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# Adhesion modification of polyolefin surfaces with sodium hypochlorite in acidic media

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## Abstract

Increased surface adhesiveness of HDPE is achieved by immersing it in an aqueous solution of sodium hypochlorite (bleach) mixed with an acid. This process results in the addition of functionality to the polymer surface vastly altering its adhesive, polarity and surface reactivity. Analysis of the modified polymer surfaces by ESCA has shown that chlorine atoms have been added to the surface. Studies regarding the chlorination of small molecules have also shown that the chlorination process is amenable to a variety of chlorination objectives and offers a route toward the functionalization of a variety of polymeric and non-polymeric substrates. In particular, this treatment renders unpaintable substrates such as HDPE more receptive to application of paints and adhesives. In this paper, we report the results of paint adhesion studies on treated polymer surfaces.

*Keywords:* HDPE; Surface treatment; Adhesion

## 1. Introduction

Polymeric materials provide excellent and versatile mechanical qualities and find use in a wide variety of applications. In certain instances, it is necessary to coat or otherwise modify the surface of polymeric materials to meet adhesion requirements or to provide a protective surface to help the polymeric substrate withstand degradation or abrasion. Providing a high quality durable painted surface on certain polymeric substrates has been problematic due to generally poor surface adhesion qualities exhibited by various polymeric substrate materials. Poor surface adhesion is also problematic in situations in which other laminates, films or metallic layers are to be imparted onto the polymer.

Polymer adhesion technology has been used within the automotive industry for the purpose of rendering polymeric components, such as automotive bumpers and the like, permanently adhesive to paints. The method by which these issues have been most broadly addressed has been to formulate the plastic to be more receptive to the application of the paint. In efforts to mitigate disadvantages associated with these thermoplastic polyolefins (TPOs) there have been a number of attempts to develop methods to chemically modify the surface of more robust polyolefins to render them paintable without substantial blending. These methods have included flame treatment and corona discharge (Wu [1]), UV irradiation (Meister [2]) and bonding of poly (ethylene oxide) to the PE surface (Kiss, Samu, Tóth and Bertóti [3]).

Chemically based adhesion promotion methods have involved the use of strong mineral acids in combination with concentrated mineral oxidants and strong mineral acid salts in aqueous treatment solutions (Orlov, Zaitseva, Sinitysn and Rostovtseva [4]). Treatment of polyolefin materials for adhesive bonding using non-chromate solutions containing sulfuric acid in the presence of either lead dioxide, potassium iodate, or ammonium persulfate were also developed (Rosti, Brook and Levi [5]). Although this later method had eliminated the chromate, other highly toxic oxidizers were used rendering this technology industrially unfriendly. Heretofore, a benign method to render polyolefin surfaces adhesive had not been developed.

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In 1997, a method was developed by which un-reactive polymeric substrates, such as polyethylene (PE), may be rendered adhesive using relatively benign chemicals and in short reaction times (Beholz [6]). This technology relies on immersing or spraying the substrate with a dilute aqueous solution of an oxidizer that has been placed in a kinetically degrading state by the addition of a carefully chosen acid. Numerous paint adhesion studies have shown that this process is simple, robust and results in substantial paintability improvement (Beholz [7]). Analytical studies characterizing the resulting alterations in adhesion, as well as mechanistic considerations are discussed herein.

## 2. Materials and methods

### 2.1. Reagents

Sodium hypochlorite solutions were prepared by dilution of a 15% aqueous sodium hypochlorite solution purchased from PVS Nolwood Chemicals, Inc. 10900 Harper Ave., Detroit, MI 48213, USA, by dilution with distilled water. Optionally, 6% sodium hypochlorite solutions were purchased directly as Clorox® bleach and used without further dilution. Concentrated acetic acid was purchased from either Aldrich Chemical Company, Inc. or PVS Nolwood. All other chemicals were purchased from Sigma-Aldrich unless otherwise indicated.

Test panels were prepared from high-density polyethylene (HDPE) plaques supplied by Standard Plaque, Inc., 17271 Francis Street, Melvindale, MI 48122, USA or other substrates as indicated. Test panels were treated by placement of the panels in an aqueous solution of the oxidizer, or oxidizer with catalyst after the temperature of the oxidizing solution had been brought up to the desired reaction temperature. With vigorous stirring, the acid was then carefully added. In general, the evolution of chlorine gas was observed. The addition of the acid to the oxidizer solution was also observed to be exothermic resulting in a ~10% increase in reaction temperature. After treatment, the panels were rinsed with copious amounts of tap water and then distilled water. The panels were then gently blotted/rubbed dry with paper towel in such a manner so as not to abrade the substrate surfaces. Panels treated under different conditions were always processed in the same manner post-treatment. Since these panels exhibited various adhesion enhancements correlating with the treatment regime, it is thought that post-treatment processing did not significantly affect the resulting adhesiveness.

### 2.2. Analytical procedures

Electron spectroscopy for chemical analysis (ESCA) was executed at Kettering University using a Mg $K_\alpha$ X-ray source (1253.6 eV) measuring to a depth of 3 monolayers. The following binding energies were quantified: C 1s (287 eV BE), O 1s (535 eV BE) and Cl $2p^{1/2}$; and $2p^{3/2}$ (202–205 eV BE). Static contact angle analysis @ 25 °C was executed as sessile drop with $H_2O$ and $CH_2I_2$. Polar, dispersive and total surface tensions were measured (dynes/cm) as well as $\gamma_p$ increases with $t_{rxn}$ and $[Cl]_{surface}$. Tensile strength analysis was executed at Kettering University using an Instron instrument according to tensile test ASTM D3163-96, 1996. Adhesives used in Instron testing were off-the-shelf 3 M 5 min epoxy, cyanoacrylate 'Super Glue' or other adhesives and paints as indicated.

Paint adhesion tests were conducted either in-house or by Technical Finishing, Inc. (TFI) as indicated. For in-house paint adhesion testing, tape adhesion test GM9071P-A and B, was used with off-the-shelf epoxy or polyurethane spray paints such as Krylon and Rust-Oleum brand paints. In general, Ace brand duct tape was used for in-house paint adhesion testing. In-house tests were further executed by attempted manual paint removal from the crosshatched area with the fingernails. Due to the inferior paints used in in-house testing, in-house tests were always found to be at least as severe as third party tests. Panels found to have acceptable in-house paint adhesion always provided excellent adhesion results in third party analyses.

Results of in-house paint adhesion were ranked as 'excellent', 'very good', 'moderate' or 'poor'. Excellent adhesion was assigned a 4, and indicated that very little ($<1\%$) paint could be removed from the painted panel. Very good adhesion was assigned a 3, and indicated that only a slight amount (~2–5%) of paint could be removed. A ranking of moderate was assigned a 2 and indicated that a significant amount (~5–20%) of paint could be removed. A ranking of poor was assigned a 1 and indicated that $>50\%$ of the paint could be removed. In general, adhesion was significant or very poor: i.e. paint adhesion was very good to excellent or poor.

Third party paint adhesion testing by Technical Finishing, Inc. was executed according to tape adhesion test GM9071P-A and B, and GM9502P using a 2 K exterior GM spec. polyurethane paint system [8]. Substrate materials examined included thermoplastic polyolefins (TPOs) CA186AC TPO-Black, considered a paintable TPO grade, CA45A TPO-natural, considered a non-paintable TPO grade, and DEFD1331 HDPE-natural. The location of the gate on all of the test panels was on one edge of each panel. Adhesion testing on the CA186AC and CA45A panels was performed on the side of the panels closest to the gates. Adhesion testing on the HDPE panels was performed 50% on the side of the panels proximal to the gates and 50% on the side of the panels furthest from the gates. There was no difference in adhesion resulting from proximity to the gates on the HDPE panels.

In-house visual examination of water sheeting was evaluated by first allowing the panels to dry completely and then placing the panels under a stream of running cold tap water. Water sheeting is poor when either the panel or the water is warm. For panels treated under very mild conditions, an increase in the number and size of adhered water droplets was noted. With increasingly more robust treatments, the water would initially adhere but run off the panels as a sheet, leaving droplets. The rate of water run-off slowed with increasingly robust treatments. Ultimately, under very robust treatment conditions, water sheeting was complete and water run-off negligible. Unless otherwise specified, for the tests discussed herein, water sheeting, in general, was low to moderate.

Treatment of plaque surfaces was accomplished according to the following procedure: 6—4×6 in. plaques were treated by suspending in a Pyrex beaker containing 1250 mL of 6% sodium hypochlorite that had previously been brought to 81 °C. With vigorous stirring 150 mL of acetic acid was carefully added as the activating agent. The reaction was allowed to progress for 60 s after which the plaques were rinsed thoroughly with tap and then distilled water as described previously.

## 3. Results and discussion

Numerous third-party paint adhesion studies indicated that outstanding paint adhesion could be achieved for HDPE panels using, for example, 6% bleach and an acetic acid concentration of 5.7% at 90 °C for 1 min (Beholz [7]). Selected results of these studies are presented below (Table 1).

When comparing entries 1 and 2, it can be seen that the choice of acid has a great effect on the adhesion of paint to the CA45A substrate surfaces. Whereas the p*K*a of acetic acid ($CH_3CO_2H$), resulting from the hydrolysis of acetic anhydride, is 4.76, the p*K*as of oxalic acid ($(CO_2H)_2$) are 4.28 and 1.27. The much lower pH of the oxalic acid solution appears to lower the extent of surface functionalization. (As will be discussed below, the pH of the solution has been determined to have a great impact on the mechanism of chlorination as well).

The extent of surface functionalization is also sensitive to the amount of acid added. This is exemplified by comparison of entries 3 and 5, again examining the effect of the treatment on the CA45A substrate. In this, the amount of acid in entry 5 was reduced ∼15 times relative to entry 3. At the reduced acid concentration reduced adhesion was observed.

When comparing entries 1 and 6, it can be seen that HDPE may be rendered adhesive under similar (slightly higher temperature) conditions to the CA45A substrate. The CA45A TPO plaques (density = 9 g/cm$^3$, elongation at break = 500%) had a matte finish and were easily scratched and flexed. The HDPE plaques (density = 0.94–0.96) had a high gloss, were not easily scratched and were significantly stiffer than the TPO substrate. As such, the HDPE substrate provided a more challenging substrate to chlorinate.

In entries 7–9, the effect of temperature on adhesion promotion was examined under reduced acid conditions. It was presumed that under these conditions, the effect of temperature on the rate/extent of treatment would be observable since paint adhesion would not be anticipated to be 100% on the HDPE substrate. It appeared that the temperature was not as significant of a parameter as pH between 50 and 100 °C as there was no apparent trend in adhesiveness observed between 56 and 96 °C. At ambient temperature though, the rate of chlorination was approximately 75 times slower.

Results of 96 h humidity testing, in which 2 of each polymer type were simultaneously treated with 1250 mL of bleach, 75 mL of acetic anhydride at 90 °C for 60 s indicated that no blistering resulted. Subsequent third party crosshatch testing indicated that there was no paint removal from these plaques as well (Fig. 1).

In-house paint adhesion resulting from the use of other acids and acid compositions has also been examined. These experiments were conducted with acid concentrations similar to those presented in entry 1, Table 1. It was determined that the use of succinic acid (p*K*as = 5.62, 4.21) provided good resultant adhesion while formic acid (p*K*a = 3.75) and citric acid (p*K*as = 6.40, 4.76, 3.13) provided poor resultant adhesion. In comparing the adhesion resulting from the use of succinic acid (p*K*as = 5.62, 4.21) to the

Table 1
Selected third-party paint adhesion results

| Entry | Polymer[a] | Bleach (mL) | Acid[b] (mL) | Temperature (°C) | Time (s) | Paint removal (Ave.%/Pull) |
|---|---|---|---|---|---|---|
| 1 | CA45A | 1250 | 75 | 73 | 120 | 0 |
| 2 | CA45A | 1250 | Oxalic acid (35 g) | 71 | 120 | 33 |
| 3 | CA45A | 1250 | 75 | 81 | 60 | 0 |
| 4 | CA45A | 1250 | 75 | 81 | 30 | 0 |
| 5 | CA45A | 1000 | 5 | 84 | 60 | 0.96 |
| 6 | HDPE | 1250 | 75 | 89 | 120 | 0 |
| 7 | HDPE | 1000 | 10 | 56 | 60 | 0.3 |
| 8 | HDPE | 1000 | 10 | 82 | 60 | 2.6 |
| 9 | HDPE | 1000 | 10 | 96 | 60 | 0.2 |

[a] 5 or 6—4×6 in. plaques were treated in each of the experiments.

[b] The acid used was acetic anhydride unless otherwise indicated. One acetic anhydride molecule hydrolizes to form two acetic acid molecules in aqueous environments.

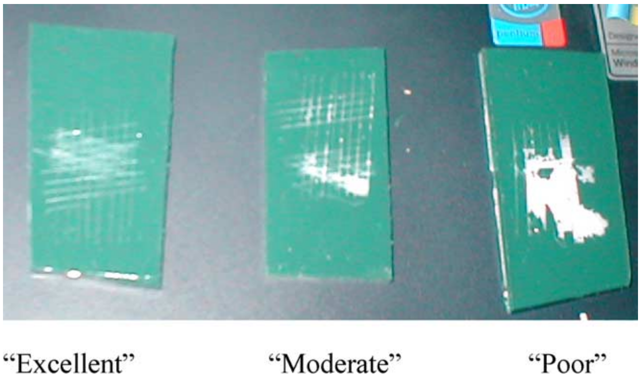

“Excellent” “Moderate” “Poor”

Fig. 1. In-house paint adhesion ranking based on crosshatch followed by attempted manual paint removal with the finger nail.

adhesion resulting from the use of oxalic acid (p*K*as = 4.28, 1.27) it can again be seen that the oxalic acid p*K*a of 1.27 correlates with the observed poor adhesion associated with the use of oxalic acid. Since formic acid (p*K*a = 3.75) also provided poor resulting adhesion, it has been determined that p*K*a values of greater than approximately 4 are necessary to promote adhesion. The highest p*K*a examined, 4.78, provided the best resulting adhesion.

Of the inorganic acids examined, tetra-boric acid (p*K*a = 9, 4) provided poor adhesion by in-house adhesion testing while $H_3PO_4$ (p*K*as = 12.38, 7.2, 2.15) provided excellent adhesion. $H_2SO_4$ (p*K*as = 1.99, −3) and HBr (p*K*a = −9) provided no adhesion either with or without a catalytic amount of $I_2$ while surprisingly, hydrochloric acid (p*K*a = −6.1) provided very good to excellent adhesion with a catalytic amount of $I_2$ under the following conditions: 200 mL 7.5% bleach, (2.5 mL HCl diluted to 10 mL water) and 200 mL 7.5% bleach, (5 mL HCl diluted to 20 mL water). It is felt that HCl reacts with the NaOCl to generate $Cl_2$ which provides a route to radical chlorination of the substrate surface. With respect to the oxidizer, it has been found that calcium hypochlorite ($Ca(OCl)_2$) purchased as a 67% dispersion in $CaCO_3$ works equally well to NaOCl.

### *3.1. Surface modification and resultant adhesion correlation studies*

Studies regarding the surface modifications subsequent to treatment indicate that the resulting adhesive effects are due primarily to the addition of chlorine atoms to the polymer surface (Aronson, Beholz, Burland and Perez [9]). ESCA analysis of the surface of chlorinated HDPE indicated that the amount of surface chlorine needed to elicit a substantial increase in adhesiveness is only 2–3% of available sites (Fig. 2).

In the chlorination method presented herein, the polymeric surface to be chlorinated is placed in a pre-heated solution of the oxidizer, generally a 3–15% aqueous sodium hypochlorite, and the acid added to effect liberation of the chlorinating species, making them available for surface chlorination, through placement of the oxidizer in a kinetically degrading state (Scheme 1). Surface chlorination using only sodium hypochlorite without the use of an acid occurs as well but at a very greatly reduced rate. This was expected, as aqueous solutions of sodium hypochlorite are unstable in contact with air, heat and light. Through the use of acid catalysts, the increase in the rate of chlorination at 100 °C is on the order of ∼75 times (in-house crosshatch paint adhesion testing). The lowering of pH through the addition of the acid shifts the equilibrium of chlorine species, kinetically degrading the oxidizer, as follows.

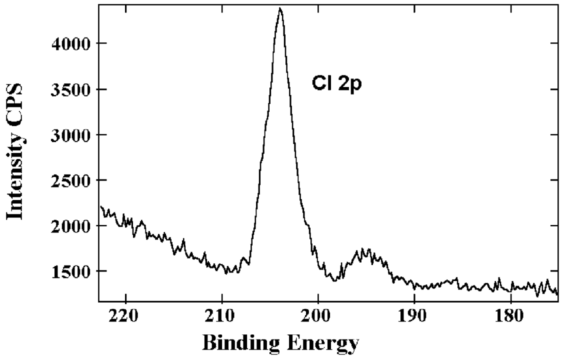
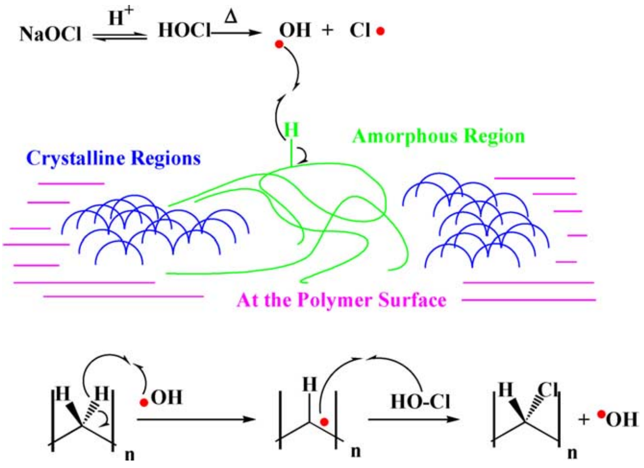


Fig. 2. ESCA analysis of the surface of chlorinated HDPE surface.

Chlorine atoms added to the polymer surface are susceptible to elimination catalyzed by exposure to UV light resulting in the formation of alkene functionality (Aronson, Beholz, Beloskur, Burland and Perez [10]). Thus treated polymer samples are stored in the dark prior to painting. Interestingly, UV-curable paints have been successfully cured to treated surfaces providing excellent adhesion results.

The rate of surface chlorination has also been shown to decrease as a function of time from the addition of the acid (Figs. 3 and 4). This is logical since chlorine gas provides a



Scheme 1. Early hypothetical kinetic degradation of sodium hypochlorite model and subsequent reaction of liberated chlorine with the polymer surface. Studies refining the mechanistic understanding of the chlorination process will be discussed below.

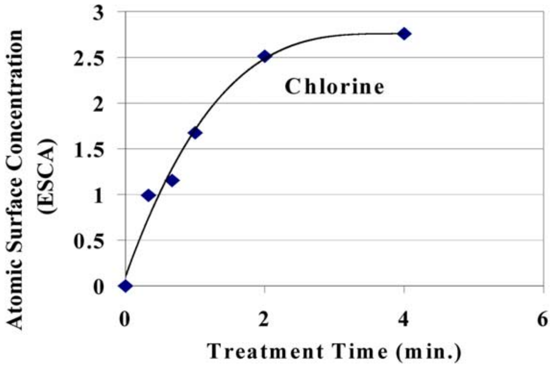


Fig. 3. Mole percent of surface chlorine by ESCA vs. reaction time for an HDPE surface treated with 6% sodium hypochlorate and 2% acetic anhydride at 95 °C.

conduit through which chlorine species may exit the treatment solution becoming unavailable for surface chlorination.

In Fig. 3 above, 6 test panels were placed in the treatment solution at $t=0$ and the acetic anhydride added. Panels were then removed at the time intervals indicated and analyzed for surface chlorine content by ESCA. As indicated in Fig. 3, the rate of chlorination decreases somewhat exponentially with time resulting in very little additional chlorination after 2 min of treatment.

Fig. 3 strongly supports the mechanistic interpretation that the chlorination of the surface results from species liberated through degradation of the oxidizer. Whereas the experiment presented in Fig. 3 suggested that the maximum extent of surface chlorination is under 3% and that the chlorination process is nearly complete within 2 min, in Fig. 4 it is shown that doubling the concentration of the acid results in a ∼17% increase in the extent of surface chlorination within 2 min. The rate of surface chlorination is dependent on the acid concentration, however, the extent of chlorination appears to be dependent on surface characteristics.

Static contact angle measurements were also conducted on the surfaces of virgin and treated HDPE panels (Fig. 5).

In general, the increases in surface tension by static contact angle correlate well with increases in chlorine concentration over the first minute. The static contact angle appears to be less sensitive to increases in chlorine concentration after the first minute of chlorination time. Also note that whereas the polar surface tension increases over the first minute, the dispersive surface tension does not appear to be affected.

Analysis of the Instron lap shear tensile adhesive strength using an epoxy glue as the adhesive demonstrated an increase in adhesive strength with an increase in the extent of chlorination (Fig. 6). Interestingly, the increase in adhesive strength was linear throughout the 6 min of chlorination. This is in contrast to the apparent leveling of surface chlorine concentration exhibited in Fig. 3 and the leveling of static contact angle measurements presented in Fig. 5.

The apparent discrepancy between the linear increase in adhesion and the exponentially decreasing addition of chlorine atoms to the polymer surface with time was initially puzzling. However, this discrepancy may be explained through the use of a simple model (Fig. 7).

For the subsequent inclusion of two additional chlorine atoms, five randomized additions were averaged.

In this model, a grid length of 11.25 mm corresponded to the length and width of one cell. Chlorine atoms within 45.07 mm of one another are indicated by lines. First, 16 chlorine atoms were randomly placed on the grid (a., blue), then 8 additional chlorine atoms (b., red) and finally 4 additional chlorine atoms (c., green). The number of chlorine atoms within some distance of each other increases linearly although the number of chlorine atoms added is

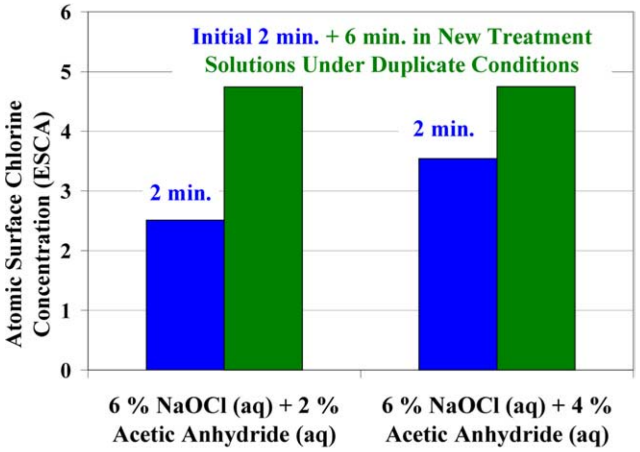


Fig. 4. Mole percent of surface chlorine by ESCA vs. reaction time for HDPE surfaces treated with 6% sodium hypochlorite and variable concentrations of acetic anhydride at 95 °C for 2 min and for 6 additional minutes using new treatment solutions.

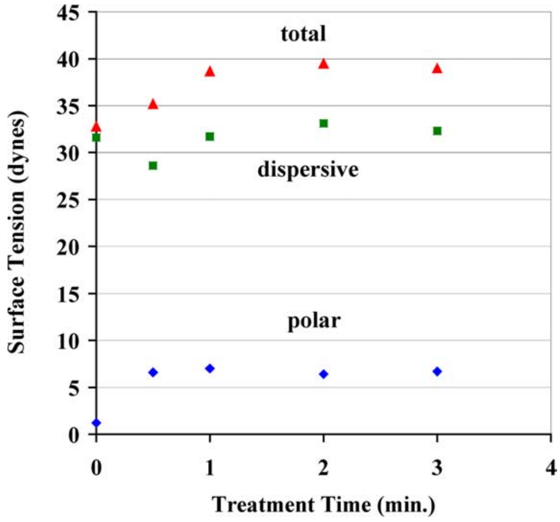


Fig. 5. Static contact angle analysis of HDPE surfaces vs. reaction time @ 25 °C sessile drop with $H_2O$ and $CH_2I_2$.

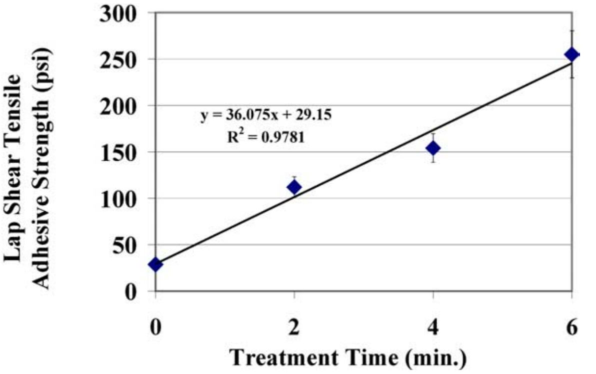


Fig. 6. Instron lap shear tensile adhesive characterization [ASTM D 3163] 1×4 in. samples; 1.0 in.$^2$ overlap; 0.05 in./min. Using an epoxy adhesive.

halved in each addition (Fig. 8). This corresponds well with the increase in surface adhesiveness being linear although the number of chlorine atoms added to the surface is not.

While the number of chlorine atoms within some distance of one another increases linearly, the average distance between chlorine atoms decreases only slightly. For 16 atoms, the average distance between atoms was 34.16 mm. For 24 atoms, the average distance between atoms was 33.56 mm. For 28 atoms, the average distance between atoms was 32.16 mm. For 30 atoms, the average distance between atoms was 31.69 mm. The inclusion of the final 2 atoms indicated that when one of the two atoms was placed near the edge of the grid, the number of atoms within some distance of one another increased from 61 to 69–71. As expected, imbedding these final 2 atoms within the grid provided a greater number of atoms within some distance of each other (72–74). On an actual surface, the reduced number of 'edge' chlorines as well as the very large number of chlorine atoms added would be expected to provide a better correlation between adhesiveness and the number of atoms within some distance of one another.

The adhesive strength resulting from the use of a cyanoacrylate adhesive (super glue) was very poor relative to the epoxy adhesive. Numerous manual tests using a variety of adhesives (gluing treated HDPE pieces together and pulling them apart by hand) indicated the following order of adhesiveness to various glue and paint formulations (Fig. 9).

According to the observations presented in Fig. 9, it appears that the aromatic character of the adhesive matrix is important in the adhesion to the treated HDPE surface. The adhesion of epoxies and urethanes is very similar. In the Instron test mentioned above, the failure mode for the epoxy glue was mixed, both cohesive and interfacial. Silicone caulking also appeared very adhesive but since the silicone caulk has poor mechanical properties, test pieces caulked together could be torn apart by hand leaving approximately equal amounts of caulk on each test piece (cohesive failure). The adhesives containing hydroxyl, ester, acid and amide groups and no aromatic character provided relatively poor adhesion when compared to adhesives containing aromatic functionality. The adhesion of cyanoacrylate, for example, provided an average tear strength of 128 psi in Instron testing of adhered panels that had been treated for 2 min in the same manner as those used in the testing of the epoxy adhesive. Test panels that had been treated for up to 6 min provided no significant increase in adhesiveness to the cyanoacrylate glue (an average of 134 psi for all test pieces treated between 2 and 6 min combined). The mode of failure in these samples was always interfacial. Since, the failure mode of the aromatic adhesives was always mixed and the failure mode of the non-aromatic adhesives always interfacial, it is believed that the surface chlorination model presented in Figs. 8 and 9 is operative and that increases in adhesiveness are not due to chlorination deeper into the substrate which would be anticipated to increase the degree of cohesive failure particularly in the cyanoacrylate system.

The outstanding adhesion of the aromatic adhesives is thought to be due to the polarizability of the aromatic systems allowing greater interaction with the surface chlorine atoms.

The method of silicone caulk application is interesting as well. Whereas, silicone caulk (Ace Hardware 100% clear silicone) adheres tenaciously to chlorinated surfaces when applied directly, isooctane solutions of this caulk applied to the treated surface provided virtually no adhesion when cured. The ranking of silicone in Fig. 9 was that resulting from adhesion of the unadulterated silicone caulk.

Interestingly, although the surface of HDPE has been successfully rendered adhesive in the gas phase, post

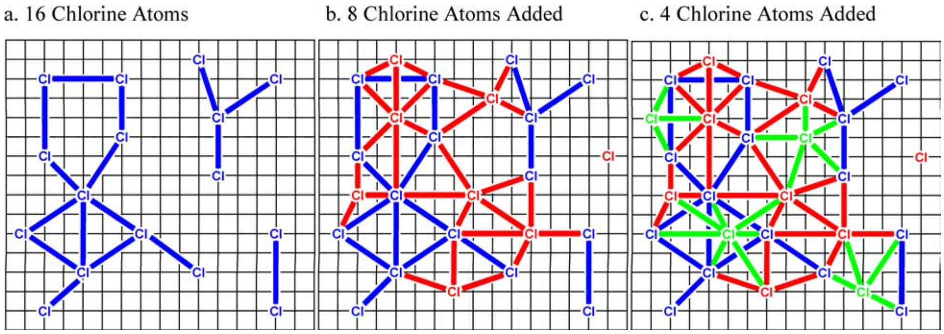

a. 16 Chlorine Atoms b. 8 Chlorine Atoms Added c. 4 Chlorine Atoms Added

Fig. 7. Model suggesting that the number of chlorine atoms some distance from one another influences adhesiveness.

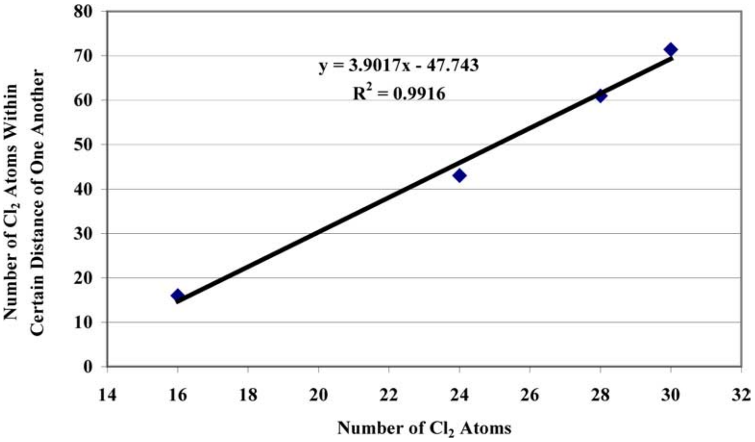


Fig. 8. Plot of the number of chlorine atoms within some distance of one another vs. the number of chlorine atoms.

treatment water sheeting is visually greatly reduced. The adhesion characteristics are altered as well, generally providing more inconsistent results. Whereas, panels treated in the liquid phase provided adhesive strengths with less than 10% variability, panels treated in the gas phase exhibited a very large range of adhesiveness. Thus, it appears in general, more difficult to render the surface adhesive in the gas phase than in an aqueous media. Possible reasons for this effect have been contemplated to include the aqueous media being better able to remove surface impurities, the aqueous environment being better able to provide intimate contact between the reactive species and the polymer surface or possibly even allow accessibility to a larger percentage of reactive sites through very slight solvation of the polymer surface. The later possibility is supported in that radical chlorination of HDPE by other methods has been shown to occur only in amorphous regions on the polymer surface (Bikson, Grodzinski and Vosfi [11]). In these studies, the percent of crystallinity in the polyethylene was varied and chlorination of the surface was mediated by photo-activation of elemental chlorine. It was determined that not only the extent of surface chlorination decreased with increased crystallinity but that the rate of chlorination was reduced as well. This rate reduction was attributed to the amorphous regions being more surrounded by the crystallites in the more crystalline polymers thus making the amorphous regions less accessible to chlorination (Bikson, Grodzinski and Vosfi [12]).

Examination of direct chlorination of non-polymeric systems under similar reactions has also been examined (Zand, Kokosa and Beholz [13]). Treatment of pentane with bleach and acid resulted in the synthesis of a variety of chloropentanes, while treatment of benzene resulted in chlorobenzene as the major product. Synthesis of chlorobenzene was quite interesting since it involves an electrophilic substitution reaction. These studies suggested a mixed mechanism is involved in the chlorination of these compounds: a radical mechanism being proposed responsible for the aliphatic chlorination products while an ionic mechanism proposed to account for aromatic chlorination (Scheme 2).

Since HDPE has no aromatic character, the only reaction path available would thus be the proposed addition of chlorine by a radical mechanism. In fact, attempted chlorination of HDPE under ionic conditions resulted in no improvement in paint adhesion.

These findings tend to also correlate well with the observed surface chlorination of HDPE in that surface chlorination rates increase substantially with the addition of catalytic amounts of $I_2$, a radical initiator. At room temperature, the rate of surface chlorination has been observed to increase approximately 18 times with the addition of $I_2$ as indicated by in-house and third-party paint adhesion tests. The degree of water sheeting too increases substantially in these $I_2$ catalyzed systems indicating that a greater degree of chlorination is being achieved or that other more hydrophilic species are ultimately being added to the polymer surface. Upon extended chlorination reactions in the presence of $I_2$, up to 24 h at room temperature, complete wetting of the surfaces has been achieved.

The use of $I_2$ was also interesting in that it formed a precipitate when dissolved in the sodium hypochlorite at elevated temperatures. In these experiments, the $I_2$ was added to sodium hypochlorite solution and the solution heated to the desired temperature. This resulted in the formation of a light precipitate at temperatures below ~70 °C and the formation of a more substantial flocculent at temperatures above ~80 °C. In these high temperature regions, excellent adhesion was never obtained as indicated in Fig. 10, below.

In an additional set of experiments, 200 mL 7.5% bleach with a catalytic amount of $I_2$ was heated to 60 °C. Samples were added and 2.5 mL HCl diluted to 10 mL water. Alternately, at 30 and 90 °C, 5 mL HCl diluted to 20 mL water. These results correlated well with the results presented in Fig. 11 indicating that the dilution of the diluted HCl provides a reduced rate of reaction (Fig. 11). Note again that the 90 °C reaction did not provide excellent adhesion even after 10 min.

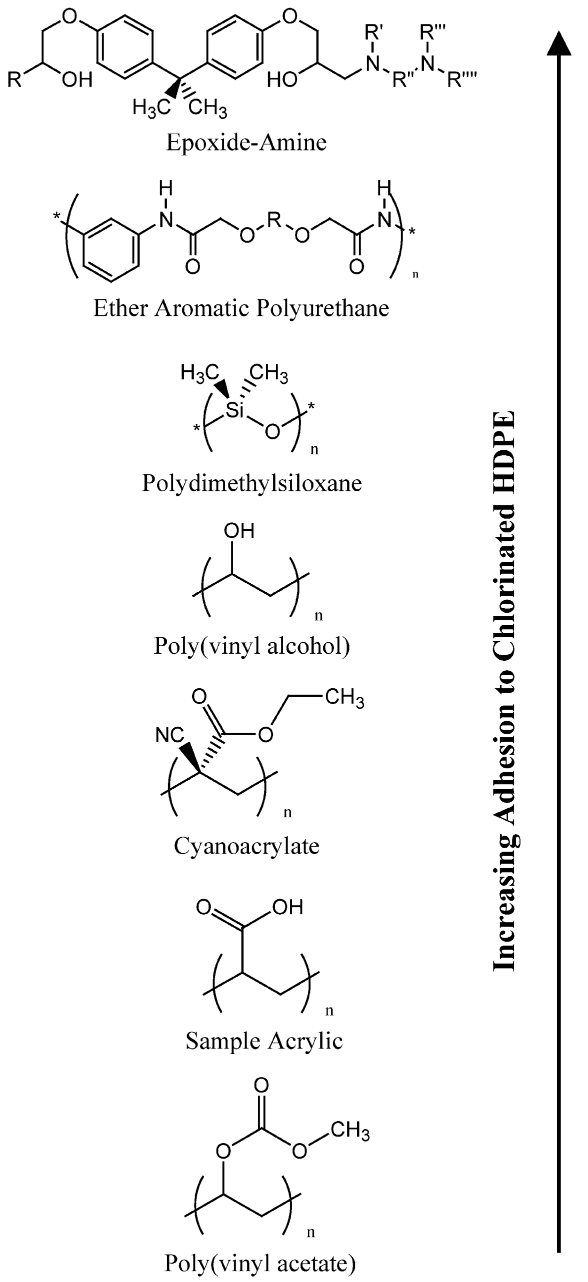


Fig. 9. Qualitative adhesive–functional group relationships.

When $I_2$ was allowed to stir in an aqueous solution of sodium hypochlorite at room temperature over night, the formation of the flocculent was also observed with disappearance of the yellow color normally associated with the sodium hypochlorite solution as well as any chlorine odor. Subsequent reduction of pH always results in dissolution of the precipitate. Although this effect is not fully understood, it has been shown that the stability of binary compounds of halogens in aqueous solutions decreases in the order of $Cl_2 > Br_2 > I_2$ and the tendency to form ternary compounds increases in the order of $Cl_2 < Br_2 < I_2$ (Eigen and Kustin [14]). It has also been shown that supersaturation of water with $Cl_2$ results in the formation of an insoluble chlorine-octahydrate complex ($Cl_2 \cdot 8H_2O$) (Lifshitz and Perlmutter-Hayman [15]). It has thus been contemplated that the $I_2$ may promote formation of this hydrate, reducing the availability of reactive $Cl_2$.

The non-polymeric chlorination studies provided above (Scheme 2) also suggest that reaction conditions may be selected to promote chlorination of different functionalities within a copolymer. For example, reaction conditions may be chosen to chlorinate either the aliphatic and aromatic functionality in a copolymer containing both. Further, a variety of polymer surface compositions in addition to polyolefins such as polystyrene may be chlorinated.

### *3.2. Industrial applications*

In recent experiments, 19 pieces of 1.5 × 1.5 in. plastic plaques were treated using 300 mL of 50% diluted 15% bleach with $I_2$ in a dip chamber fashioned from an isopropyl alcohol bottle. Thirty milliliters of acetic acid was used as the activator. There was a significant amount of ‘dead-volume’ unoccupied by plastic pieces at either end of the dip chamber (Fig. 12).

In these studies, the approximate surface area was 144 square inches for the faces of the plastic pieces. The plastic pieces were treated for 10 min at 40 °C providing excellent adhesion results by in-house paint adhesion analysis. From this study, a crude reagent cost estimate was developed to determine the cost of treating a square foot of material under these conditions. Neither the edges of the plastic pieces or the internal surface area of the HDPE dip chamber were considered in the reagent cost estimate. ‘Bulk’ reagent prices were obtained PVS-Nolwood (Table 2).

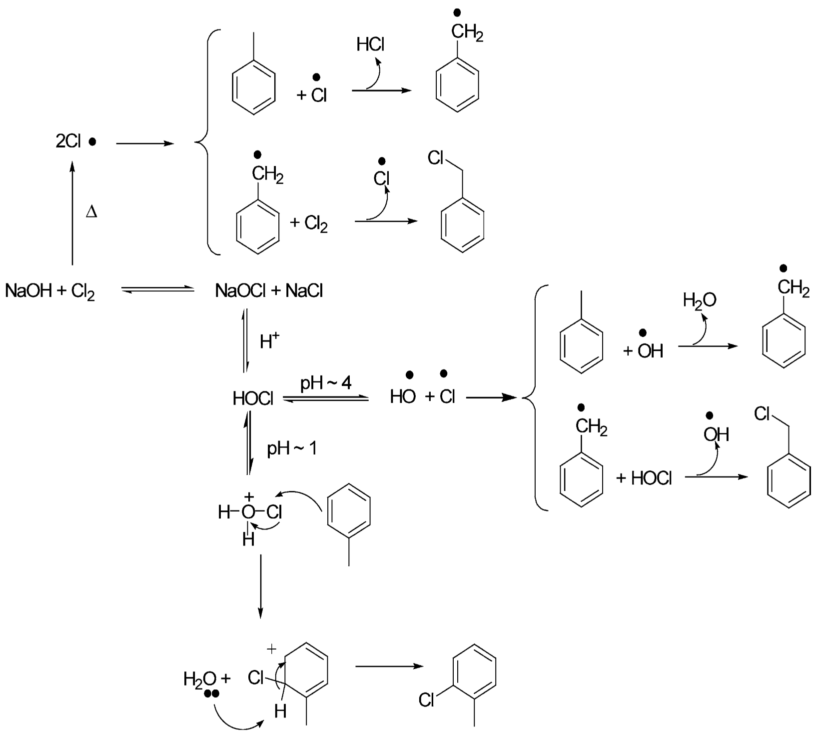
Using the model presented in Fig. 12 and reagent prices, the cost to treat a square foot of material was calculated to be ~\$0.27 in reagents including $I_2$. Note that this price includes stoichiometric amounts of reagents to quench effluent and residual materials resulting in a pH ~ 7 salt water effluent. A variety of ‘treatment chamber’ aspects and configurations have been examined and submitted for patent protection.

It is felt that this surface treatment method will provide advantages in industry over existent plastic pre-treatment methods including it is: water-borne and effectively replaces current organic adhesion promoters, simple, fast, renders the substrate polymer permanently adhesive and allows the

Table 2
Reagent prices per 50 lbs or 55 gal (prices are from PVS-Nolwood)

| Reagent | Price per quantity indicated[a] |
|---|---|
| HCl | \$1.5/gal |
| Acetic acid | \$0.6725/lb (0.7054525/gal) |
| NaOCl | \$3.03/gal 15% NaOCl |
| NaOH | \$0.51/lb |
| $Na_2S_2O_5$ | \$0.702/lb |

[a] Iodine is used in catalytic amounts (<0.002% by weight relative to the other reagents). Iodine from Aldrich costs \$250.00 per 2.5 kg (5.51 lbs).



Scheme 2. Mixed radical and ionic mechanism accounting for variable product mixture in the chlorination of toluene using aqueous sodium hypochlorite placed in an acidic state.

potential for great cost reduction by permitting adhesion to very inexpensive substrate materials. For example, recycled polypropylene secured from paradigm polymers ($0.17/lb) was treated equally well relative to other materials.

A further advantage of this process is that it may be tailored to meet a variety of processing constraints. For example, in Table 1 it was shown that HDPE may be rendered adhesive in as little as 2 min and that CA45A may be rendered adhesive in 30 s at 80–90 °C. Fig. 10 suggests that HDPE may also be rendered adhesive within 4 min at 40 °C. Thus, the time, temperature and treatment chemicals may be adjusted to maximize speed or minimize temperature and ultimately minimize the cost of treatment relative to the application.

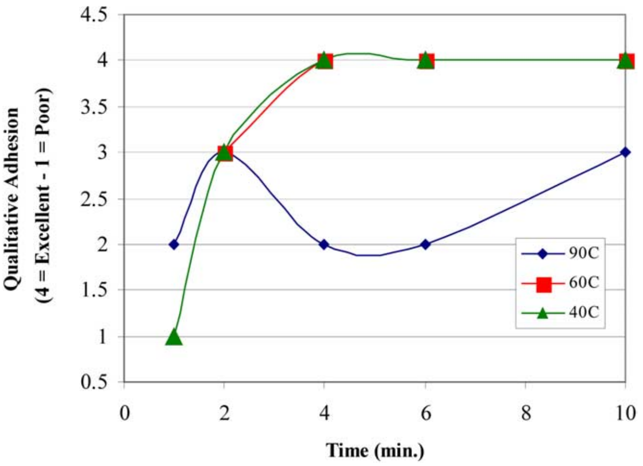


Fig. 10. Representative in-house paint adhesion results using HCl as the activator and $I_2$ as a catalyst at varying temperatures; 200 mL 7.5% bleach, $I_2$, 2–4 mL HCl.

## 4. Conclusions

Chlorination of the surface HDPE has been achieved under relatively mild aqueous conditions using sodium hypochlorite at reduced pH. Only a very small percentage of the surface of HDPE needs be chlorinated to provide a substantial increase of adhesiveness, particularly toward adhesives and paints containing aromatic functionality.

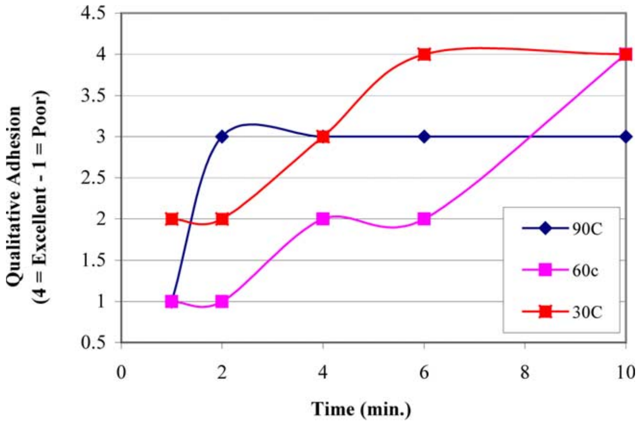


Fig. 11. Additional in-house paint adhesion results using diluted HCl as the activator and $I_2$ as a catalyst at varying temperatures.

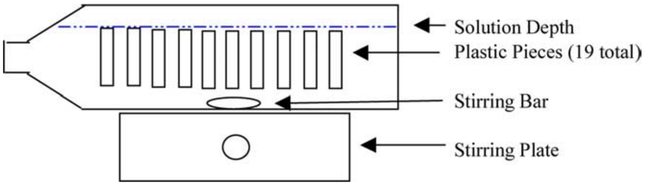


Fig. 12. Small scale pilot study treatment chamber model.

Adhesiveness of a variety of polyolefin substrates toward a variety of paints and adhesives has been demonstrated. Chlorination studies involving non-polymeric species have led to an understanding that the mechanism of HDPE chlorination under the conditions examined herein is likely through a radical mechanism. These same non-polymeric studies have shown that a variety of other polymer surface compositions, particularly those having aromatic functionality may be chlorinated as well. Chlorination of aromatic species has been shown to occur through an ionic mechanism in which chlorine is attacked by the aromatic ring. The mechanisms by which these different chlorination reactions are affected may be adjusted to preferentially add chlorine to either aliphatic or aromatic functionalities. The current method thus presents a versatile method of modification of polymer surfaces for adhesive applications.

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[8] (a) Tape Adhesion Test GM9071P-A and B, (b) Knife Cross-Hatch GM9502P, (c) 96 h Humidity GM4465P, (d) Paint System: White Base Coat (PPG CBCK9753B, Actual DFT 1.3 mL), Galaxy Silver Basecoat (PPG CBC519, Actual DFT 0.8 mL), Basecoat Catalyst (PPG Cat123), 2K Clearcoat (PPG TKU200B, Actual DFT 2.0 mL), Clearcoat Catalyst (PPG CAT110, Actual DFT 1.8 mL).

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