Sonochemically-Assisted Modification of Polyethylene Surfaces

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ABSTRACT: The oxidation of polyethylene surfaces with a range of mild oxidizing agents enhanced by the use of ultrasound is described. The use of sonochemical methods allows significant levels of surface modification to be achieved using oxidizing agents such as hydrogen peroxide and persulfate salts around ambient temperatures under mild conditions. Changes in the water contact angle and attenuated total reflection IR spectroscopy were used to follow the changes in surface chemistry. Variation of the experimental conditions such as treatment time and sound intensity allowed control over the extent and nature of the surface oxidation. Although the changes achieved with laboratory equipment are relatively slow, more significant effects could be obtained at higher ultrasound intensities.

Introduction

Polyolefins, including polyethylene, are commonly used for a wide range of applications. They are usually considered to be stable and inert while being relatively inexpensive. However, their inert nature leads to materials with low surface energies and consequent problems in the adhesion of coatings as well as other materials.[1,2] There is thus great interest in modifying the surface to make it more receptive to other components. A second area of interest in modifying the surface of such polymers is to take advantage of their bulk economy and material properties while presenting a functional or active surface. Finally, an area of considerable current activity is that of producing biocompatible polymeric articles.[3]

A number of methods have been developed for modifying polymer surfaces[4,5] including free-radical chlorination and sulfonation. Most methods rely on oxidation to introduce the polar groups to the surface, which raises the surface energy and hence promotes adhesion *etc.* Techniques[4,5] for achieving this include corona and plasma discharges, photooxidation, ozonation, and chemical reaction. For example, Rånby *et al.*[6] have carried out extensive studies of photografting of acrylic acid onto polyethylene and polypropylene. Others workers have utilized methacrylic acid,[7] acrylamide,[8] methacrylonitrile,[9] or polyacrolein[10] to introduce hydrophilicity at the surface.

The most commonly used chemical oxidant is chromic acid. Blais *et al.*[11] showed that hydroxyl groups and several different types of carbonyl functions were introduced at the surface, while Rasmussen and coworkers suggested[12] that the main product was carboxylic acid functionality. Clearly, the large-scale use of chromic acid is undesirable and it would be more convenient to employ a milder oxidizing agent. In addition, environmental considerations for modern commercial processes mean that an aqueous system would be preferable to one employing organic, particularly chlorinated, solvents.

The oxidation of polyethylene by wet chemical methods generally requires very strong oxidizing agents. In a search for a milder system, the following systems were selected as candidates for study on the basis of their electrode potentials.[13]

acidified dichromate:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad E° = 1.36\ V$$

hydrogen peroxide:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E° = 1.76 V$$

persulfate salts:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \qquad E° = 1.96\ V$$

$$2SO_4^{\bullet -} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet} \qquad E° = 2.08\ V$$

Hydrogen peroxide is a commonly used oxidizing agent due to the ready formation of hydroxyl radicals although under normal conditions the effect of polyethylene surfaces is negligible. Metal persulfates are well-known[14] sources of radicals in aqueous solution, for example in the initiation of polymerization. The mechanism of the thermal decomposition is believed[15] to involve the two steps outline above where either of the radical species can remove a hydrogen from the PE surface after which hydroxylation can occur to give an oxidized surface. In a recent report,[16] Bamford and Al-Lamee described the persulfate oxidation of the surfaces of several polymers, although high temperatures were used to generate the effects.

Over the past two decades, the use of high-intensity ultrasound has become a common technique in synthetic chemistry.[17−19] A number of reactions, especially those in heterogeneous systems, have been shown to give enhanced rates and yields under ultrasound, leading to a branch of chemistry sometimes termed *sonochemistry*. The best known effect in polymer sonochemistry is the cleavage of chains when irradiated in solution,[20,21] although ultrasound has recently been successfully applied to polymer synthesis reactions.[22]

The main effects of sonication are due to *cavitation* or the growth and explosive collapse of microscopic bubbles on a microsecond time scale.[23] This can result in the formation of relatively high concentrations of excited species such as radicals which can be used to initiate reactions.[24] Motion of the solvent molecules

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around bubbles causes very efficient mixing and dispersion of multiphase systems. An extra effect occurs near a solid surface when cavitational collapse is asymmetric[25] and results in a microjet of solvent impinging at high speed on the solid[26] which increases the rate of transfer of reactants and products to and from the surface.

Urban and Salazar-Rojas[27] utilized these effects to remove HF from the surface of poly(vinylidene difluoride) (PVF_2) to give extended sequences of conjugation. The conventional approach is to treat the polymer with a hot solution of a strong base together with a phase transfer catalyst. The use of ultrasound accelerated the dehydrofluorination, particularly at low temperatures, and produced extended sequences of unsaturation and conjugation. The unsaturation gives sites which can be further modified by subsequent chemical reaction. Examples[28] of this have been seen with the grafting of silicon- and germanium-centered phthalocyanines onto the surface of PVF_2.

There are two main effects of ultrasound which could be beneficial in promoting the oxidation at polymer surfaces. First, the enhanced mass transfer and phase transfer properties around solid surfaces caused by ultrasound could accelerate the oxidation. Second, the production of radicals could be accelerated by enhanced decomposition of the oxidizing agents. In an early report, Schumb and Ritner[29] showed that the rate of decomposition of potassium persulfate was slightly increased (~10%) during sonication at 8.7 kHz. More recently, Lorimer *et al.*[30] reported an increase in the rate of decomposition, although only temperatures between 50 and 70 °C were used. Related work by the authors[31] has shown that the rate of radical formation in this system is accelerated approximately threefold at 55 °C but by a factor of 10 at 35 °C.

At present, it is generally regarded[4] that to chemically modify polyethylene surfaces, it is necessary to first generate some form of oxidized layer which can be subsequently derivatized. In the present work, a number of ultrasonic oxidation routes for polyethylene have been investigated and the most promising of these used to generate the starting material for further sonochemical derivatization studies. Finally, the ability of ultrasound to bring about grafting and chemical modification in a single step has been investigated for a few of these systems.

Experimental Section

Sonication Procedure. Films cut from the PE sheets were cleaned with methanol and dichloromethane followed by drying in a stream of dry air. The sonication system used is shown schematically in Figure 1. The films were clamped in a steel holder immersed in approximately 150 cm^3 of the appropriate reagent solution contained in a jacketed beaker. Thermostated water was circulated to maintain temperature control to ±0.5−1.0 °C, depending on the starting temperature. Except where noted, experiments were carried out at 35 °C since cavitation in water is maximized at this temperature.[32] A Sonics and Materials VC600 ultrasound horn system was fitted so that the horn tip was 3 cm above the PE film. The intensity of ultrasound, measured calorimetrically[33] was 26.2 ± 1.5 W cm^{-2}. Blank experiments were carried out in the same apparatus without switching on the ultrasound but with magnetic stirring. After treatment, the films were rinsed with clean water and acetone before being dried under vacuum.

Materials. The polyethylene (PE) was a commercial, LDPE sample with a weight-average molecular weight of 145 000 and polydispersity of 7.0 and was melt pressed into sheets of thickness 0.2−0.3 mm. All reagents and solvents were of the purest grade available from Aldrich Ltd.

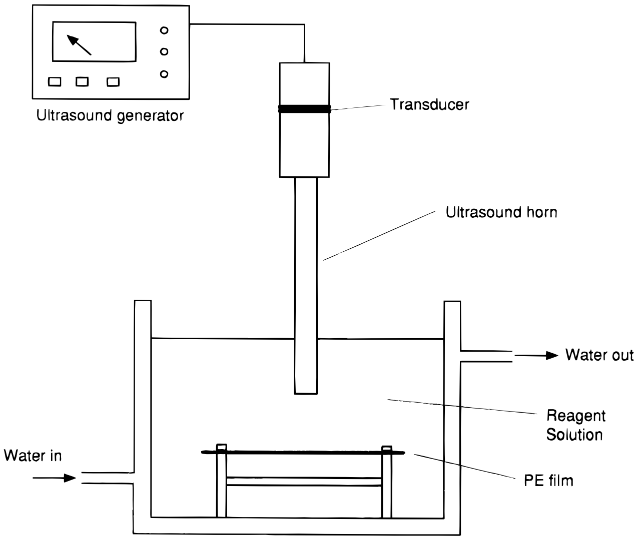

Figure 1. Schematic diagram of sonication apparatus.

Polymer Analysis. Infrared spectra were recorded on a Nicolet 510P spectrometer with a variable-angle attenuated total reflectance (ATR) accessory utilizing a KRS-5 prism. Spectra were measured with a resolution of 4 cm^{-1} by averaging 150 scans. Contact angles were measured on a home-built apparatus using water purified by ion exchange. The treated PE films were clamped horizontally on a steel base inside a Perspex box, the inside or which was maintained at relatively constant, high humidity. Droplets of 10 ± 1 μL were placed on the film from a microsyringe and observed through a traveling microscope fitted with a goniometer eyepiece. All measurements were made at 21 ± 1.5 °C and were the average of at least ten readings at different positions across the surface. The uncertainty in the values was at most ±5°. In most cases, measurements were performed shortly after treatment while for other experiments, measurement was delayed for up to 12 h. No significant differences in the measured values were noted for these cases. To assist with spectral interpretation, some films were further derivatized[34] with trifluoroacetic anhydride (TFAA). Treated PE films were suspended in a sealed tube above approximately 2 cm^3 of TFAA for 15 min at 35 °C. The films were removed and dried under high vacuum for 5 h prior to recording infrared spectra.

Results and Discussion

The contact angle of water on the untreated PE films was 98.6 ± 2.5°. As noted above, a method in common current use for oxidizing PE prior to reaction is the use of chromic acid which results in contact angles of 45−66°.[11,35] Treatment of the PE used here with chromic acid according to the method of Rasmussen *et al.*[12] yielded films with contact angles of 60 ± 2.5°, in satisfactory agreement with literature values.

To isolate the effects of the oxidants, preliminary reactions were performed under the appropriate ultrasound conditions at 35 °C in pure water in order to maximize cavitation.[32] The contact angle obtained after ultrasonic treatment was 94° compared with 97° in a control experiment without ultrasound. It is well known[17,31] that sonication of water can produce significant concentrations of $H^\bullet$ and $OH^\bullet$ radicals, reaction with which may be responsible for the small amount of change observed.

Reactions with Dichromate. The highly corrosive nature of the chromic acid oxidizing system renders it unsuitable for widespread use, particularly on a large scale. In an attempt to determine whether ultrasound

Table 1. Water Contact Angles for Hydrogen Peroxide[a] Treated PE Surfaces

reagents	water contact angle/deg	
	ultrasound	control
6% H_2O_2	94	96
30% H_2O_2	89	95
6% $H_2O_2 + Fe^{2+}$ [b]	91	100
30% $H_2O_2 + Fe^{2+}$ [b]	89	94

[a] Reactions were performed at 35 °C in air for 5 h at an ultrasound intensity of 26.2 W cm^{-2}. Percentage concentrations are on a volume basis. [b] 1.0 g dm^{-3}.

would allow the use of less harsh conditions, PE films were treated with a more dilute solution consisting of 5 g of $K_2Cr_2O_7$ dissolved in 150 cm^3 of 32% sulfuric acid solution. Sonication and stirred control reactions were conducted for 5 h, and the resulting contact angles were 93 and 94°, respectively. Both samples therefore showed a small, but barely significant, change from the starting polyethylene. Neither sample showed any signs of oxidation by ATR-IR in the region 2000−1500 cm^{-1} These results would suggest that some oxidation might have been achieved with this but, if so, the levels were very low. Furthermore, ultrasound appears to have little accelerating affect on the oxidation process in this case and produced no more change than sonication in pure water. Accordingly, this system was abandoned in favor of study of reactions with strong oxidizing power, judged by their $E°$ values.

Reaction with Hydrogen Peroxide. Samples of polyethylene film were then sonicated in a variety of hydrogen peroxide solutions. The precise conditions and the water contact angle values of the resulting films are shown in Table 1. None of the stirred control reactions gave significant changes in contact angle from the starting film. Although there was an indication that some reaction occurred with Fe^{2+}-accelerated 30% solution, this was at a very low level and no signs of oxidation were observed in the ATR-IR spectrum of this sample. The application of ultrasound to these systems clearly gives an increased level of surface modification as shown by the contact angle values. The largest change was obtained with the 30% peroxide concentration although addition of Fe^{2+} appeared to have no further effect on the oxidation. Since addition of Fe^{2+} is known to accelerate the formation of radicals, this observation suggests that this part of the process is not the rate-limiting step. Further information on the nature of the modification can be gleaned from the ATR-IR spectrum of the film treated sonochemically with 30%/Fe^{2+} shown in Figure 2. The broad absorption band at ~1724 cm^{-1} is consistent with the formation of carbonyl groups, including those in ketones and esters. Also shown is the spectrum after treatment of the film with trifluoroacetic anhydride (TFAA) vapor. This derivatization would have selectively reacted with any hydroxyl or epoxide groups[36] present on the surface, generating trifluoro ester functionality. The reacted sample has a new absorbance band at ~1785 cm^{-1}, which is characteristic of the carbonyl group of fluoroesters. The absorption at ~1725 cm^{-1} remains in the spectrum, albeit at a reduced intensity, indicating that the oxidation reaction produces a range of different functionality at the surface.

Reactions with Persulfates. Given the low extent of reaction achieved with hydrogen peroxide, attention was then focused on oxidation of PE films with aqueous persulfate solutions. The results produced in a range of initial reactions are shown in Table 2.

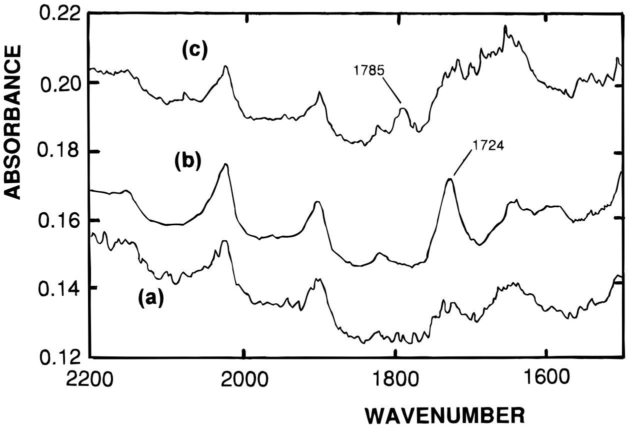

Figure 2. Attenuated total reflectance IR (60°) spectra of PE surfaces: (a) control reaction; (b) reacted with 30% H_2O_2 and Fe^{2+} at 35 °C with ultrasound; (c) as (b) and then treated with TFAA vapor.

Table 2. Water Contact Angles for Persulfate[a] Treated PE Surfaces

reagents	conditions	water contact angle/deg	
		ultrasound	control
$K_2S_2O_8$	air, 35 °C	82	96
$K_2S_2O_8$	N_2, 35 °C	84	99
$K_2S_2O_8$	air, 75 °C		95
$K_2S_2O_8$	air, 35 °C, 33 g dm^{-3} + 2.0 g dm^{-3} $FeCl_3$	82	95
$K_2S_2O_8$	air, 35 °C, 33 g dm^{-}13 in 0.05 mol dm^{-3} NaOH	93	95
$K_2S_2O_8$	air, 35 °C, 33 g dm^{-3} in 0.05 mol dm^{-3} H_2SO_4	89	95
$(NH_4)_2S_2O_8$	N_2, 35 °C	92	98

[a] All reactions times were 5 h. The persulfate concentration was 33 g dm^{-3} and the sonication intensity was 26.2 W cm^{-2}.

It is clear that all of the ultrasonically promoted reactions gave changes in contact angle from the untreated polyethylene larger than the uncertainly of ±5° while none of the stirred, control reactions showed significant changes.

Reaction with potassium persulfate under air or nitrogen at 35 °C gave similar results with a decrease in contact angle of around 16°. Other work[31] has shown that the conventional decomposition reaction at 75 °C yields a similar rate of radical formation as the sonochemical system at 35°C. However, the change in contact angle for the latter system was larger, indicating that ultrasound is enhancing the reaction at the surface as well as accelerating the production of radical species. Addition of trace amounts of metal ions has also been reported to increase the rate of decomposition of the persulfate system.[37] In this work, Fe^{2+} and Fe^{3+} were added to the system but no further improvement was noted over the use of persulfate alone. Again, this suggests that production of radicals is not the rate-limiting step.

Studies of the thermal decomposition kinetics for sodium and potassium persulfate in basic, neutral, and dilute acid solutions by Green and Mason[38] and later by Kolthoff and Miller[39] showed that the reaction is catalyzed by the addition of acids so that these were also used here. Again, the contact angles after treatment were significantly different from those of the starting polyethylene, but the changes were less than those obtained using ultrasound in neutral media. These results are consistent with the radical mechanism suggested above. Kolthoff and Miller suggested that in acidic media the reaction proceeded via HSO_4^- so that the intermediates are ionic rather than the radicals involved in neutral media. These mechanisms are consistent with sonochemically enhanced reactions since a number of workers have reported that in heterogeneous systems radical reactions are preferentially accelerated by ultrasound over those proceeding by solely ionic pathways.[40] Indeed, it has been observed[41] in some heterogeneous sonochemical reactions that only the single electron transfer pathway operates even where the major product in the absence of ultrasound arises from an ionic mechanism. The contact angle changes in Table 2 also signify that some reaction occurred with ammonium persulfate although modification in these terms appeared to be more substantial with the potassium salt.

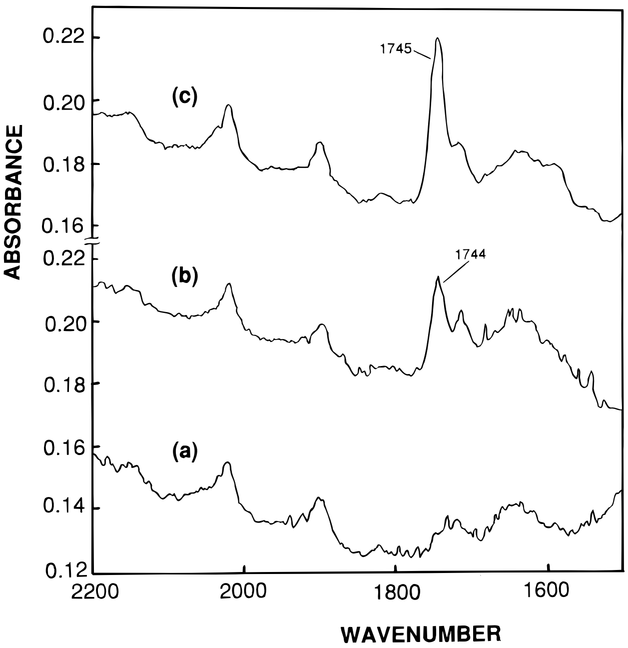

Figure 3. Attenuated total reflectance IR (60°) spectra of PE surfaces: (a) control reaction; (b) reacted with $K_2S_2O_8$ at 75 °C; (c) $(NH_4)_2S_2O_8$ at 35 °C with ultrasound.

In an attempt to identify the chemical species responsible for the change in surface properties, ATR-IR spectra were recorded. Unfortunately, at the sensitivity available, no differences could be found between untreated PE films and those which had been sonicated in any of the potassium persulfate solutions. The ATR-IR spectrum from the reaction carried out by heating to 75 °C did however suggest the presence of a carbonyl stretching band at ~1744 cm^{-1} as shown in Figure 3b. The spectra recorded from the film treated with ammonium persulfate, shown in Figure 3c, also showed the presence of a new strong absorbance band at ~1745 cm^{-1}. The position of this band is consistent with the carbonyl stretching of organic esters.

The difference in the potassium persulfate results is likely to be due to the much softer surface and hence increased mobility of polymer chains at higher temperatures, which allows deeper penetration of reagents into the film, and hence a greater degree of reaction occurs within the IR sampling depth. At 35 °C, the polymer is harder and hence functionalization will be more localized at the surface.

The contact angle changes and ATR-IR results appear to be somewhat conflicting since the former suggest that the potassium salt causes greater oxidation of the surface while the spectra suggest that the ammonium salt causes greater functionalization. These observations can be reconciled by suggesting that a greater level of oxidation is achieved with ammonium persulfate but that the oxidized layer is more diffuse and distributed over a deeper region of the infrared sampling depth (~0.75−1 μm). Oxidation caused by the potassium salt seems to be confined to the outermost layers and so is insufficient to be detected by ATR-IR.

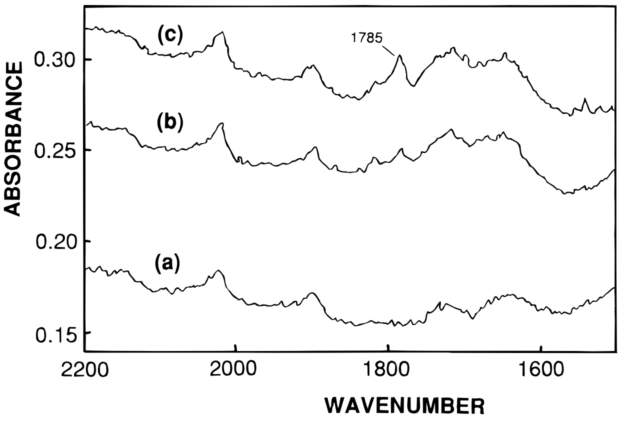

Figure 4. Attenuated total reflectance IR (60°) spectra of PE surfaces: (a) unreacted PE; (b) PE reacted with TFAA; (c) sonochemically oxidized with $K_2S_2O_8$ at 35 °C and then treated with TFAA vapor.

Previously, Morris found that treatment of PE with dilute solutions of ammonium persulfate treatment caused large increases in the adhesive joint strengths[42] for PE. Although only small changes in the critical surface tension were observed, small carbonyl peaks were reported to be visible in the ATR-IR spectra. Treated samples were also reported to be partially insoluble and the increased adhesive joint strength was attributed to surface cross-linking. In our work, no evidence for cross-linking was obtained with any of the films as they remained completely soluble in hot decalin.

An alternative explanation of the absence of spectral information in the potassium persulfate treated films is that the modification produced a highly hydroxylated surface rather than introducing carbonyl functionality. Samples of the PE film oxidized under the conditions above were further reacted with TFAA vapor, and the ATR-IR spectra of the original and derivatized samples are shown in Figure 4. The characteristic fluoroester peak at ~1785 cm^{-1} is clearly present in the oxidized polyethylene sample to a much greater degree than in the untreated PE.

The encouraging initial results of obtaining significant levels of surface oxidation led us to investigate the effect of persulfate concentration, treatment time, and variation of the ultrasound intensity in order to maximize the oxidation and to determine the available degree of control over the process. Figure 5 shows the variation in contact angle with treatment time under the conditions described above. The displayed error bars indicate the variation observed over at least ten measurements across the film. The plot indicates that the extent of oxidation increases markedly with longer treatment times and, after 24 h, reaction to give surface energies equivalent to those obtained after treatment with chromic acid can be achieved. The ATR-IR spectrum of the PE film after 24 h sonication is shown in Figure 6. The two absorption bands at 1716 and 1736 cm^{-1} are in positions characteristic of carbonyl functions including carboxylic acid or ester groups, which could arise from further oxidation of hydroxyl substituents at

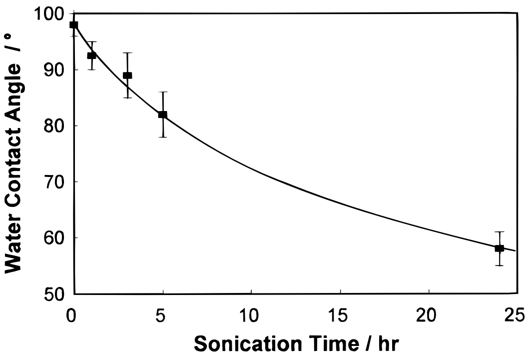

Figure 5. Change in water contact angle of PE surface during sonochemical treatment with $K_2S_2O_8$ at 35 °C and 26 W cm^{-2}.

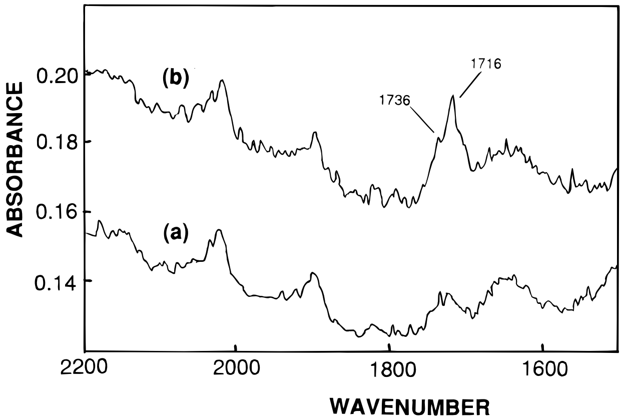

Figure 6. Attenuated total reflectance IR (60°) spectra of PE surfaces: (a) control reaction; (b) 24 h sonication with $K_2S_2O_8$ at 35 °C and 26 W cm^{-2}.

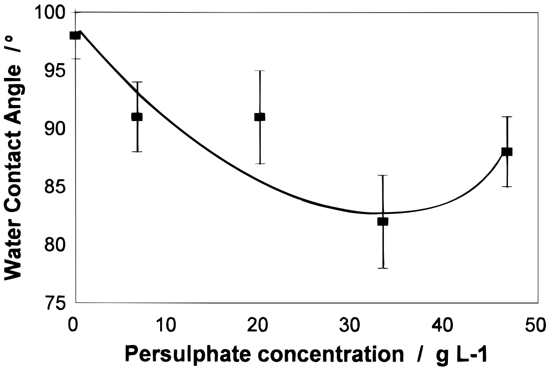

Figure 7. Water contact angles of PE surfaces after 5 h sonochemical treatment at 35 °C and 26 W cm^{-2} with varying concentrations of $K_2S_2O_8$.

the surface. The dependence of the sonochemical oxidation on persulfate concentration was investigated for reaction at an intensity of 26.2 W cm^{-2} for 5 h. The results, shown in Figure 7, show no clear dependence on concentration, indicating that this is not the rate-determining parameter.

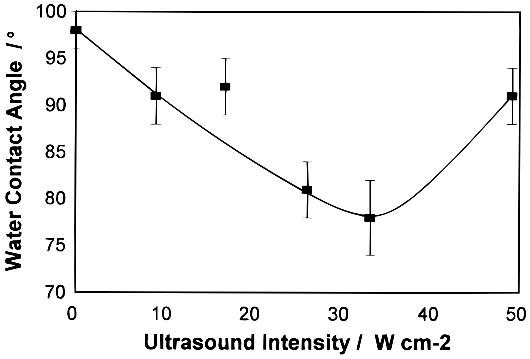

Figure 8. Water contact angles of PE surfaces after 5 h sonochemical treatment with $K_2S_2O_8$ at varying intensities at 35 °C.

An alternative method for increasing the reactivity in terms of the number of cavitation bubbles produced is to increase the sound intensity. Figure 8 shows the results for varying this at fixed reaction times of 5 h and demonstrates that the extent of oxidation does increase although the effect is relatively small. There is a maximum intensity, in this case 32 W cm^{-2}, above which the benefit of increasing the intensity is lost. This has been noted in a number of sonochemical systems and can be attributed to the intense cavitation field near the horn disrupting passage of sound into the liquid and hence reducing the overall degree of cavitation. It should also be noted that the plot in Figure 8 mirrors that measured elsewhere[31] for the decomposition of potassium persulfate, suggesting that the rate of oxidation appears to be limited by the number of cavitational events.

Nature of the PE Surface. Previous workers have investigated changes in the nature of the PE surface after treatment. The characteristic doublet at 720−730 cm^{-1} in the infrared spectrum has been shown to be sensitive to crystallinity changes in the polymer surface during the acid etching of polyethylene. The 730 cm^{-1} component of this doublet is associated with the crystalline regions and the 720 cm^{-1} component mainly with the amorphous regions. The absorbance ratio I_{720}/I_{730} can therefore be used as a measure of the relative amounts of crystallinity. The values of this ratio obtained in the present work were 1.25 prior to treatment, 1.27 after 5 h oxidation with aqueous $K_2S_2O_8$, and 1.36 after 24 h.

These values are similar to those reported by Haridoss and Perlman during the acid etching of polyethylene films,[43] where the values of R increased from 1.09 for the untreated polyethylene to 1.45 for chromic acid oxidized samples. While the changes in the present work are lower, they also suggest that the ultrasonically promoted oxidation occurs in the same regions of the polymer. The smaller change in the value of R observed in this work is unsurprising since the persulfate oxidation is more surface selective than chromic acid treatments. Urban and co-workers recently suggested[44] that this method is not accurate for studying crystallinity changes in the surface since the absorbance ratio of these bands is also sensitive to sample preparation and crystallite orientation so that accurate determination of surface crystallinity requires detailed polarization studies. Thus, the results from this work can only be regarded as approximate although the trend seems to be consistent with other workers.

Further Reaction of Oxidized Polyethylene Films. The final stage of this investigation was to determine whether the oxidized surfaces could be used as a starting point for further reaction. PE films were oxidized for 5 h with potassium persulfate using the conditions described above. The films were then rinsed with distilled water and subjected to further reaction with the systems included in Table 3, which also includes the contact angle values for the resulting films. The further change in contact angle caused by grafting these hydrophilic compounds is clearly apparent. However, no significant conclusions could be drawn from the ATR-IR spectroscopy, implying that surface modification

Table 3. Contact Angle Data for Oxidized Polyethylene Films after Secondary Grafting Reactions[a]

oxidant	reagents	water contact angle/deg
H_2O_2	maleic anhydride	84
$K_2S_2O_8$	10% acrylic acid	78
	0.1% poly(acrylic acid)	71
	0.1% polyacrylamide	88
	10% HEMA	79
	maleic anhydride	84

[a] Reactions were performed at 35 °C in air for 5 h at an ultrasound intensity of 26.2 W cm^{-2}.

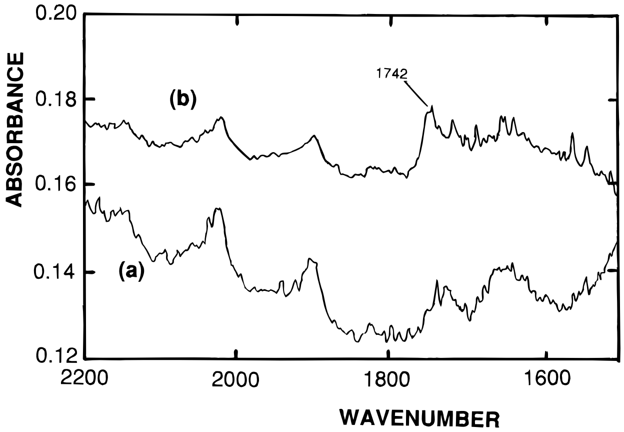

Figure 9. Attenuated total reflectance IR (60°) spectra of PE surfaces: (a) control reaction; (b) 5 h sonication with trimethylsilyl methacrylate at 35 °C and 26 W cm^{-2}.

was restricted to a very thin layer of <0.1 μm. A more sensitive technique such as ESCA would be necessary to determine the functionality unambiguously.

An alternative approach to modifying PE surfaces has been to initiate a radical polymerization to graft a hydrophilic polymer onto the oxidized surface using UV radiation or a radical initiator.[6,9,10,45] As well as other uses described here, it has been shown that ultrasound can also be used to initiate radical polymerization.[14,46] Another common method of modifying surface functionality is the introduction of silicon-containing species. In an attempt to determine whether the ultrasound method could be useful in this area, a reaction was carried out on oxidized PE films under the same conditions as those in Table 3 using a 5% solution of trimethylsilyl methacrylate in 3:1 water:isoproyl alcohol. The resulting film was found to have a contact angle of 44°, clearly showing that a high degree of reaction had occurred with this system. The ATR-IR spectrum of this sample, Figure 9, shows an absorbance at 1742 cm^{-1} due to the carbonyl of the silyl ester group.

Further Discussion. Although it is a rather straightforward technique, the measurement of contact angles is a sensitive indication of the chemical nature of a surface[5] in terms of the outermost 10−100 Å. The significant changes measured in this work indicate that properties of this region are being considerably modified. It is well recognized that one effect of cavitation is the erosion of surfaces. This roughening could, in principle, change the contact angle. However, in this case, it would be expected to increase the value rather than the observed decrease. Furthermore, the relatively large droplet size used for measurements would be expected to minimize any inaccuracies introduced.[47] Although ATR-IR spectroscopy is very sensitive, the depth of material sampled depends on the incident angle of the IR beam but is of the order[5] of 1000−10000 Å and also depends to some extent on the orientation of functional groups in the beam. Hence, in some cases, surface changes cannot be detected by this method and it can be regarded as complementary to the contact angle measurements.

The goal of this work was to provide a method to modify the surface properties of polymers using relatively mild reagents in an aqueous system. We have shown that, by using ultrasonic enhancement, this can be achieved using hydrogen peroxide or, more effectively, using persulfate salts. Oxidation by potassium persulfate proceeds initially through the generation of surface hydroxyl groups which are oxidized further to give carboxylic acids and esters. At extended sonication times, the oxidation layer produced gave a similar contact angle to the more conventional chromic acid oxidized samples although the spectroscopic results suggest that the oxidation is limited to a region of the polymer surface much less than 1 μm. This is due in part to the lower operating temperatures which the sonochemical acceleration allows so that the polymer surface is harder and reagents do not penetrate the polymer. The oxidation functionality gives sites where further modification such as grafting of polymers or other hydrophilic molecules can be performed.

The question of the precise mode of action of the ultrasound remains uncertain. The acceleration of radical production is not sufficient to explain the enhanced oxidation and some modification to the surface or interfacial interactions is achieved. Under some circumstances[26] the impact of the microjets arising from cavitational collapse can remove significant amounts of material from the surface. However, under the conditions used in this work, no changes or surface damage to the PE films was visible although some microscopic changes were noticable under high magnification. However, the impacts will produce local heating and appreciable deformation of the surface. Although no chain breakage has been detected, this is another possible source of the enhanced surface reactivity.

Bamford and Al-Lamee[16] found that persulfates could be used to produce reactive sites on the surface of a range of polymers including polyolefins. In their process, temperatures in the range of 70−100 °C were used for the oxidation and the grafting was carried out as a second step, initiated by, for example, Ce^{4+}. In our work, we have achieved comparable results on polyethylene at much lower temperatures and without the need for a separate graft initiator. Hence, in principle, the sonochemical reaction could be carried out as a single-step process with sequential addition of reagents under mild conditions. Since polyethylene can be regarded as an inert surface, sonication may well have a role to play in the activation of other polymer surfaces. Under the conditions used here, the process is relatively slow but equipment is now available to operate at higher power densities and much higher scale.[33,48] The results from this work further suggest that the degree and nature of the surface functionality could be controlled to some degree by varying the sonication time, sound intensity, and reaction temperature.

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References and Notes

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