Polymer Bulletin 53, 401–412 (2005)
DOI 10.1007/s00289-005-0344-y

Polymer Bulletin

New Pathways for Modifying the Surface of High Density Polyethylene: Chemically Benign Adhesion Promotion and Subsequent Reactivity

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Received: 5 September 2004 / Revised version: 20 January 2005 / Accepted: 26 January 2005

Summary

The surface of high density polyethylene (HDPE) was modified using a two-step chemical process. HDPE panels were initially immersed in a heated, aqueous hypochlorite solution containing a carboxylic acid promoter and quenched with deionized water at room temperature following a heterogeneous chemical reaction process patented by Beholz *(U.S. Patents 6,077,913 and 6,100,343*). 1-5 mole percent chlorine heteroatoms were identified on the resulting HDPE surface using ESCA techniques. The surface chlorine concentration was optimized as a function of reaction time, reaction stoichiometry and number of repeated chemical treatments. The chlorinated HDPE surface was subsequently exposed to ultra-violet (UV) light and surface alkene moieties were noted using ATR FT-IR methods along with a concomitant reduction in surface chlorine from ESCA measurements. The photochemically induced free radical surface dehydrochlorination mechanism was observed to follow first-order kinetics and potentially produce a focussed pattern for information storage. Facile subsequent reactivity of the isolated surface alkene groups was demonstrated using electrophilic addition of Br_2. Furthermore, poly(4-hydroxy styrene) architectures were covalently tethered to either the chlorinated or unsaturated HDPE surface in an effort to ultimately tailor surface polarity and adhesiveness as well as create laminate poly(α-olefin) containing structures. This economical and benign surface chlorination/photochemical two-step treatment process produced relatively small disposal risks as well as no apparent polymer degradation.

Introduction

Despite the engineering versatility of metallocene catalyzed high density polyethylene (HDPE), its pristine surface is *non*-polar and has no inherent attraction to conventional paints as well as inorganic or organic based glues. The most common method used to improve paint adhesion in HDPE is blending with paintable, less inert, less robust thermoplastic polymers. Nevertheless, the resulting thermoplastic polyolefin (TPO) blends are generally far less mechanically sturdy than virgin HDPE, easily abraded prior to painting and much more expensive. In efforts to mitigate the high cost and poor mechanical properties of TPO blends, a number of physical and chemical treatments have been developed to significantly increase the polymer's total surface tension and concomitant adhesion. Sources used to modify the HDPE surface include flame, laser, ultraviolet radiation as well as discharge from electrical corona or plasma. These physical methods produce a combination of both desirable as well as undesirable chemical and morphological modifications including crosslinking, oxidation, grafting of active/polar groups, chain scission, ablation and roughening at the polymer surface [1]. Nevertheless, each physical treatment listed above possesses at least one major drawback such as ephemeral-transient modification, photosensitizer requirement, extreme expense or extensive technical complexity. The HDPE surface can also be oxidized using mixtures of concentrated, corrosive mineral acids combined with inorganic salts. However, these solutions pose severe handling and disposal risks with the potential of degrading/compromising the polymeric surface. Hence, other solutions are clearly desired. Much effort has been expended in order to find a safe, inexpensive and relatively mild post-manufacturing chemical means of tailoring the polarity of the HDPE surface including direct *photo*-initiated free radical surface grafting reactions of acrylic acid and acrylamide monomers [2].

A technology was developed in our laboratory that relies on initially immersing the HDPE substrate in a dilute aqueous solution containing a chemical oxidizer and a carefully chosen carboxylic acid as described previously [3-5]. Although permanent, the halogen moiety created by the initial chemical surface modification can be subsequently reacted photochemically to produce a still more versatile alkene moiety. The isolated alkene moieties can be used as a starting template for organic chemistry at the poly(α-olefin) surface in an effort to ultimately tailor the adhesiveness and/or polarity. Furthermore, the surface alkene moieties can be used to covalently tether macromolecules as detailed herein.

Experimental

Materials

0.125 inch thick and 4 inch high injection molded HDPE (Union Carbide DMDA 8007 NT7) engineered test plaques were cut into 1.00 inch wide rectangular panel strips. 4-hydroxyphenylmethylcarbinol (4-HPMC) and poly(4-hydroxystyrene) branched grade (PHS-B) [6-8] were donated by DuPont® Electronic Polymers (Dallas, Texas) and used as received. Reagent grade methanol, sodium hydroxide, bromine, *n*-pentane, toluene, ethylbenzene, acetic anhydride ($(CH_3CO)_2O$), glacial acetic acid, concentrated sulfuric acid and succinic acid were purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. Ultra Clorox® bleach (6.00% aqueous sodium hypochlorite) was used as received. West Marine West Coat® epoxy resin 105/hardener 205 and cynoacrylate adhesives were used as received.

Surface Modification Chemical Reactions

Surface Chlorination

140 ml of 6% aqueous sodium hypochlorite (NaOCl) solution was magnetically stirred while being heated to 85°C in air. Immediately after dropwise addition of 3 ml

of acetic anhydride, a HDPE test panel was immersed in the solution and allowed to react heterogeneously for a prescribed amount of time. A 10°C increase in temperature was consistently observed upon addition of the acidic promoter due to a reaction exotherm. The reaction was quenched by pouring both the hot solution and polymer into 2 L of room temperature deionized water. The polymer was isolated, subsequently dried in air at room temperature and completely covered from room light.

Surface Dehydrochlorination

NaOCl/acetic anhydride treated (*i.e.* surface chlorinated) HDPE was continually exposed to a relatively soft (20 Watt, 16 footcandle intensity), long wave mercury ultra-violet (UV) laboratory lamp (F20T12-BL, General Electric, GE®, Fairfield, CT) at ambient conditions. The separation distance between the light and polymer surface was held constant at 7.0 mm. The resulting irradiated surface was characterized at prescribed exposure times for chemical structure using both Electron Spectroscopy for Chemical Analysis (ESCA) and attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy techniques as well as for wetting contact angle.

Polymer Grafting Reactions

Chlorinated Surface

A 1”x 4” HDPE test panel that was previously reacted heterogeneously with $(CH_3CO)_2O/NaOCl$ at 95°C for 6 minutes, quenched and dried as described hereinabove, was cut length-wise and width-wise into 8 equal parts. The HDPE panel parts were suspended in a homogeneous PHS-B/NaOH solution in methanol solvent [9-10]. The blood red phenoxide solution was gently stirred magnetically in a 3-necked flask at room temperature under nitrogen. The system was allowed to react heterogeneously for 4 hours at room temperature and then neutralized with 10% HCl (aq). The resulting modified HDPE was carefully isolated, rinsed with excess methanol and finally dried in air completely covered from room light.

Alkene Surface

In the first case, a HDPE plaque that was previously surface chlorinated and UV irradiated for 720 hours was simply suspended in bromine (Br_2) liquid and gently stirred for 20 minutes at room temperature in air within a fume hood. In another set of experiments, a 1”x 4” HDPE test panel that was treated with $(CH_3CO)_2O/NaOCl$ at 95°C for 6 minutes, quenched, dried and subsequently UV treated for 600 hours as described hereinabove, was cut length-wise and width-wise into 8 equal parts. The HDPE panel parts were place in a 3-necked flask and suspended in a 7:1 mole ratio solution of glacial acetic acid and 4-HPMC under nitrogen [6-8]. A catalytic amount of concentrated sulfuric acid was added and the ice bath subsequently removed. The flask was allowed to gradually warm to room temperature wherein the HPMC all dissolved. The reaction was stirred overnight at room temperature under $N_2(g)$. The reaction was poured into a large excess of room temperature deionized water. The resulting modified HDPE was carefully isolated from the white PHS-B homopolymer precipitate, rinsed with excess deionized water and dried in air covered from room light.

Characterization

Electron Spectroscopy for Chemical Analysis (ESCA) was performed on a VG Microtech (East Sussex, England) ESCA-Q spectrometer equipped with a MgKα X-ray source (1253.6 eV) and operated at 120 W (8 kV and 15 mA). Surface elemental analysis was accomplished by integrating the atomic% of chlorine (Cl) *2p*, carbon (C) *1s*, oxygen (O) *1s* as well as bromine (Br) *3d and 3p* absorptions from high resolution ESCA spectra using the corresponding atomic sensitivity factors. The standard deviation for atomic compositions calculated from ESCA was approximately ±5%. All infrared spectra were recorded on either a Thermo Nicolet® Avatar 360 E.S.P. Fourier transform infrared spectrometer operating at a resolution of 2 cm^{-1} in attenuated total reflectance mode using a cesium iodide (CsI) plate. Gas chromatography/mass spectrometry (GC/MS) analysis was accomplished using an Agilent® 5973N GC/MS system equipped with a splitless front inlet and a HP-5MS capillary column (Agilent model number 19091S-233, 0.25 mm x 30m x 1μm, 250 μm nominal diameter). Initial flow was set at 1.0 ml/min and the average velocity was 36 cm/s. MS scans were taken from 35-550 amu. Adhesion strength was tested at 22.0±1.0°C using an Instron® 8511 dynamic tensile testing apparatus with a 5 inch initial jaw separation, 0.05 inch/minute separation rate and polymer samples in lap-shear geometry according to American Society for Testing and Materials (ASTM) test D3163–96. For tensile testing, either Loctite Prism 401® cyanoacrylate adhesive or West Marine West Coat® epoxy resin 105/hardener 205 was first applied to the treated polymer's surface. The rectangular strips were then overlapped by 1.000±0.005 $inch^2$ surface area and glued (polymer-adhesive-polymer). Adhesive strength values were reported as average tensile force (lb_f) at adhesive failure for 3-10 samples. Contact angle measurements were made using an AST 2500XE Video Contact Angle System [ASTM D5725-97] with ≤ 2 μL sessile drops of either 99% methylene iodide or *ultra*-filtered triple distilled water [ASTM D1193]. Surface tension was calculated from contact angles using the geometric mean method [11]. Aggressive paint adhesion testing was done at Technical Finishing, Incorporated, Flint, Michigan [ASTM D3924–80] according to the paint performance approval tests of the General Motors (GM®) Corporation (Detroit, Michigan). These tests included the GM4388M paint performance flexibility test; GM9071P-A & B and GM9502P tape adhesion tests [rigorous versions of ASTM D3359-97]; GM9502P knife crosshatch/crosscut test [ASTM F1842-97 and ASTM D3359-97] and GM4465P 96 hour humidity-adhesion test [ASTM D2247-97] with rinse evaluation followed by size 8 blister qualitative distribution/density analysis according to the ASTM D714-87 standard test method. The Pittsburgh Paint and Glass (PPG®) brand paint system used for this study consisted of either PPG® white basecoat (CBCK9753A,B; DFT=1.3 mils) or PPG® Galaxy® silver basecoat (CBC519; DFT=0.8 mils) with PPG® basecoat catalyst (CAT123) using a basecoat letdown of 0.5% by volume with CAT123; as well as 2K clearcoat (TKU200B DFT=1.8-2.0 mils) and clearcoat catalyst (CAT110) with a clearcoat letdown of paint:catalyst = 3.0:1.0 by volume. Paint films of uniform thickness were produced according to the ASTM D823-95 test specifications.

Results and Discussion

A broad, monomodal ESCA absorption centered at a binding energy of 202-205 eV was observed in the treated polymer spectra as shown in Figure 1. This absorption was identified as a superposition of the $2p^{1/2}$ and $2p^{3/2}$ electrons of chlorine heteroatoms on the treated HDPE surface. The ESCA Cl *2p* absorption was not observed in the untreated HDPE spectra. Carbon *1s* electrons (287 eV binding energy) as well as a small amount of oxygen *1s* electrons (535 eV) were also noted on the untreated HDPE surface using ESCA techniques. Polar oxygen containing functionalities on the HDPE surface have been previously noted to result from thermal oxidation catalyzed at the mold surface during melt processing [11-12]. Nevertheless, no consistent increase in surface oxygen concentration was observed using ESCA upon treatment of HDPE with heated NaOCl/$(CH_3CO)_2O$ solutions.

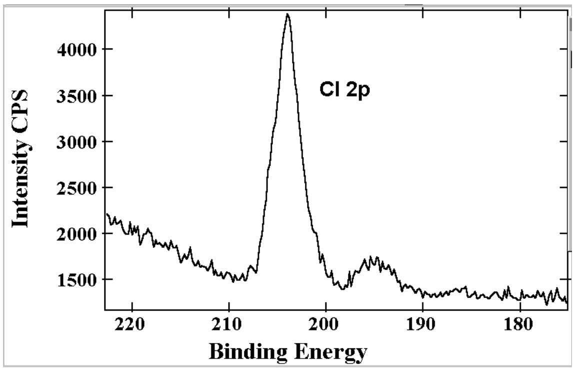


Figure 1. ESCA Cl $2p^{1/2}$ and $2p^{3/2}$ absorption for HDPE polymer surface treated with NaOCl (aq)/$(CH_3CO)_2O$ at 85°C for 2 minutes.

Using ESCA techniques the surface concentration of chlorine was determined to lie between 1 and 5 mole% as a function of treatment time and chemical reactants used as shown in Figure 2. Hence, a maximum of about 6 mole% of surface ethylene ($-CH_2-CH_2-$) monomers were observed to be *mono*-chlorinated on average using NaOCl/$(CH_3CO)_2O$ at 85°C (Figure 2).

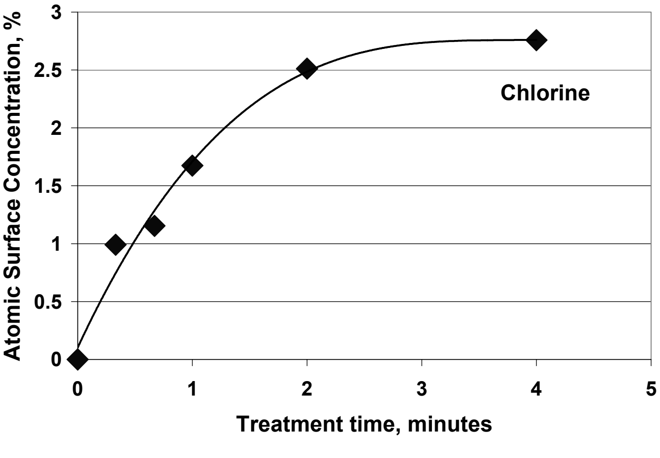


Figure 2. Mole percent chlorine versus reaction time characterized by ESCA for 9.25 in^2 surface area of HDPE surface treated with a solution of 140 ml of 6% NaOCl (aq) and 3 ml of $(CH_3CO)_2O$ at 95°C.

Although the extent of chlorination here appeared modest, treatment for 2-4 minutes was observed to significantly enhance the wettability, surface tension and lap-shear tensile adhesive strength of the polymer surface. For example, the average water contact angle was observed to decrease from 93° to 81° whereas the polar surface tension component (γ_p) was observed to increase from 1.2 to 6.0 dynes/cm for treatment times up to 3 minutes (Figure 3). Nevertheless, the dispersive surface tension component (γ_d) was observed to remain virtually constant at 31.6 dynes/cm as shown in Figure 3.

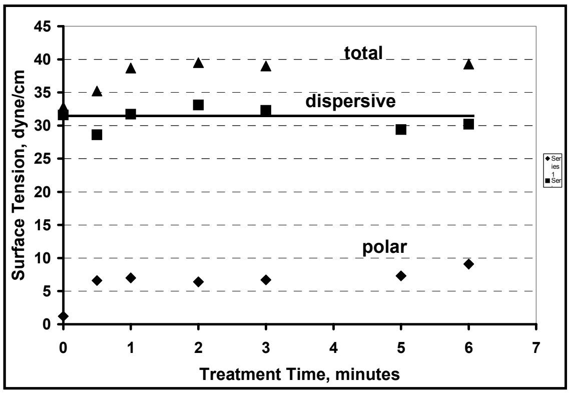
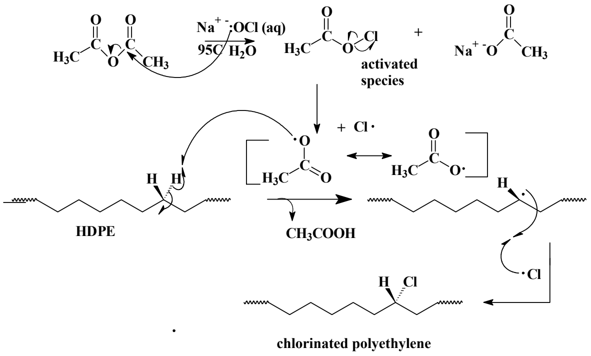


Figure 3. Surface tension analysis from static contact angles measured with H_2O and CH_2I_2 sessile drops at 25°C for HDPE treated with NaOCl (aq)/$(CH_3CO)_2O$ at 85°C as a function of reaction time.

The replacement of a fraction of the hydrogen atoms by chlorine atoms on the HDPE surface led to a significant increase in the polar force but a negligible increase in the dispersive force due to the large polarizability and weak hydrogen bonding capability of covalent chlorine [13]. The increase in wettability attributed to surface chlorination was observed to level off after one minute of treatment (Figure 2) when the surface chlorine concentration was 1 mole% (Figure 3). Nevertheless, further increases of $[Cl]_{surface}$ up to 2.8 mole% (Figure 2) had no major effect on surface wettability (Figure 3). Hence, the surface tension appeared to be somewhat insensitive to further increases in $[Cl]_{surface}$ beyond the initial change. This phenomena is currently under investigation in our research laboratory. The lap-shear tensile adhesive strength of the HDPE treated for 2 minutes using epoxy glue was 236.7 psi compared to only 28.5 psi for the untreated material. This 8 fold enhancement in tensile adhesive strength was more than enough to render the substrate highly adhesive to both the PPG® white and silver colored paint systems with 0.0% paint removal during tape adhesion peel, cross hatch, cross cut and knife cross hatch paint removal testing. Furthermore, no size 8 blisters were observed post either 96-hour humidity testing or subsequent water rinse.

In another series of experiments, HDPE was treated for 2, 4, and 6 minutes using an aqueous treatment solution comprised of 4% succinnic acid and 6% calcium hypochlorite at 72°C. The resulting lap-shear tensile adhesive strengths using epoxy adhesive were 112, 154, and 225 psi respectively for the indicated treatment times in cohesive failure mode compared to 28.5 psi in adhesive failure mode for the untreated case. The tensile adhesive strength was observed to increase linearly for reaction times up to 6 minutes using the NaOCl//$(CH_3CO)_2O$ system. Our research has shown that the surface chlorine concentration at the molecular level is somewhat proportional to the adhesive strength observed on the macroscopic engineering mechanical level. Nevertheless, the lap shear tensile adhesive strength with cyanoacrylate glue was observed to remain constant at 130±10 psi for HDPE treated up to seven times repetitively with the $NaOCl/(CH_3CO)_2O$ system at 95°C for 6 minutes each time. An adhesive *structure-property* relationship was observed. Epoxide-amine and ether aromatic polyurethane type glues adhered very well to the chlorinated HDPE surface. Sanding/abrading the HDPE surface (ASTM D2093-97) prior to treatment was not observed to significantly enhance the tensile adhesive strength irregardless of the particular glue used. The single step-rinse, post-manufacturing, paint adhesion promotion process possesses the advantages of being aqueous based, chemically benign, quick, inexpensive (*i.e.* treatment reagent cost ≤ \$0.25/100 ft^2 HDPE surface area), while not effecting pre-existing pigmented colors. Furthermore, this process is environmentally benign since the used treatment solution and gaseous effluents, Cl_2 and RCOOH, can be conveniently neutralized with $NaHSO_3$ and either NaOH or $NaHCO_3$ respectively.

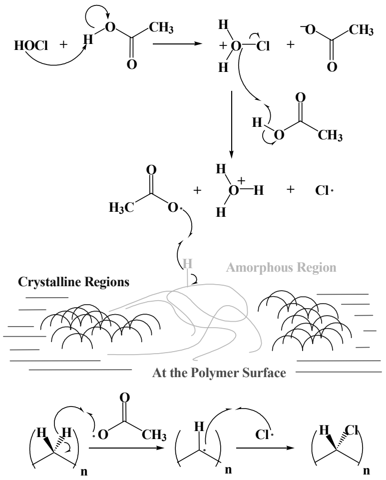
One plausible mechanistic pathway for this novel, heterogeneous surface treatment is the initial production of an acyl hypochlorite (chlorine carboxylate) activated oxidizer species from the reaction of the hypochlorite ion with the acidic promoter as shown in Scheme 1.



Scheme 1. Hypothetical chemical reaction mechanism pathway using acetic anhydride as the promoter.

The acyl hypochlorite is hypothesized to subsequently react *in situ* by releasing a chlorine radical and extracting a hydrogen atom from a methylene group on the HDPE substrate surface [14-15]. This mechanistic step produces a carbon radical on the polymer backbone as well as the corresponding carboxylic acid molecule *by*-product. The backbone carbon radicals remaining on the polymer surface chains are hypothesized to react with the previously released chlorine radicals ultimately yielding the observed chlorinated polyethylene surface. An alternative hypothetical free-radical mechanism using acetic acid as the reaction promoter is illustrated in Scheme 2 where free-radical attack was envisioned primarily on the amorphous phase of the HDPE surface. A third plausible theoretical mechanism involves free radical chlorination of the polymer following hydrogen abstraction from the HDPE backbone by hydroxyl radicals, produced from the reaction of hypochlorous acid (HOCl) with the acidic promoter.

Immersion of HDPE into an aqueous treatment solution of 6% sodium hypochlorite at 85°C at 2 minutes after addition of the acetic anhydride promoter was observed to cause a three-fold reduction in surface chlorine concentration compared to HDPE immersion immediately after promoter addition as determined using ESCA techniques. Hence, the chemical reactivity and resulting surface chlorine concentration appear to be maximum during the initial reaction stage. These results were in agreement with a mechanism favoring formation of a highly reactive acyl hypochlorite type activated species. Nevertheless, eventual production of a chlorine free radical species (Cl·) is hypothesized here *via* radical cleavage of the *in situ* generated hypochlorous acid (HOCl) and/or molecular chlorine (Cl_2). Further evidence for simple *mono*-chlorination of the HDPE surface using $(CH_3CO)_2O$/NaOCl was provided by analogous chemical reactions with model small molecular weight compounds. Heterogeneous reaction of *n*-pentane with $(CH_3CO)_2O$/NaOCl at pH=4 and room temperature for 24 hours yielded a mixture of 1-, 2- and 3-chloropentane derivatives as evidenced using GC/MS techniques. In addition, reaction of either toluene or ethyl benzene with $(CH_3CO)_2O$/NaOCl under identical conditions yielded predominantly benzyl chloride (α-chlorotoluene) or a combination of 1- and (2-chloroethyl)benzene derivatives respectively.



Scheme 2. HDPE surface treatment reaction scheme using acetic acid as the promoter.

Branched poly(4-hydroxy styrene) (PHS-B) was heterogeneously reacted with surface chlorinated HDPE in methanol as detailed hereinabove [6-8]. The resulting grafted polymer surface had an average water contact angle of 39°, which was very close to the water contact angle of PHS-B (38°). The average water contact angle of the NaOCl/$(CH_3CO)_2O$ treated HDPE chlorinated surface prior to grafting PHS-B was 51° [13]. Hence, despite the steric restrictions conventionally associated with grafting macromolecules to polymer surface substrates, PHS-B was apparently covalently tethered to the HDPE surface using a facile Williamson ether synthesis. Covalent ether bond graft formation, as depicted in Figure 4, was envisioned to proceed *via* an oxygen-alkylation of the phenoxide ion [9-10]. The polar nature of both the chlorine and phenol substituents would likely cause collapse of the tethered PHS-B onto the chlorinated HDPE surface unlike Figure 4. Hence, a relatively small concentration of covalent ether grafts would result in significant overall coverage of the HDPE surface area by PHS-B in agreement with the static wetting contact angle data.

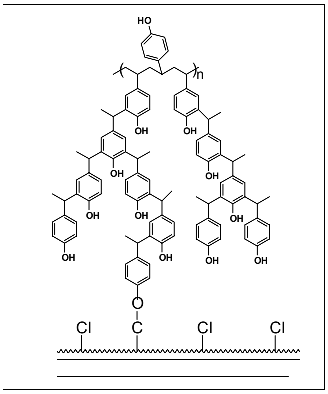
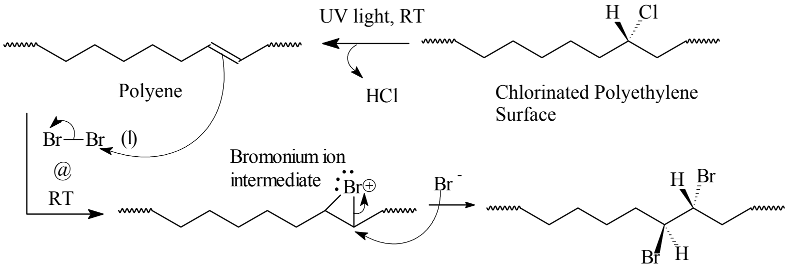


Figure 4. PHS-B covalently tethered to the chlorinated HDPE surface.

Exposing the effectively chlorinated polymer surface to ultraviolet (UV) light in air at room temperature (*i.e.* ambient conditions) yielded isolated alkene groups (carbon-carbon double bonds or unsaturations) with a concomitant decrease in chlorine on the polymer surface as shown in Scheme 3. Alkene formation and chlorine loss were observed using both attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) (indicated by a broad alkene absorption centered around 1650 cm^{-1}) and ESCA spectroscopic techniques (noted by a concomitant monotonic decrease in the chlorine $2p^{½}$ and $2p^{3/2}$ absorptions centered at 202-205 eV).



Scheme 3. Photochemical treatment of the chlorinated HDPE surface followed electrophilic addition of bromine (Br_2).

NaOCl/acetic anhydride treated (*i.e.* surface chlorinated) HDPE was continually exposed to relatively soft laboratory UV light at ambient conditions and chlorine loss was quantified over time using ESCA techniques as shown in Figure 5. The *photo*-induced free radical dehydrochlorination reaction was observed to be first-order in surface chlorine concentration $[Cl]_{surface}$ with a reaction rate constant (*k*) of $9x10^{-7}$ s^{-1} as shown in Figure 6. A homolytic, free-radical *photo*-induced dissociation reaction lead to carbon-carbon double bond formation with concomitant cleavage and ejection of HCl (*i.e.* surface dehydrochlorination). It is hypothesized that the amorphous regions of the HDPE surface were more susceptible to initial chlorination than the crystalline regions of the pristine HDPE surface (Scheme 2). In addition, it is believed that a single chlorine was added to the surface polymer chain monomer units in a region isolated by at least two vinyl group spacers (4 carbon polymer backbone atoms) on average rather than in a consecutive (*i.e.* poly(vinyl chloride) [PVC] like) manner. Hence, the isolated chlorine groups are *photo*-chemically transformed *via* dehydrochlorination into isolated alkene groups rather than the conventional *photo*-chemical degradation pathway of PVC [16].

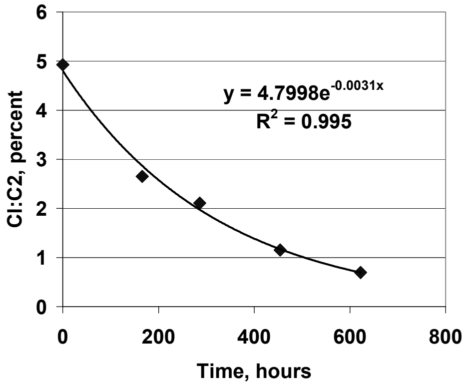


Figure 5. Chlorine concentration (normalized to the carbon *1s* ESCA absorption) as a function of room temperature UV exposure time for HDPE.

Facile electrophilic *anti*-addition of bromine (Br_2) to the alkene groups, confirmed using ESCA techniques with $3d^{5/2}$ and $3p^{3/2}$ bromine absorptions centered at 220 and 95 eV respectively, was carried out by simply immersing the unsaturated HDPE panel surface in Br_2 (*l*) at room temperature in air for 20 minutes in an effort to further demonstrate the surface chemical reactivity and ability to tailor/functionalize the polymer surface as shown in Scheme 3 hereinabove.

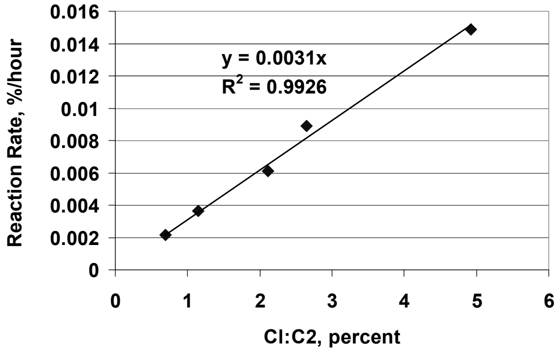
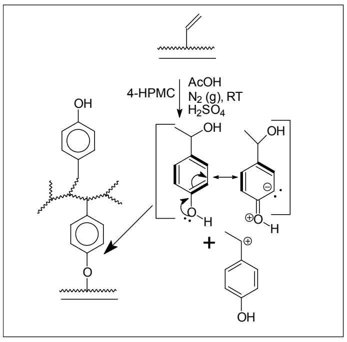


Figure 6. Reaction rate (%Cl/hour) as a function of surface chlorine content at room temperature for HDPE initially treated with NaOCl (aq)/$CH_3(CO)_2O$ at 85°C for 6 minutes.

Macromolecules were also grafted to the unsaturated high density polyethylene surface shown in Figure 7. Branched poly(4-hydroxystyrene) was tethered to the alkene functionalized polyethylene surface using an acid-catalyzed, carbocationic Friedel-Crafts alkylation/polycondensation *ortho*-scaffolding-type polymerization of 4-hydroxyphenylmethylcarbinol (4-HPMC) following the chemistry of U.S. patent nos. 5,554,719 and 5,565,544 by J. Sounik [6-7] as shown in Scheme 4.



Scheme 4. Simultaneous acid-catalyzed carbocationic polymerization of 4-HPMC with hydro-alkoxy addition to surface alkenes *via* cationic intermediate for macromolecular scaffolding on HDPE surface.

The resulting grafted polymer surface had an average water contact angle of 39°, which was very close to the water contact angle of PHS-B (38°). The average water contact angle of the UV treated HDPE unsaturated surface prior to grafting PHS-B was 45° [13].

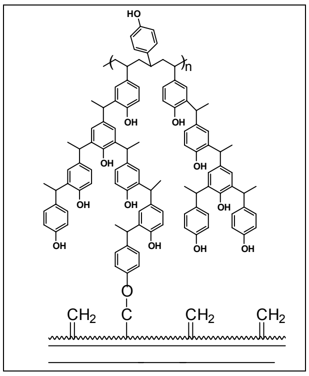


Figure 7. PHS-B covalently tethered to the UV treated, unsaturated HDPE surface.

Conclusions

Treatment of HDPE by the herein described heterogeneous chemical reaction process had the function of adding chlorine to the polymer surface and rendering it adhesive to both inorganic paints and glues. Nevertheless, surface chlorination was not observed to affect the desirable chemical, thermal and mechanical engineering characteristics of the bulk HDPE material, pigment or molded sample geometry. Although the increases in adhesiveness shown here are significant, it is anticipated that far greater chlorination and concomitant adhesive strength can be obtained through continued optimization of surface treatment reactants, reaction conditions, application methods, and adhesive film characteristics. Differences in polymer surface morphology (*i.e.* degree of crystallinity) resulting primarily from changes in cooling rate, mechanical stress and mold surface may significantly effect the maximum achievable bondability [11].

The chlorinated HDPE surface was subsequently exposed to ultra-violet (UV) light and surface alkene moieties were noted using ATR FT-IR methods along with a concomitant reduction in surface chlorine. The photochemically induced free radical surface dehydrochlorination mechanism was observed to follow first-order kinetics and potentially produce a focussed pattern for information storage *via* UV laser treatment. Feng and Ranby [2] have demonstrated efficient grafting of either acrylic acid or acrylamide with 10-20 seconds of UV laser irradiation time following a short pre-soak of the HDPE in the monomer/photo-initiatior solution. While the two-step chemical reaction demonstrated herein ultimately produces an extremely versatile surface alkene moiety, this technology cannot compete with the speed of laser-induced processes such as Feng and Ranby [2] to date. It is hypothesized that increasing the light intensity using a UV laser with $\lambda<355$ nm would increase the efficiency of homolytic C-Cl bond scission and significantly shorten the 600 hours of irradiation required here using a soft laboratory UV lamp [2,16]. Dehydrochlorination reaction kinetics using UV laser treatment on the HDPE surface chlorinated *via* reaction with $NaOCl/(CH_3CO)_2O$ is currently being investigated in our laboratory. Facile subsequent reactivity of the isolated surface alkene groups was demonstrated using electrophilic addition of Br_2. Furthermore, a branched poly(4-hydroxy styrene) architecture was covalently tethered to either the chlorinated or unsaturated HDPE surface in an effort to ultimately tailor surface polarity, hydrophilicity and adhesiveness. In addition, the tethered PHS can be used to create poly(α-olefin)s with laminate coatings *via* conventional urethane, epoxy, novolac or resole condensation step-growth polymerization reactions. This economical and environmentally benign surface chlorination/photochemical two-step treatment process produced relatively small disposal risks as well as no apparent polymer degradation.

Acknowledgements. The authors wish to thank DuPont® Electronic Polymers (Dallas, TX) for the generous donation of both branched poly(4-hydroxystyrene) (PHS-B) and 4-hydroxyphenylmethylcarbinol (4-HPMC) materials for this research.

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