Evaluating UV/H$_2$O$_2$ Exposure as a DEHP Degradation Treatment for Plasticized PVC

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ABSTRACT: Millions of tons of plasticized poly(vinyl chloride) (PVC) materials are disposed every year. A biologically sustainable and green method for removal of toxic plasticizers from polymer systems after disposal is highly desired since plasticizers can leach out into the environment over decades. Here we compare the surface and bulk structural changes of DEHP-plasticized PVC after two treatments intended to degrade bis-2-ethylhexyl phthalate (DEHP) in PVC plastic: short wave (254 nm) UV with and without the addition of 35 wt % H$_2$O$_2$. Sum frequency generation vibrational spectroscopy (SFG) reveals the addition of aqueous H$_2$O$_2$ decreases CH$_3$ signals on the surface of the films up to 8 h, due to increased molecular disorder and the removal of alkyl chains. Secondary ion mass spectrometry demonstrates that the degradation of DEHP after 8 h of reaction is similar with and without the use of H$_2$O$_2$. However, FTIR results reveal that the introduction of H$_2$O$_2$ reduces bulk DEHP degradation and leads to competing radical chain scission reactions with PVC. Therefore, simple short wave UV exposure may be an effective means to degrade DEHP within and on PVC plastic and the addition of H$_2$O$_2$ is only beneficial if additional degradation of PVC is needed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40649.

INTRODUCTION

Bis-2-ethylhexyl phthalate (DEHP) plasticized PVC remains heavily utilized in the plastic market worldwide, with millions of tons of this plastic currently in use across the globe, and millions more tons of disposed plastic scattered throughout urban and rural ecosystems.[1–7] DEHP is a proven rodent endocrine disruptor and suspected human and marine toxin. In the human body, DEHP is rapidly metabolized to mono-ethylhexyl phthalate (MEHP). Studies have indicated that MEHP is the active toxic metabolite of DEHP and may damage human endothelial cells and sperm cells, among others.[8–17]

Because of the impending environmental threat DEHP poses, the removal of DEHP after plastic disposal from the polymer matrix is vital; surface DEHP molecules on the plastic are at risk of contaminating the environment and often end up in water supplies, air currents, and soils as the plasticizers slowly leach out from the bulk.[2,4,7,18–21] However, there currently exists no energy and cost efficient means to degrade the plasticizer and eliminate or reduce the risk of DEHP exposure. Thus, it is of utmost importance to remove as much DEHP as possible after disposal to prevent environmental contamination in a safe and green manner.

We have previously studied the surface and bulk effects of short and long wave UV (254 and 365 nm, respectively) treatments on DEHP-plasticized PVC materials in air to better understand what molecules remain present on the plastic surfaces after exposures

to UV in industrial or natural environments. Exposure to short wave UV was found to rapidly degrade DEHP molecules on the surface of the plastic and in the bulk to form products including MEHP, phthalic acid, hydroxylation of phenyl rings, and complete breakdown of DEHP.[22] From an environmental perspective, this demonstrates that plastics exposed to short wave UV over time will yield surfaces containing a number of different phthalate related molecules. However, if short wave UV is applied to plastics for a predetermined amount of time, it may be possible to remove phthalate molecules from the surface or bulk almost completely. In addition, free DEHP molecules in aqueous systems have been shown to be effectively removed by treatment of UV light and hydroxyl radicals.[23–28] The addition of oxygen radicals in H_2O_2 was believed to increase the pseudo first order degradation kinetics of phthalates as compared to just using UV light alone, resulting in faster bulk removal of dimethyl phthalate from water systems as demonstrated by Tawabini and Al-Suwaiyan in 2004 and Xu et al. in 2009.[23,28] Therefore, we decided to study photochemical reaction processes in the presence of 35 wt % H_2O_2 as well as a UV light treatment. To the best of our knowledge, this is the first time that UV and UV/H_2O_2 exposures have been studied as phthalate degradation treatments for phthalates on and within plastics.

Our first goal was to evaluate the effectiveness of H_2O_2/UV systems on removing or reducing the amounts of phthalate molecules from the surface and bulk of plastics in comparison to short wave UV exposure. Our second goal was to understand how the addition of hydroxide radicals present in an aqueous environment affects the molecular surface and bulk of plastics exposed to UV in an environmental setting. The model short wave UV and UV/H_2O_2 treatment systems presented are intended to degrade phthalates throughout flexible clear PVC materials, which typically contain the highest weight percentage of phthalates of PVC products, as well as opaque thin film PVC products. In addition, the UV exposures may be applied to treat the surfaces of decades old PVC materials in the cases where most phthalates have already migrated to the surface layers of the plastic. In this article, the descriptor "bulk" refers to non-surface plasticizers/plastic. Further discussion on the depth penetration of UV light into PVC films can be found in the supplemental information file.

To achieve a molecular-level understanding on surface changes to plastics without damage or disturbance to the samples, we obtained analytical data before and after UV treatments using sum frequency generation vibrational spectroscopy (SFG). SFG data yielded information on molecular surface group type and ordering changes. In turn, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to determine what stable surface molecules were formed after treatments. Because SIMS data were obtained several days after UV treatment, we were able to determine that all products found using SIMS were stable and persist on the surface of the plastic. To obtain additional information about vibrational molecular bulk changes, Fourier transform infrared spectroscopy (FTIR) was utilized.

Using this combination of analytical techniques, it was determined that the addition of H_2O_2 to short wave UV light treat-

ments changed the surface ordering of plastics, but yielded similar surface degradation products. In addition, samples exposed to UV/H_2O_2 treatment rather than UV light exhibited larger amounts of polymer breakdown and higher DEHP bulk content. Long wave UV/H_2O_2 treatment was ineffective at degrading DEHP or polymer molecules, as the addition of DEHP to PVC reduced molecular breakdown under these conditions.

EXPERIMENTAL

Materials
Poly(vinyl chloride) ($M_w = 62,000$; $M_n = 35,000$) in pellet form, tetrahydrofuran (THF) $\geq 99.9\%$ purity, concentrated sulfuric acid (reagent grade), hydrogen peroxide (stabilized, 35 wt % in water), and potassium dichromate were obtained from Sigma Aldrich (St. Louis, MO). Bis 2-ethylhexyl phthalate (analytical standard) was obtained from Fluka (St. Louis, MO).

Sample Preparation
General Sample Preparation. Fused silica windows (ESCO Products) were used for SFG measurements and were sequentially cleaned using a concentrated sulfuric acid bath saturated with potassium dichromate overnight, rinsed with deionized water, dried under a stream of nitrogen gas, and then further cleaned by exposing windows to a glow discharge air plasma for 4 min using a PE-50 series Plasma System (Plasma Etch) before plastic sample preparation. For FTIR experiments, calcium fluoride windows (ESCO Products) were used in place of silica. Calcium fluoride windows were first soaked in THF and then cleaned using a dilute Contrex soap solution, rinsed with Milli-Q deionized water, dried under a stream of nitrogen gas and further cleaned with the same glow discharge plasma as previously mentioned. For SIMS experiments, clean silicon wafers [Wafer World, 250–300 μm thickness, (100) orientation, prime grade] were cut into 10 × 15 mm pieces and dusted with nitrogen before film deposition.

PVC pellets were dissolved in THF to prepare the PVC-based thin films. A 30 : 1 weight ratio of THF/PVC was used for all PVC-based films. DEHP was added by weight percent to PVC. Solutions were mixed using a vortex mixer (Vortex-Genie 2T, Scientific Industries) until clear. A P-6000 spin coater (Speedline Technologies) was used to prepare all plastic films. Samples were spin coated at 3000 rpm for 30 s on silica windows, calcium fluoride windows, or silicon wafers. Film thicknesses were ~200 nm.

UV Treatment for Spectral Analysis. Films were placed in a blacked out chemical hood in air and exposed to either a 60 W short wave UV (254 nm) lamp (Cole Palmer) at about 30 cm from the film surface ($I = 53$ W/m^2) or a 100 W long wave UV (365 nm) lamp (Ted Pella) at about 30 cm from the film surface ($I = 88$ W/m^2) for 30, 60, 90, 300, or 480 min. SFG spectra were collected from PVC or PVC/DEHP thin films deposited on fused silica as reference spectra in air before UV exposure. After UV exposure, SFG spectra were obtained again at the air interface. Films spin coated on Si substrates were placed on plasma cleaned glass slides and exposed to UV light as mentioned above for 5 or 8 h prior to SIMS analysis. For samples
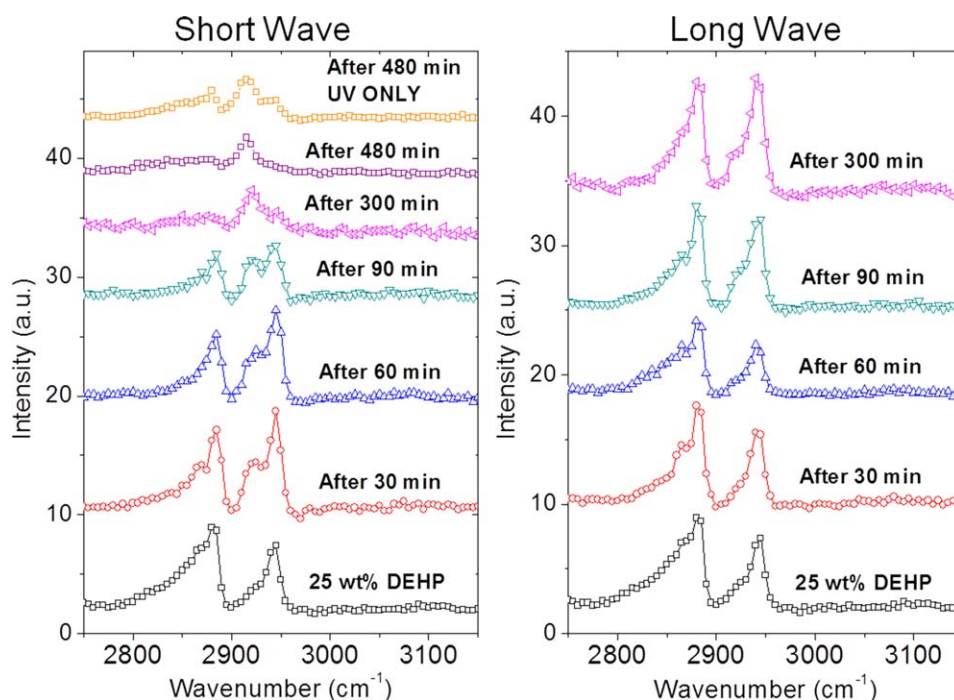
Figure 1. Left panel: SFG ssp spectra collected from plasticized PVC with 25 wt % DEHP before and after 30, 60, 90, 300, or 480 min of short wave UV exposure with H_2O_2 and after 480 min of short wave treatment with no H_2O_2. Right panel: SFG spectra of plasticized PVC with 25 wt % DEHP before and after 30, 60, 90, or 300 min long wave UV exposure with H_2O_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

undergoing UV treatment with H_2O_2, 35 wt % H_2O_2 was added by glass pipette to cover film surfaces. After UV exposure and before spectral analysis, H_2O_2 liquid was removed by glass pipette.

Instrumentation

SFG. SFG has been widely applied to gain information on molecular level changes of polymers at interfaces including air, water, and other buried interfaces.[29–39] The details of SFG theory and setup have been extensively outlined in previous articles from our lab.[32,40,41] The SFG experiments conducted for this article were taken using the ssp (s-polarized signal, s-polarized 532 nm input beam, and p-polarized tunable frequency IR input beam) polarization combination. All SFG spectra were obtained at the same visible and IR beam powers. SFG spectra in this article were obtained in the C—H stretching frequency region only as C=O signal intensities were low.

SIMS. Time-of-flight secondary ion mass spectrometry was performed on a TOF.SIMS 5 instrument manufactured by ION-TOF GmbH, Münster, Germany. This instrument is equipped with a Bi cluster liquid metal ion source and a reflectron type time-of-flight analyzer. Short primary ion pulses (<1 ns) of Bi_3^+ with an energy of 25 keV were applied providing high mass resolution secondary ion spectra together with a spot size of about 5 μm (bunched mode). Spectrometry was performed on 500 × 500 μm fields of view under static SIMS conditions by limiting the primary ion dose to 10^{11} ions/cm^2. No charge compensation was required. The pressure in the sample compartment of the spectrometer was <2 × 10^{-9} mbar. Spectra were calibrated on omnipresent C^-, CH^-, and CH_2^- peaks.

SIMS has been widely used to study molecular surface changes of polymer networks previously.[42–47]

FTIR. A Nicolet 6700 FTIR spectrometer was used to study the vibrational molecular signatures of the bulk of plastic films before and after UV exposure. The FTIR sample stage was purged with nitrogen gas prior to and during data collection. Pure PVC films were compared to FTIR PVC reference spectra. Spectra were obtained of pure PVC and 25 wt % DEHP plastic PVC films spin coated on calcium fluoride windows from 100 to 4000 cm^{-1} before UV exposure and after 1, 5, or 8 h of short or long wave UV or UV/H_2O_2 treatment, identical to the UV treatment for SFG analysis. Spectra are shown between 1000 and 3600 cm^{-1} for image clarity. The presented spectra were corrected for atmospheric water interferences and baseline anomalies.

RESULTS AND DISCUSSION

SFG and SIMS Results on Short Wave UV Treated Materials

SFG Analysis of 25 wt % DEHP. The surface of PVC with 25 wt % DEHP before UV/H_2O_2 exposure has been characterized by SFG and discussed in previous publications.[22,34] Briefly, two dominant peaks at 2880 and 2945 cm^{-1} are associated with the $CH_3(s)$ and corresponding Fermi resonance of the DEHP molecule, whereas a smaller shoulder at 2915 cm^{-1} is associated with the $CH_2(s)$ stretch of PVC (Figure 1). The smaller signal intensity from PVC compared to DEHP indicates that DEHP molecules dominate the plastic surface. Figure 2 contains the molecular structures of both PVC and DEHP for reference.

As observable in the SFG spectra in the left panel of Figure 1, after 30 min of exposure to short wave UV/H_2O_2, there is an
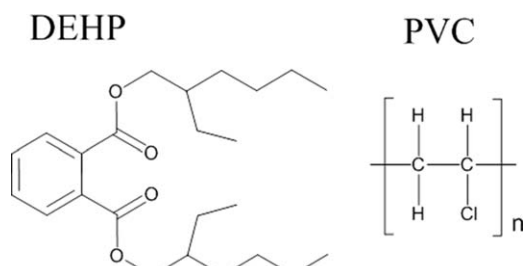
Figure 2. Molecular structures of bis-2-ethylhexyl phthalate (DEHP) (left), and poly(vinyl chloride) (PVC) (right).

increase in the $CH_2(s)/CH_3(s)$ peak intensity ratio. From our previous publication studying UV-induced reactions of plasticized PVC films in air, we were able to associate this change in peak ratio with DEHP surface reactions.[22] Interestingly, in the previous article it was after 1 h exposure to short wave UV without H_2O_2 that this peak ratio change was observed for 25 wt % DEHP. Here, with the addition of H_2O_2, the surface molecular changes are evident much faster at 30 min. This is immediately indicative that the surface reactions may occur faster with the addition of hydroxyl radicals.

The $CH_2(s)/CH_3(s)$ signal ratio change continues as the $CH_3(s)$ peak continues to decrease in intensity up to 5 h of treatment, where the only peak distinguishable is the dominant $CH_2(s)$ peak (Figure 1), which indicates CH_2 groups from PVC remain ordered on the plastic surface. The SFG data suggests after 5 h of treatment, almost all DEHP molecules have been removed or converted to different molecules. This spectrum after 5 h of treatment is very similar to the SFG spectrum we found after 5 h of short wave UV exposure in the previous article, except after UV exposure only, there was a small 2880 cm^{-1} peak of $CH_3(s)$ still clearly visible.[22]

After 8 h of short wave UV/H_2O_2 treatment, only the $CH_2(s)$ signal remains resolvable, suggesting almost all CH_3 groups have either been removed or are disordered. This is different than the surface of the plastic after 8 h of short wave UV exposure only, where the CH_3 signals remain present (Left panel, Figure 1). As stated earlier, in our previous publication, we found that the surface of the plastic after 5 h of short wave UV yielded SFG surface signals dominantly from CH_2 groups. The increase in CH_3 signals after 8 h of UV may suggest that either the DEHP molecules have been reacted even further to yield small alkyl groups, or that the PVC surface itself is now beginning to undergo scission once DEHP has been removed. Further reasoning behind the changes in surface signals after 5 and 8 h of reaction will be discussed in the next section.

SIMS Analysis of 25 wt % DEHP. Because SFG results indicated that the surface removal and conversion of DEHP molecules may occur faster with the addition of H_2O_2 and may yield different surfaces after 5 and 8 h of treatment, we obtained SIMS data after 5 or 8 h of exposure to short wave UV only, and to short wave UV with the addition of 35 wt % H_2O_2. SIMS data complements the molecular ordering data obtained by SFG with information on the types of molecules that remained on surfaces after treatment, allowing us to identify

molecular reaction products. A 25 wt % DEHP sample without any reaction was utilized as a control. The negative secondary ion spectrum of the control sample contained a peak at 277.1 m/z, associated with a phthalic monoester, attributed to the *in situ* fragmentation of DEHP during the sputtering process initiated by the primary ion bombardment (Figure 3), and a weaker signal at 391.3 m/z, $[C_{24}H_{38}O_4+H]^-$, originating from the parent DEHP molecule. Although all samples were analyzed by applying a constant Bi_3^+ dose, the total secondary ion count rate in negative polarity is low in the case of the untreated sample as compared to the UV treated samples. This is mainly due to the introduction of oxygen by any type of UV treatment, increasing the ionization yield.

SIMS data obtained after 5 h of exposure to only short wave UV revealed evidence of phthalic acid formation at a 165.0 m/z, $[C_8H_5O_4]^-$, phenyl ring hydroxylation of the phthalic acid molecule at 181.0 m/z, the appearance of the peak at 277.1 m/z associated with the phthalate monoester, a peak at 293.1 m/z hydroxylation of the monoester, and hydroxylation of the parent molecule at 405.2 m/z (see Table I). The evidence of phthalic acid formation and phenyl ring hydrogenation is consistent with results we previously found of molecules contained in the bulk after short wave UV exposure. Now, however, we have additional evidence of multiple phenyl ring hydroxylation types.

Exposure of the film to 5 h of short wave UV and 35 wt % H_2O_2 resulted in large peaks at 165.0, 181.0 m/z, 277.1 and 405.2 m/z. The intensities of the peaks associated with the monoester and hydroxylated parent molecule were compared to the nontoxic molecules that are larger than those observed after 5 h of short wave UV exposure, indicating different reaction pathways.

After 8 h of short wave UV exposure, peaks associated with phthalic acid at 165.0 m/z, hydroxylated phthalic acid at 181 m/z, and hydroxylated phthalic monester at 293.1 m/z were apparent. The intensity of peaks at 165.0 and 181.0 m/z were
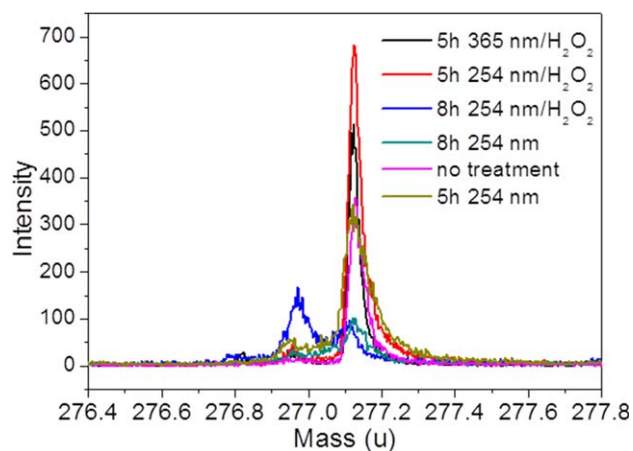

Figure 3. SIMS spectra of the phthalic monoester fragment before and after a variety of long or short wave UV treatments, with or without the addition of 35 wt % H_2O_2.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Poisson Corrected Peak Areas and Total Counts in Neg. Secondary Ion Mass Spectra

Experimental conditions	PVC with DEHP, untreated	5 h, short UV	8 h, short UV	5 h, short UV with H_2O_2	8 h, short UV with H_2O_2
O ($\times 10^3$)	117	353	322	510	420
CCl, 47 m/z ($\times 10^3$)	28.0	15.4	36.4	24.7	27.5
$[C_8H_5O_4]^-$, 165 m/z ($\times 10^{3)}$	1.7	28.1	13.3	5.8	7.9
$[C_8H_5O_5]^-$ 181 m/z ($\times 10^3$)	n.d.	12.9	11.5	1.9	12.3
$[C_{16}H_{21}O_4]^-$ 277.1 m/z ($\times 10^3$)	6.1	8.6	2.4	16.2	2.1
$[C_{16}H_{21}O_5]^-$ 293.1 m/z ($\times 10^3$)	n.d.	4.3	2.4	1.6	n.d.
$[C_{24}H_{39}O_4]^-$ 391.3 m/z	500	n.d.	n.d.	900	n.d.
$[C_{24}H_{37}O_5]^-$ 405.2 m/z ($\times 10^3$)	n.d.	1.2	n.d.	11.0	n.d.
Total ions ($\times 10^6$)	7.5	15.3	16.0	14.2	25.3

much larger than the intensity of the peak at 293.2 m/z collected on the same sample, indicating that a small percentage of the surface products were hydroxylated monoesters. The lack of signals at 391.3 and 405.2 m/z in turn suggest that most of the DEHP molecules were converted to smaller molecules. Thus the surface contained very few toxic molecules after treatment.

SIMS results after 8 h of short wave UV exposure with 35 wt % H_2O_2 are similar to those after 8 h of pure UV. The intensities of the peaks at 165.0 and 181.0 m/z are still large. However, the peak at 293.1 m/z is smaller than the sample after 8 h of short wave UV only. The results indicate that there is still a small percentage of the hydroxylated monoester left on the surface (or possibly the hydroxylated parent before sputtering and fragmentation during the secondary ion generation) but most of the surface DEHP molecules have been converted to smaller molecules.

At first glance, it may appear that the SIMS results after 5 or 8 h of short wave treatment do not directly agree with the SFG results. For instance, there are lower intensity SFG CH_3 peaks visible after 5 h of UV/H_2O_2 treatment as compared to short wave UV only,[22] which is suggestive that the addition of H_2O_2 has resulted in further reaction on the surface. But SIMS results reveal there are more DEHP molecules on the UV/H_2O_2 treated surface than the UV treated surface. Similarly, there are lower intensity SFG CH_3 peaks for the UV/H_2O_2 treated surfaces after 8 h as compared to UV treatment alone, but SIMS demonstrates there are similar surface products after both 8 h UV and UV/H_2O_2 exposure. However, the assumption that the decrease in SFG CH_3 signals directly relate to DEHP content does not take into account the differences in UV treatment methods. With H_2O_2 solution added, two complications may result: the addition of liquid to the system may increase the degree of disordering of hydrophobic groups on the surface, and the removal of the liquid by pipette may have aided in removing smaller aliphatic alkyl groups in water soluble degradation products as well. Since SFG is sensitive to the ordering of molecules as well as the number of molecular vibrational groups, it is most likely that the changes in SFG signals with UV/H_2O_2 treatment compared to UV treatment are due to increased surface disorder. The few DEHP molecules and/or DEHP reaction products remaining on the surface after UV/H_2O_2 treatment were likely

disordered, giving lower or no CH_3(s) signals compared to treatment without the addition of liquid. With this information in mind, the increase in the CH_2 peak intensity compared to CH_3 peaks observed after 30 min of UV/H_2O_2 exposure in the beginning of the discussion may be due to the different experimental conditions of UV/H_2O_2 treatment. Rather than an indication in increased reaction time, the CH_2/CH_3 ratio change is more likely attributed to differing CH surface ordering.

SIMS results indicate that the addition of hydroxyl radicals to the UV treatment for the purpose of DEHP removal is not immediately beneficial as there are no major differences in the surfaces after 8 h of treatment. The data from SIMS measurements allows us to form a slightly more complex reaction scheme for the degradation of DEHP molecules at the air/film interface as well. As expected, the hydroxylation of the phenyl ring occurs at many steps in the degradation process and may occur multiple times on a single molecule for both reaction setups, with or without H_2O_2. For the UV/H_2O_2 reactions, the DEHP molecules are expected to almost entirely cover the surface of the plastic, and therefore be readily available for reaction with OH radicals from H_2O_2. The increase in surface present OH radicals may compensate for the slower reaction kinetics in water compared to air, which may explain why the surfaces of films eventually contain similar reaction products after 8 h of short wave UV treatment or UV/H_2O_2 treatment. The DEHP degradation scheme under UV/H_2O_2 conditions will be discussed in greater detail later in this article.

SFG Analysis of Neat PVC. To determine what surface molecular changes occurred to pure PVC due to short wave UV/H_2O_2 treatment, SFG spectra were obtained before and after treatment. Similar to previous results, the SFG spectrum of pure PVC surface contains a large CH_2(s) peak at 2915 cm^{-1} and a small peak at 2880 cm^{-1}, the CH_3(s) end group (Figure 4).[22,34,48] After 60 min of exposure, the CH_3(s) peak decreases in intensity compared to the CH_2 peak. This trend continues at 1.5 h of exposure. However, after 5 h of exposure, the 2880 cm^{-1} peak reappears, and a peak near 2945 cm^{-1} appears as well. The intensities of these peaks are equal to the intensity of the CH_2(s) peak. This indicates that now both CH_3 and CH_2 groups are ordered on the plastic surface. This may suggest that
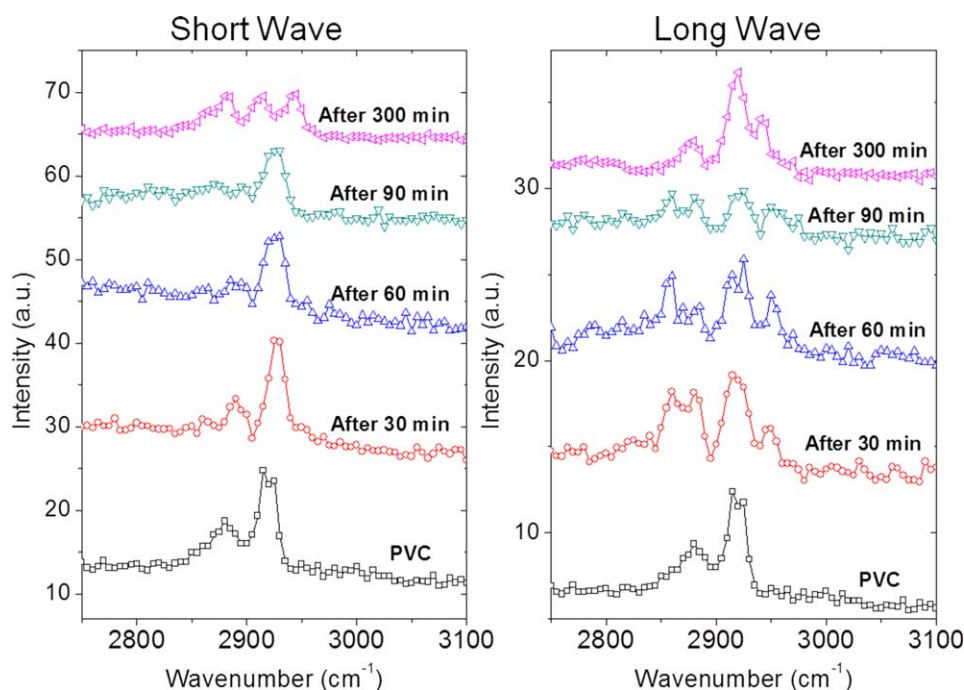
Figure 4. SFG ssp spectra collected from PVC before and after 30, 60, 90, or 300 min of short (left panel) versus long (right panel) wave UV exposure with H_2O_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

first, susceptible CH_3 end groups are removed from the PVC surface from radical reactions. Once all of the groups are removed, the chains themselves undergo radical attack, resulting in scission, removal of chlorine, and double bond formation. With ozone present under short wave UV conditions, these double bonds may have been attacked to form more CH_3 groups. In addition to these peak intensity changes, the 2915 cm^{-1} peak red-shifts after 30–90 min of short wave UV exposure. This peak shift is likely due to the differing chemical environments surrounding the $CH_2(s)$ bond resulting from radical reactions, although the exact nature of the surrounding environment after different reaction times remains unknown.

SFG and SIMS Results on Long Wave Treated Materials
SFG Analysis of PVC and 25 wt % DEHP. We previously discovered that exposure to long wave UV induced fewer surface and bulk molecular changes to DEHP-plasticized PVC films than pure PVC as evidenced with SFG and FTIR. To determine if the same surface trends occur with the long wave UV/H_2O_2 treatment, we obtained SFG data before and after UV/ H_2O_2 exposure to 0 and 25 wt % DEHP films. As shown in Figure 1, exposure to UV/H_2O_2 for 25 wt % DEHP films, even after 5 h, did not induce any observable changes in the $CH_2(s)$ to CH_3 ratios in SFG spectra, indicative that the molecular surface ordering of CH groups did not occur to any major extent.

Results from pure PVC exposure to long wave UV/H_2O_2, shown in Figure 4, demonstrate that there is likely a complex reaction process occurring at the PVC surface. There is an intermediate increase in the $CH_3(s)$ peak, Fermi resonance, and a $CH_2(as)$ peak at 2860 cm^{-1} after 30 min of treatment. In addition, the CH signal intensities overall decrease with increasing reaction time up to 90 min, indicative of increased CH disorder. After 5

h, however, there is a dramatic increase in $CH_2(s)$ in comparison to the intensity of the other CH peaks.

The difference in SFG spectral trends for long wave UV/H_2O_2 treatment versus short wave treatment may be due to different equilibrium reactions between hydroxide radicals and ozone radicals. Unlike the environment under short wave UV exposure, this system likely contained a lower concentration of ozone. A change in the balance of radical reactions between ozone and hydroxyl radicals may have led to more surface chain scission (hence the increase in intensity of the $CH_3(s)$ peak) and Cl removal, and eventually more double bond formation with the elimination of the chlorine atoms. The double bonds would not be as susceptible to further scission with less ozone present. However, this theory is difficult to prove with our current evidence and it is unclear as to exactly why CH_3 peaks are dominant at the surface after shorter treatment times.

SIMS Analysis of 25 wt % DEHP. To determine what molecular products may have been formed on the surface of the plastics from long wave exposure, if any, we obtained SIMS data after long wave UV exposure to 25 wt % DEHP films (Table II) and after long wave UV/H_2O_2 exposure. SIMS results after 5 h of exposure to long wave UV only reveal peaks at 277.1 and 391.3 m/z, the phthalic monoester and parent molecule. The addition of hydrogen peroxide appears to make little difference, with major peaks at 277.1 and 391.3 m/z, and a very small signal at 181.0 m/z, the hydroxylated phthalic acid after 5 h long wave UV/H_2O_2 treatment. The combined SFG and SIMS results demonstrate that the addition of OH radicals to the long wave UV treatment is not enough to induce major surface reactions on DEHP molecules. From this we can determine that long

Table II. Poisson Corrected Peak Areas and Total Counts in Neg. Secondary Ion Mass Spectra

Experimental conditions	PVC with DEHP, untreated	5 h, Long UV	5 h, Long UV, with H_2O_2
O ($\times 10^3$)	117	122	426
CCl, 47 m/z ($\times 10^3$)	28.0	25.7	26.6
$[C_8H_5O_4]^-$, 165 m/z ($\times 10^3$)	1.7	1.6	2.7
$[C_8H_5O_5]^-$ 181 m/z ($\times 10^3$)	n.d.	n.d.	1.1
$[C_{16}H_{21}O_4]^-$ 277.1 m/z ($\times 10^3$)	6.1	6.0	7.2
$[C_{16}H_{21}O_5]^-$ 293.1 m/z ($\times 10^3$)	n.d.	n.d.	n.d.
$[C_{24}H_{39}O_4]^-$ 391.3 m/z	500	350	400
$[C_{24}H_{37}O_5]^-$ 405.2 m/z ($\times 10^3$)	n.d.	0.2	0.6
Total ions ($\times 10^6$)	7.5	14.2	14.4

wave UV should not be used for any DEHP-removal process and will do little to affect the surface of the film.

Evidence for Bulk Reactions from UV Treatments

FTIR spectra were obtained before and after long or short wave UV/H_2O_2 exposure to 25 wt % DEHP and pure PVC (Figures 5 and 6). PVC with 25 wt % DEHP films after short wave UV exposure with H_2O_2, similar to our previous results, contained dramatic spectral bulk changes across CH and C=O stretching frequency ranges (Figure 5, top panel). The decreases in intensity across both spectral regions may be due to partial phthalate evaporation. Still, we are able to obtain information about molecular structural changes of the plastic by studying peak ratio changes. Large decreases in signal intensity were observed at 1027 and 1127 cm^{-1}, (the aromatic O—CH$_2$ group of DEHP), and 1280 cm^{-1} (the conjugated aromatic ester COO group of DEHP). Additionally, a decrease in intensity and broadening of the 1725 cm^{-1} C=O stretch, suggests that the number of C=O groups decreased and that the neighboring chemical environment around the C=O bond changed, as evidenced in our previous publication. These spectral changes are indicative that the ester bond of DEHP was broken to form smaller molecules. Possible molecules formed include phthalic acid, phthalic anhydride, phthalic monoesters, and phthalate-related molecules with hydroxylated phenyl rings as observed with HPLC/MS in the previous articles and with SIMS in the current study. However, the decrease in intensities in the C=O region of spectra are not as dramatic as previously found with exposure to short wave UV only. Comparatively, there are greater decreases in intensity across the C—H region of spectra, indicative of CH bond elimination. Collectively, this is evidence that a greater amount of reactions may have occurred with PVC molecules over DEHP molecules.

This suspicion was confirmed by the FTIR spectra of PVC before and after 1 or 5 h short wave UV/H_2O_2 treatment. There is a major decrease in CH signal intensity overall, which continues to decrease with longer treatment times from 1 to 5 h. Decreases in signal intensity include both CH$_2$ and CH$_3$ groups at 2880 cm^{-1} (CH$_3$), 2860 cm^{-1} (CH$_2$), and 2845 cm^{-1} (CH$_2$(s)). These decreases in signal intensities for pure PVC are much larger than the signal decreases previously observed in

our first article. Thus, the addition of hydroxide radicals to our treatment system demonstrated preferred radical reactions with PVC chains rather than DEHP molecules, leading to a larger amount of bulk polymer breakdown.

Additionally, after 8 h of 25 wt % DEHP treatment, it is obvious from FTIR data that exposure to short wave UV only results in complete removal of DEHP in the bulk (up to the
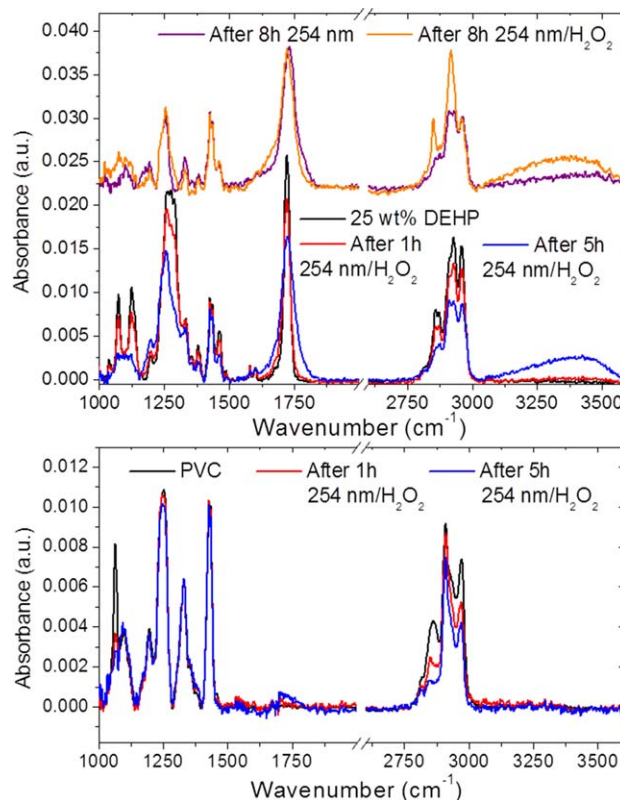

Figure 5. Top panel, top row: FTIR data of PVC with 25 wt % DEHP after 8 h of short wave UV exposure (purple) and 8 h short wave UV exposure with H_2O_2. Top panel, bottom row: PVC with 25 wt % DEHP before (black) and after 1 h (red) and 5 h (blue) UV exposure with H_2O_2. Bottom panel: FTIR data of PVC before (black) and after 1 h (red) and 5 h (blue) short wave UV exposure with H_2O_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
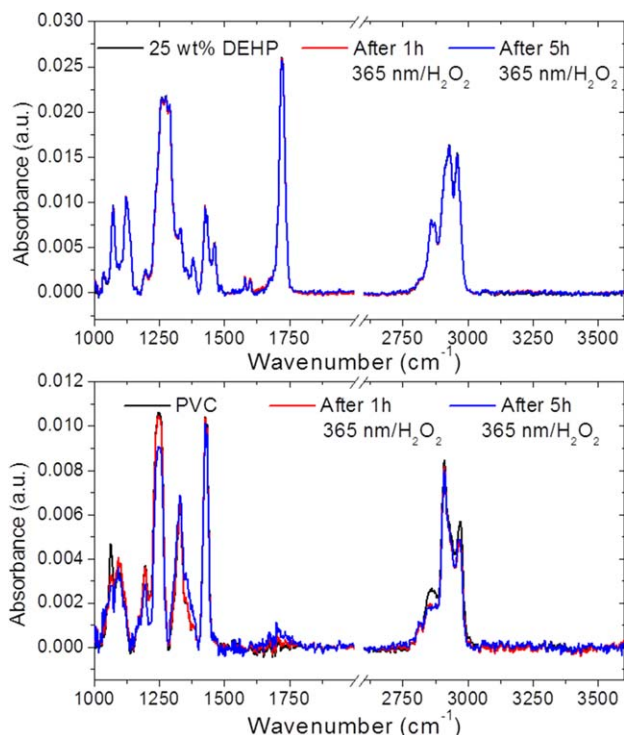
Figure 6. Top panel: FTIR data of PVC with 25 wt % DEHP before (black) and after 1 h (red) and 5 h (blue) long wave UV exposure with H_2O_2. Bottom panel: FTIR data of PVC before (black) and after 1 h (red) and 5 h (blue) long wave UV exposure with H_2O_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR detection limit) with no DEHP signals, whereas 8 h short wave UV/H_2O_2 exposure does not result in elimination and DEHP FTIR signals remain. It is at this point in time that the pure UV reaction is still faster than UV/H_2O_2 and is successful in removing almost all DEHP molecules from the bulk (Figure 5, top panel). It is interesting that this means the surface and bulk reaction kinetics may be different. At this point on the surface, SIMS results reveal that the removal of DEHP via UV or UV/H_2O_2 is virtually the same.
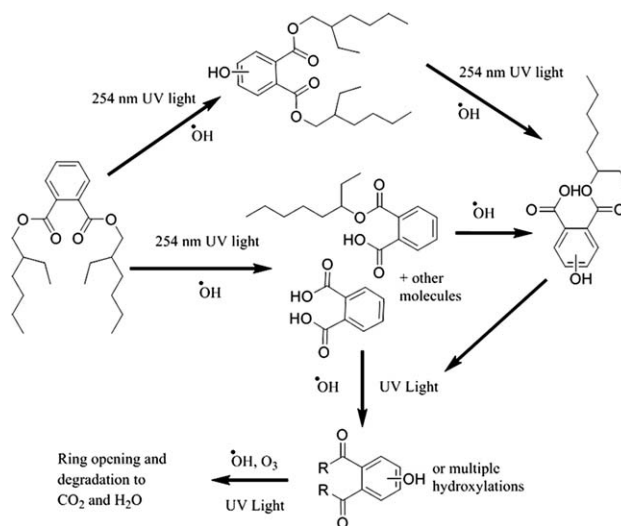
We additionally obtained FTIR data to determine the bulk molecular changes for DEHP plasticized and pure PVC exposed to long wave UV/H_2O_2 compared to the surface changes. Similar to before, pure PVC exposure to long wave UV treatment resulted in CH signal decreases, likely due to crosslinking, scission, or radical scavenging. Once again, the decrease in signal intensity after long wave UV treatment was less dramatic than that after short wave UV treatment. Also there are virtually no changes in signal intensity when the DEHP has been added to the PVC matrix, demonstrating that the molecules have a protecting effect on both the surface (from SFG data) and throughout the bulk (Figure 6). This is concrete evidence that the use of long wave UV for DEHP removal is not effective for either surface or bulk removal.

We can deduce from FTIR results that reaction processes for DEHP molecules in the bulk due to short wave UV/H_2O_2 exposure are similar to reaction processes induced from short wave

UV exposure only, but complicated by preferential hydroxyl and ozone radical reactions with PVC chains. Using information from all three analytical techniques, it is clear that the addition of hydrogen peroxide was less effective in degrading DEHP molecules contained within the plastic matrix than pure UV, and was comparable at converting DEHP on the surface of the plastic. The following is a simplified reaction scheme for the degradation of DEHP in the short wave UV/H_2O_2 system (Scheme 1). In the bulk, a competing reaction pathway with PVC and OH radicals results (pathway not shown). Hydroxylation of the phenyl ring occurred at all steps of degradation. First step major products included hydroxylated DEHP, and the formation of MEHP and hydroxylated MEHP. Eventually, these products would give way to phthalic acid, hydroxylated phthalic acid, and other smaller molecules formed from the breaking of the CO ester bond of the phthalate. The small alkyl legs of the molecule may have volatilized or been removed with the removal of the H_2O_2 liquid after treatment. The addition of O_3 in the system from the short wave UV would break open phenyl rings, with further radical attack leading to complete degradation of the plasticizer. A similar molecular degradation would likely results for phthalates in plastics exposed for long periods of time to short wave UV in aqueous environments with hydroxyl radicals.

There are a few reasons as to why the bulk DEHP removal was less effective with hydrogen peroxide. First, these bulk reactions took place in aqueous media rather than air. The aqueous phase kinetics would therefore be much slower than gas phase in the bulk of the plastic, yielding a slower start of OH reactions with DEHP. This may explain why FTIR results show much more DEHP degradation at 5 h for UV reactions in air, and only a small difference at 8 h.

Second, the influx of water into the PVC system would swell the polymer matrix further than the plasticizers already had and increase the areas in which PVC chains are susceptible to radical attack. The behavior of water to act as a plasticizer has been

Scheme 1. Simplified reaction scheme for DEHP degradation at 254 nm UV light with 35 wt % H_2O_2 (aq).

previously demonstrated in published polymer systems[49,50] and in our unpublished data. Perhaps the influx of radicals at new regions within the plastic leads to the preferential attack on the PVC chains rather than the DEHP molecules.

CONCLUSION

The molecular structural surface and bulk changes of plasticized PVC materials after UV/H_2O_2 exposure were studied using SFG, SIMS, and FTIR. The addition of 35 wt % H_2O_2 to short wave UV exposure for the purpose of improving DEHP degradation was found to yield different surface molecular ordering, but comparable phthalate-related products to surfaces exposed to short wave UV only at longer (8 h) treatment times. In addition, surface CH_3 groups were found to be ordered to a greater extent in samples exposed to short wave UV only than UV/H_2O_2. The lack of SFG CH_3 signals in the UV/H_2O_2 samples were not attributed to decrease in DEHP content, but a change in CH ordering once aqueous solution was added and a possible removal of alkyl components. The DEHP molecules underwent radical attack at the ester bond to form smaller molecules. Surface products identified using SIMS after short wave UV and short wave UV/H_2O_2 treatment included phthalic acid, hydroxylated phthalic acid, MEHP, and hydroxylated MEHP. By 8 h, most toxic surface molecules were eliminated from either treatment methods. However, it was found that the UV/H_2O_2 treatment was less effective in degrading DEHP molecules in the bulk up to 8 h of treatment. This was determined to have occurred due to preferential radical reactions with the polymer.

The addition of DEHP to PVC was found to protect the surface and bulk from damage from long wave UV/H_2O_2. Without DEHP, the polymer was susceptible to radical attack by OH radicals, resulting in increased CH_3 surface groups after exposure and chain scission in the bulk. Results from our study indicate that extended short wave UV exposure may be an effective means to degrade toxic DEHP and MEHP molecules after plastic disposal, and the addition of H_2O_2 to this treatment system is only beneficial if additional degradation of the polymer bulk is desired. If commercial UV absorbers are added to the plastic matrix during plastic processing, the treatment times indicated in this study are not directly applicable, and longer UV exposure times must be used.

ACKNOWLEDGMENTS

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