheme 3, with polymer samples of higher



Scheme 3. Formation of carboxylic acids in poly(vinyl butyral).



Scheme 4. Formation of carbonyls in poly(vinyl butyral).

alcohol substitution accumulating a lower maximum peroxide concentration.¹¹

While the processes discussed above may provide some explanation for the decrease in peroxides observed in poly(vinyl butyral) during photooxidation, it is notable that degradation seems to proceed steadily despite this change in the abundance of the peroxide species thought to propagate it. Indeed, neither the reaction between peroxides and aldehydes nor the acid-catalyzed decomposition of peroxides is likely to result in broken chains that would contribute to the generation of volatile degradation products or a decrease in the molecular weight of the polymer, yet both of these processes continue to occur.¹¹ Norrish photo-reactions, however, which occur in the absence of peroxides and can lead to chain breaking, may become more important in the advanced stages of oxidation.¹⁰ Carbonyls formed in the main chain of poly(vinyl butyral) via beta-scission of an alkoxy radical at a tertiary carbon in the backbone, followed by scission of the C—O bond of the side group, as shown in Scheme 4, might undergo Norrish II reactions that would introduce unsaturation into the polymer while causing scission of the main chain.²⁸ This reaction could also occur at the acetate side group, forming acetic acid and introducing a C=C bond into the polymer backbone.²⁹

Many products of the reactions discussed above—alcohols, ketones, aldehydes, carboxylic acids, and water—are identical to those formed in the reaction sequences beginning with the homolysis of hydroperoxides; the similarities among these products may account for why these pathways might be overlooked in studies of polymer oxidation. Furthermore, reactions that might remove peroxides may only be relevant to a subset of polymers—those whose structures are conducive to the fast formation of aldehydes and carboxylic acids and are polar enough to facilitate reactions involving ions. Indeed, no peak was observed in the emission rate of volatile peroxides from photo-oxidizing polypropylene.¹⁷ While acids are known to form in this material during oxidation,³⁰ the nonpolar nature of the polymer matrix may not have allowed them to effectively decompose peroxides in the bulk samples during the time scale of the experiment. A more complete understanding of the factors that influence the evolution of peroxides during oxidation of polymers like poly(vinyl butyral), as well as those that affect the course of oxidation at lowered peroxide levels, requires further investigation.

CONCLUSIONS

The level of peroxide species found in polymers during oxidation is determined by the balance between the processes by which they are generated and destroyed. Thus, the peak in solid-state peroxides observed during the photooxidation of thin films of poly(vinyl butyral) may have multiple origins.

In addition to consumption of the substrate, the release of volatile peroxides and the reactions of peroxides with other oxidation products may also play roles in the decline of peroxide species in this polymer. The peak observed in the emission rate of volatile peroxides suggests that these reactions may also consume small, volatile peroxides before they migrate out of the polymer. It is possible, however, that these phenomena are more relevant to polymers containing oxygen in their original structure, for which less additional oxidation is needed to produce the aldehydes and acids that may react with peroxides, and whose polar structures may be more conducive to these reactions.

ACKNOWLEDGMENTS

The authors thank Val Colaluca and Dr. Muditha Senarath-Yapa for assistance with initial validation of the method for measuring volatile peroxides. This work was done at the Art Conservation Research Center under an operating grant provided by the Andrew W. Mellon Foundation. CHB gratefully acknowledges support from ARCS.

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