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Microwave-Induced Chemistry at Functionalized Polyethylene Surfaces

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Polymer surface chemistry is an area of practical and academic interest.[1] A principal concern in this area is the development of methods that selectively introduce, manipulate, and affect functional groups at surfaces. In the case of functionalized polymer surfaces that are commonly produced in modification of nonpolar polymer films,[2–4] good selectivity for chemistry at the surface versus the bulk can often be achieved in the initial functionalization chemistry either through the use of highly reactive reagents or through the use of reagents or solvents that minimally interact with bulk polymer. However, mild methods by which the initial functional groups can be further modified remain of interest. In addition, the surfaces formed often are high-energy surfaces which can reorganize and reconstruct on heating.[5–7] Such reconstruction alters the location of functional groups vis-à-vis the polymer/solution interface typically by movement of the polar groups into the organic polymer matrix. Here we describe preliminary results which show that microwave energy is a useful alternative to bulk heating for inducing both chemical changes and surface reorganization. This is evidenced in a mild procedure for esterification or esterification/ketalization of chromic acid-etched polyethylene (PE–[CO_2H]) and annealing of a sulfonated polyethylene (PE–[SO_3H]). In both cases, microwave radiation inputs energy selectively into a polar surface or surface phase.

Microwave radiation is absorbed and dissipated in a medium in the form of heat. The extent of heating depends on a number of factors including the dielectric constant of the medium being irradiated.[8] Many organic polymers including polyethylene are low dielectric media. It is common knowledge that such materials heat slowly in a microwave in comparison with a high dielectric medium. We have found that it is possible to use the disparity in microwave heating of a bulk nonpolar polymer and a polar surface phase to affect chemical processes involving surface groups.[9,10]

Formation of carboxylic acid esters from carboxyl groups is a relatively facile process. For chromic acid-etched polyethylene film (PE–[CO_2H]), routes analogous to solution state methods can accomplish this transformation.[3b,c] These include the use of diazomethane as well as multistep procedures involving activated carboxyls (e.g., acid chlorides) as intermediates at 25 °C. However, Fischer esterification (e.g., with 1-octanol/H^+ catalyst)[6] requires longer times (e.g., 72 h at 40 °C). We verified this using oxidized polyethylene and methanol at 25 °C for 1 h showing that little esterification occurred (Table I below). We have found that irradiation of PE–[CO_2H] coated with polar alcohol solutions containing catalytic acid using an ordinary microwave accelerated esterifications.

IR analysis of the carbonyl region of PE–[CO_2H] coated with a thin film of methanol containing methane sulfonic acid as a catalyst after irradiation with microwaves showed substantial esterification (Figure 1). The changes in the IR spectra in this carbonyl region paralleled changes in surface wettability listed in Table I. Experimentally, a thin film of the reagent mixture (CH_3OH/CH_3SO_3H, 20/1 (w/w)) was applied to the PE–[CO_2H] before microwave exposure by simply dipping the film into a methanol solution containing methanesulfonic acid. To avoid bulk heating of the polyethylene films, repeated short microwave exposures (30 1-min exposures with a low power setting of a standard 2.45-GHz kitchen microwave) were used. In a typical experiment, two films samples were placed in loosely covered polystyrene Petri dishes on a rotating carousel on either side of a separate beaker containing 100 mL of water. Other experiments with other alcohols that have high dielectric constants were similarly successful. For example, use of 1,2-dihydroxyethane in place of methanol also led to clear changes in the carbonyl groups of PE–[CO_2H] (Figure 1b) presumably through esterification and/or ketalization.

Microwave irradiation induces other thermal processes in organic and polymer chemistry.[9,10] As is shown in Figure 2, contact angle analysis indicates that a sulfonated polyethylene anneals in a microwave just as it does on heating in vacuum.[11] However, unlike vacuum heating which is a bulk process requiring longer periods of time, the microwave process is quite rapid. Using an inexpensive 500-W microwave at a low power (220 W) setting, the sulfonated film reorganization is complete in about 30 s in a microwave using the setup described above.

The time frame for microwave annealing of the sulfonated surface is significantly different than that for thermal annealing. Figure 2 shows the differences seen

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Table I. Wettability Changes in Functionalized Medium-Density Polyethylene from Microwave Treatment[a]

sample	θ_a (deg)	θ_r (deg)
PE–H	110	78
PE–[CO_2H]	64	26
PE–[CO_2CH_3][b]	100	40
PE–[CO_2CH_3][c]	85	25
PE–[CO_2H]·[$HOCH_2CH_2OH$][d]	77	16
PE–[CO_2H]·(CH_3OH/CH_3SO_3H)[e]	71	25
PE–[CO_2H]·($HOCH_2CH_2OH/CH_3SO_3H$)[e]	64	18

[a] Contact angles were measured using the pendant drop technique with doubly distilled water and are the average of 6–8 measurements. The estimated error in these values is ±2°. [b] This ester was prepared from the carboxylated surface by successive treatment with $SOCl_2$ and CH_3OH. [c] This ester was prepared from the carboxylated surface by microwave treatment using CH_3OH/CH_3SO_3H. [d] This sample was treated with ethylene glycol in the presence of 10% CH_3SO_3H using microwave irradiation to accelerate esterification and acetal formation. [e] This sample was a control film treated with either methanol or ethylene glycol and 10% CH_3SO_3H but without microwave irradiation.

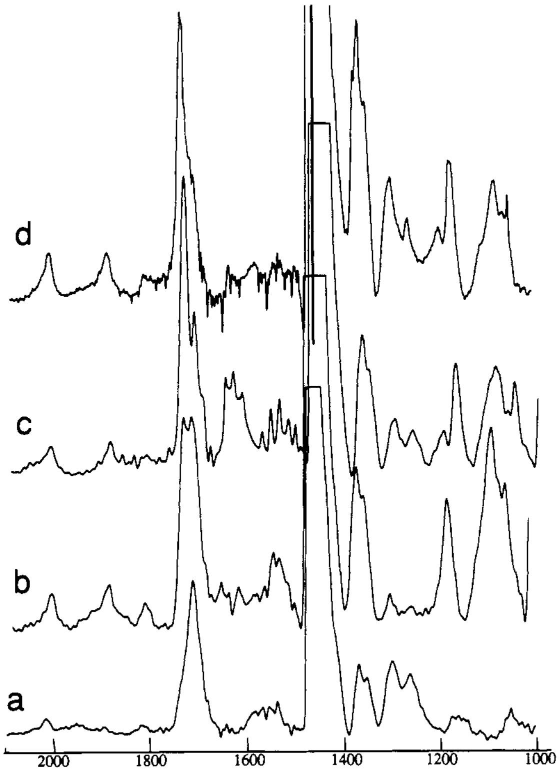

Figure 1. ATR-IR spectra showing changes in the region 1000–2100-cm^{-1} region: (a) initial PE–[CO_2H]; (b) PE–[CO_2R], R = ethylene glycol; (c) PE–[CO_2CH_3] from microwave irradiated PE–[CO_2H] in the presence of CH_3OH containing a 10% CH_3SO_3H (catalyst); (d) PE–[CO_2CH_3] from PR–[CO_2H] after $SOCl_2$ and CH_3OH treatment without microwave irradiation.

in advancing water contact angles θ_a for sulfonated surfaces heated in vacuum microwave. In general, vacuum heating at 70 °C requires about ten times longer to reach the point where further changes in surface wettability cease.

The changes in contact angle as a function of annealing time in microwave or thermal annealing seen in Figure 2 were manifest in quantitative analysis[11] and XPS analyses too. For example, a sulfonated medium density polyethylene films initially had a starting θ_a value of 61° (±2°), a titrable value of [$-SO_3H$] of 9.8×10^{-10} mol/cm^2 (±0.4 × 10^{10} mol/cm^2) and a S/C atomic ratio of 0.040 (±0.004) in XPS analysis using 300-W Mg Kα X-rays with a 75° takeoff angle. After 3 min of microwave annealing or 360 min of thermal annealing (in vacuo at 70 °C), these values changed to 51°, 10.1×10^{-10} mol/cm^2, and 0.036 for the microwaved sample and 52°, 7.8×10^{-10} mol/cm^2, and 0.026 for the thermally annealed sample, respectively. These effects are summarized in Figure 2 where similar changes in the θ_a values are seen in both experiments. However, while little change is seen in the [$-SO_3H$]$_{surface}$ by quantitative analysis with reactive dyeing for microwave annealing, a significant decrease was seen for [$-SO_3H$]$_{surface}$ in thermal heating.

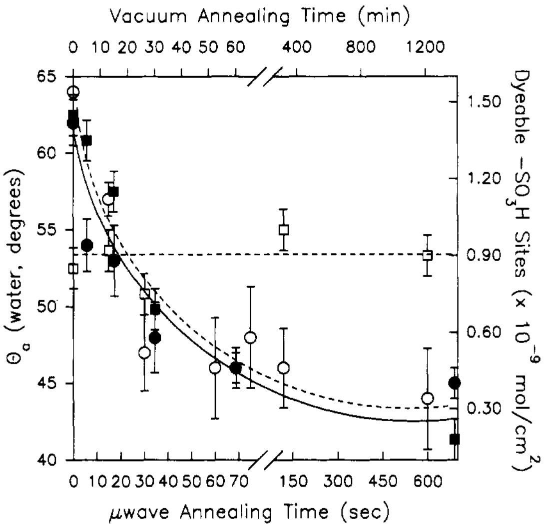

Figure 2. Microwave annealing at ambient temperature at a nominal power of 220 W (- - -) and thermal (—) annealing (70 °C) in vacuum of medium density PE–[$-SO_3H$] showing the changes in dyeable [$-SO_3H$] (□ and ■) and on advancing water contact angle (○ and ●) for microwave and thermal annealing, respectively, as a function of annealing time. The error bars for contact angles were measured standard deviations for eight measurements on the same sample. Errors for dyeing experiments were estimated to be $\pm 0.4 \times 10^{-10}$ mol/cm^2.

In the case of high density polyethylene and polypropylene, initial θ_a, XPS$_{S/C}$, and [$-SO_3H$]$_{surface}$ values were 81°, 0.018, and 3.5×10^{-10} mol/cm^2. After annealing in vacuum for 12 h or annealing in a microwave for 60 s these values changed to 73°, 0.014, 2.5×10^{-10} mol/cm^2, 76°, 0.017, and 3.2×10^{-10} mol/cm^2, respectively. Sulfonated polypropylene underwent similar changes with θ_a and [$-SO_3H$]$_{surface}$ values after sulfonation, after vacuum annealing and after microwave annealing being 89°, 76°, 86°, 1.3×10^{-10} mol/cm^2, 0.5×10^{-10} mol/cm^2, and 1.3×10^{-10} mol/cm^2, respectively. While the XPS$_{S/C}$ values for HDPE–[$-SO_3H$] are within our estimated experimental error (as were the even smaller XPS$_{S/C}$ values for PP–[$-SO_3H$], the other values show the same effects seen in Figure 2. The lower concentration of surface sulfonic acid groups in high density polyethylene and polypropylene evidently did not change the effects seen for sulfonated medium density polyethylene that had higher concentrations of [$-SO_3H$]$_{surface}$ groups. Control experiments showed unfunctionalized polyolefin films do not absorb any detectable amount of methyl red and have no sulfur detectable by XPS spectroscopy.

The simplest explanation of these effects is the shorter timeframe of the microwave process. However, our work cannot exclude other explanations involving subtle interactions of microwaves in the oven cavity with solid films. Regardless of the origin of these effects, our results show that microwave annealing produces equivalent hydrophilicity increases but with less change in the overall structure of the surface interphase. In both thermal and microwave annealing, the contact angles gradually changed to about the same extent to a more hydrophilic value. However, in thermal annealing, a decrease in dyeable [$-SO_3H$] groups occurred concomitant with the contact angle changes. In contrast, the surface concentration of dyeable [$-SO_3H$] groups in the microwave experiment was unchanged. While the surface selectivity of a dyeing experiment in which a sulfonated surface is treated with the basic azo dye *p*-methyl red in CH_3CH_2OH is unknown, S/C atomic ratios measured by XPS spectroscopy changed in thermal annealing experiment but changed little in the microwave experiment. These experiments together suggest that changes in the contact angle interface occurred more selectively with microwave irradiation.

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