Chemical Oxidation of High-Density Polyethylene: Surface Energy, Functionality and Adhesion to Liquid Epoxy

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Abstract

The application of polyolefins has increased significantly over the past few decades. However, their chemical inertness and low surface energy limits their application in many industries where high adhesion to polar materials is required, such as for composites and protective coatings. Herein, six different acids are used to create polar functional groups on High-Density Polyethylene's (HDPE) surface and to increase its adhesion to liquid epoxy (LE). Contact angle measurements, Fourier Transform Infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and pull-off strength measurements are used to analyze the surface energy and functionality of HDPE and to measure its adhesion to LE. The results show that each acid increases both the polar and disperse surface energies of HDPE to a different extent, but that this is not necessarily a function of acid strength. Chlorosulfonic acid and chromic acid increase the oxygen to carbon ratio by a factor of 8 and increase HDPE's adhesion to LE by more than 400%. Furthermore, a comparison between predicted work of adhesion values from the OWRK model and experimental results shows that the latter are significantly higher than what is predicted, especially with increasing surface polarity.

Keywords: Adhesion, Coatings, Polyolefins, Surface energy, Surfaces and interfaces

1. Introduction

The use of polyolefins in the automotive, packaging, protective coatings[1] and biomedical[2] industries has increased significantly over the last few decades due to their abundant supply, good processability, low energy demand for processing, low cost, and high chemical stability.[3-5]

Many of these applications require the polyolefin to bond to various polar materials to form a laminate, protective coating, or a strong composite product.[6] However, polyolefins are nonpolar thermoplastics, which consist of only C–H and C–C pi bonds, with a smooth surface and a very low surface energy, which results in their poor adhesion to polar materials and limits their application.[7]

For instance, to improve the bonding of polyethylene to epoxy and produce various composites and laminates, the polyethylene surface must be chemically modified.[8,9] In another industrially important application, High Density Polyethylene (HDPE) is used as a component of pipeline coatings and it has always been a challenge for industry to improve the adhesion of HDPE to liquid epoxy (LE) to form a strong and lasting girth-weld joint coating.[10]

To overcome this problem, during the last half century significant research efforts have been devoted toward modification of the polyolefin surface so as to create polar functional groups on its surface, improve its wettability, surface energy and adhesion to different polar materials, especially LE. Different methods such as corona,[11,12] plasma,[12,13] flame treatment [14] and chemical oxidation with various oxidants [5,15] were employed to create various functional groups on polyolefin surfaces to improve their poor adhesion properties.

Most of the experiments for chemically modifying PE have been performed using strong oxidants. Chromic acid has been the most popular choice [16-18] and LDPE was used more than

HDPE.[19,20] Only a few researchers have studied the effect of other oxidants on HDPE. Immersing HDPE in a solution of $KMnO_4$ and HCl for 2-8 hours created carbonyl functional groups on its surface and reduced its contact angle with water from 95° to 60°.[21] Hypochlorite and mild acetic acid introduced chlorine to the HDPE surface and improved its surface energy from 34 mN m^{-1} to 40 mN m^{-1}.[22] Soybean peroxidase and hydrogen peroxide,[9] concentrated sulfuric acid [17] and nitric acid [23] were among other acids that has been used to modify the surface of HDPE and in all cases new functional groups were introduced to the HDPE surface.

In only a few cases was adhesion measured or the work of adhesion calculated after chemical treatment. The differences in temperature, treatment duration, HDPE initial properties and lack of reproducible adhesion results make it impossible to accurately compare the effects of different acids on the creation of various functional groups on HDPE surfaces. Further, the extent of subsequent adhesion improvement or any correlation between the extent of these improvements and the strength of the acids used for chemical treatment is not available.

To calculate the work of adhesion, models such as OWRK and its variants,[24-26] which are based on the polarity match principle, are widely used and recommended for nonpolar polymers and have achieved some measure of qualitative success in estimating adhesion.[27] However, it is not clear how accurate these models would be when the polarity of polyolefin increases upon chemical treatment.

In this work, six different acids were used to modify HDPE surfaces over the same treatment time and temperature. The contact angle of all modified and unmodified samples with DI water and diiodomethane was measured to calculate the polar and disperse portions of free surface energies after each treatment. After obtaining the polar and disperse portion of LE's surface tension, work of adhesion was calculated and compared with the pull-off strength test results.

Attenuated total reflection in conjunction with infrared spectroscopy (ATR-FTIR), XPS and pull-off strength measurements were employed to analyze and compare the changes that each acid makes on the HDPE surface and to more accurately correlate these changes to the work of adhesion and experimental adhesion improvements.

2. Materials and Methods

Table 1 lists the acids that were used in this work to modify HDPE's surface wettability and adhesion properties. Some of these acids were previously used by other researchers at different temperature and exposure times [28] and some have not been applied to HDPE. The numbers for each acid are used as sample descriptors in the following text and Figures.

Table 1. Acids used to modify HDPE surface

NO.[a]	Oxidant
1	Nitric acid
2	Hydrochloric acid
3	Perchloric acid
4	Sulfuric acid
5	Chromic acid
6	Chlorosulfonic acid

[a] Unmodified HDPE will be sample 0

67% nitric acid, 98% sulfuric acid, 37% hydrochloric acid, 70% perchloric acid and 99% chlorosulfonic acid were bought from Sigma-Aldrich and Fisher Scientific and used without any further purification. Chromic acid was made by adding 0.25 M potassium dichromate and 15.8 M sulfuric acid to DI water. HDPE samples were received from Shawcor Ltd and the two-part liquid epoxy (SP 8888) was received from Specialty Polymer Coatings Inc. The samples were cut to 4 x 4 cm squares for surface energy and ATR-FTIR measurements and 1 x 1 cm for XPS measurements. HDPE panels (HDPE coated onto a pipeline steel substrate) were cut to 10 x 10 cm squares for pull-off strength tests.

All samples were washed with DI water three times, washed with acetone, and then washed again with DI water prior to being dried in an oven at 50 ± 2 ⁰C for 30 minutes. Then each sample was immersed in one of the acids listed in Table 1 at 60 ± 1 ⁰C for 20 minutes. After the immersion, the samples were washed with DI water and then were dried in the oven at 50 ± 2 ⁰C for 30 minutes in preparation for subsequent tests.

To measure the surface energy of the HDPE samples before and after each treatment, the sessile drop method, which is a geometric method for optical measurement of the contact angle of a solid surface with a liquid using drop shape analysis,[29] was employed to measure the contact angle of HDPE with DI water and diiodomethane using a Kruss DSA30E Drop Shape Analyzer. Each measurement was repeated 3 to 5 times. The Young-Laplace method was used as the fitting method for contact angle measurement and Equation 1 was used to calculate the surface energy of HDPE according to the OWRK model.[24,25]

$$\frac{\sigma_l(\cos\theta + 1)}{2\sqrt{\sigma_l^D}} = \sqrt{\sigma_s^P}\frac{\sqrt{\sigma_l^p}}{\sqrt{\sigma_l^D}} + \sqrt{\sigma_s^D} \qquad Equation(1)$$

Where θ is the angle between the solid and liquid, σ_l^p and σ_l^s are polar and disperse portion of liquid's surface tension and σ_s^p and σ_s^D are the polar and disperse surface energy of the solid, respectively.

FTIR analyses of all modified and unmodified HDPE samples were performed from 650 cm^{-1} to 4000 cm^{-1} (8 scans per spectrum with the resolution of 4 cm^{-1}) using a Perkin–Elmer Frontier Spectrometer equipped with an attenuated total reflection unit to investigate the type of different functional groups that each oxidant creates on HDPE's surface after treatment.[30]

XPS spectra were obtained by a Kratos AXIS Supra spectrometer using AlKα (1486.7 eV) radiation, running at 15 mA with the anode at 15 kV (225W). XPS survey spectra were obtained from an area of approximately 300 x 700 microns using a pass energy of 160 eV. A pass energy of 20 eV was used for high resolution spectra. The pressure did not exceed $5*10^{-9}$ Torr ($6.67*10^{-9}$ Pa) and the temperature was 20 ± 2 ºC.

The level of adhesion between modified HDPE samples and LE was measured via pull-off strength test according to ASTM D4541.[31] After chemical treatment, HDPE samples were coated with commercial LE and cured according to the manufacturer's recommendation. After the LE had cured, pull-stubs were attached to the coating with an adhesive and the pull-off strength test was conducted with a digital SEMicro PATTI Adhesion Tester. A schematic cross section of the testing instrument used in this work is shown in **Figure 1**. Each test was repeated three to five times to ensure a reproducible result.
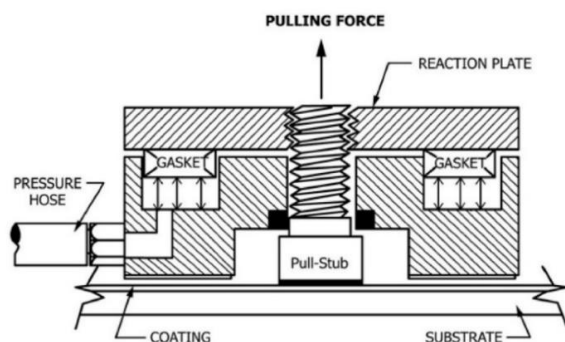

Figure 1. Schematic cross section of pull-off tester used in this work according to ASTM D4541[31]

Because the LE is a non-Newtonian liquid, a Kruss K-11 force tensiometer was used to measure the surface tension of LE with the Wilhelmy plate method. To determine the disperse and polar portion of LE's surface tension, the interfacial tension between LE and DI water was measured using the same instrument and method discussed above. Equation 2 and 3 were used to calculate the polar and disperse surface energy of LE.

$$IFT = \sigma_W + \sigma_{LE} - 2\left(\sqrt{\sigma_W^D \sigma_{LE}^D} + \sqrt{\sigma_W^P \sigma_{LE}^P}\right) \qquad Equation(2)$$

$$\sigma_{LE} = \sigma_{LE}^P + \sigma_{LE}^D \qquad Equation(3)$$

Where IFT is the interfacial tension between water and LE. The work of adhesion between the

HDPE samples and LE ($W_{HDPE,LE}$) was calculated by equation 4 based on the OWRK method:

$$W_{HDPE,LE} = 2\left(\sqrt{\sigma_{HDPE}^D \sigma_{LE}^D} + \sqrt{\sigma_{HDPE}^P \sigma_{LE}^P}\right) \qquad Equation(4)$$

3. Results and discussion

3.1. Surface energy measurements

Figure 2 presents the contact angles of DI water and diiodomethane with unmodified and

modified HDPE samples. In all cases, the contact angle of both DI water and diiodomethane with

HDPE decreased after chemical modification. However, the amount of this decrease varies

significantly for different samples. The contact angle of HDPE and DI water was 94.40⁰ with the

standard deviation (SD) of 1.79⁰ for the unmodified sample, which decreased by 69.28% after

using chlorosulfonic acid and only 3.6% after using nitric acid. The contact angle of HDPE with

diiodomethane is less than its contact angle with DI water in all cases, due to the lower surface

tension of diiodomethane. Moreover, the degree and the trend of contact angle reduction is

different. The contact angle between HDPE and diiodomethane is 53.9⁰ for the unmodified

sample. The maximum reduction, 24.68%, was observed after using chlorosulfonic acid, while

the minimum reduction was 10.2% after using sulfuric acid, which shows there is a smaller

change between the contact angle of HDPE with diiodomethane after chemical modification

compared to its contact angle with DI water.

Although in most of the previous work, the contact angle between modified polyolefins and DI water or diiodomethane have not been reported after chemical modification, the results of this work are in line with what has been reported in the literature. For instance, the contact angle of polyethylene with DI water is reported to be 66⁰ after modification with chromic acid at 70 ⁰C for 1 hour[32] and 45⁰ after 6 hours[33]. As shown in Figure 2, the measured contact angle between HDPE and DI water after treatment with chromic acid for 20 minutes is 69⁰.

Although some sources suggest different values for the level of PE surface energy improvement required to obtain a proper adhesive bonding with a polar material,[34,35] the increase in polar and disperse portions of surface energy should be analysed individually for a more thorough analysis. Using the results of contact angle measurements and equation 1, the disperse and polar components of the surface energy of all samples were calculated and they are presented in **Figure 3**. For unmodified HDPE, the disperse and polar surface energies are 33.39 mN m^{-1} and 1.15 mN m^{-1} with SD of 2.21 mN m^{-1} and 0.43 mN m^{-1}, respectively. This confirms the literature values for HDPE and also shows only about 3% of its surface energy is associated with polar forces. The biggest change in HDPE disperse surface energy was 18.57%, which was observed after chemical treatment with chlorosulfonic acid. On the other hand, sulfuric acid increased HDPE's disperse surface energy by only 2.99%. This could be explained by the fact that sulfuric acid had the lowest impact on the contact angle change of HDPE with diiodomethane, a completely nonpolar liquid with only disperse surface tension.
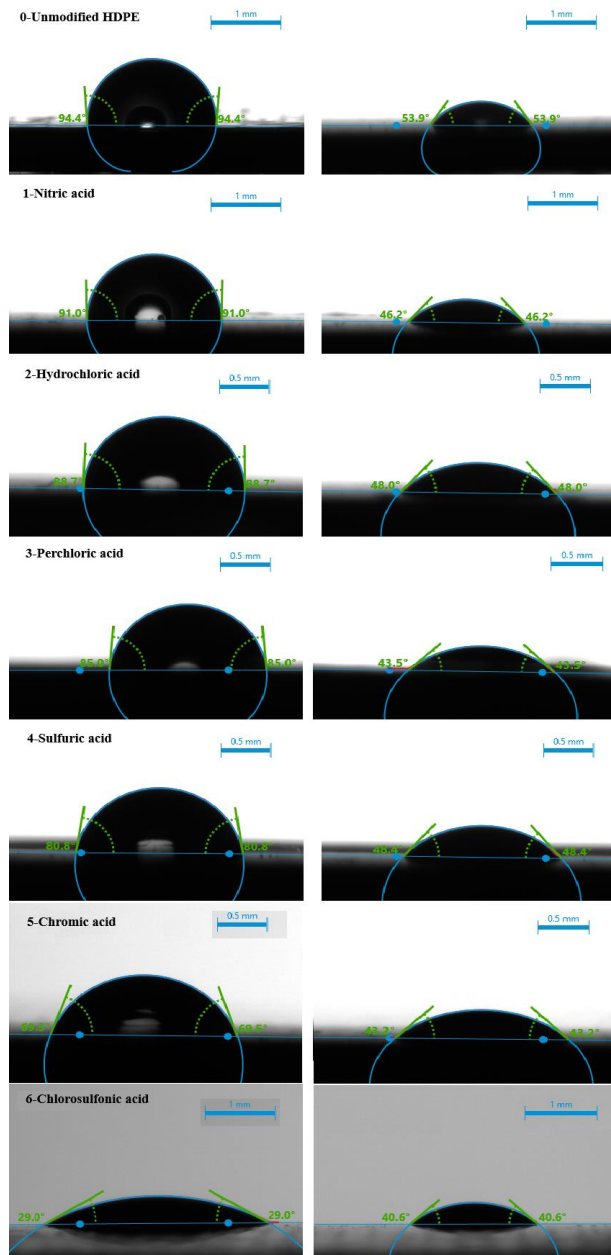
Figure 2. Contact angle measurements of HDPE samples with DI Water (left images) and their contact angle with diiodomethane (right images)

Figure 3 shows the most changes of HDPE's surface energy after chemical treatment is caused by the increase in its surface polar interactions. Perchloric acid, hydrochloric acid and nitric acid exerted the smallest influence on the polar surface energy of HDPE with 1.87 mN m^{-1}, 1.07 mN m^{-1} and 0.09 mN m^{-1} improvement, respectively. Chromic acid increased the polar part of

HDPE's surface energy by more than 7 times its initial value, while the biggest change, more than 27 times, was observed after chemical treatment with chlorosulfonic acid, which transformed the HDPE surface from an almost nonpolar surface to a highly polar surface with the polarity of 44.24%.
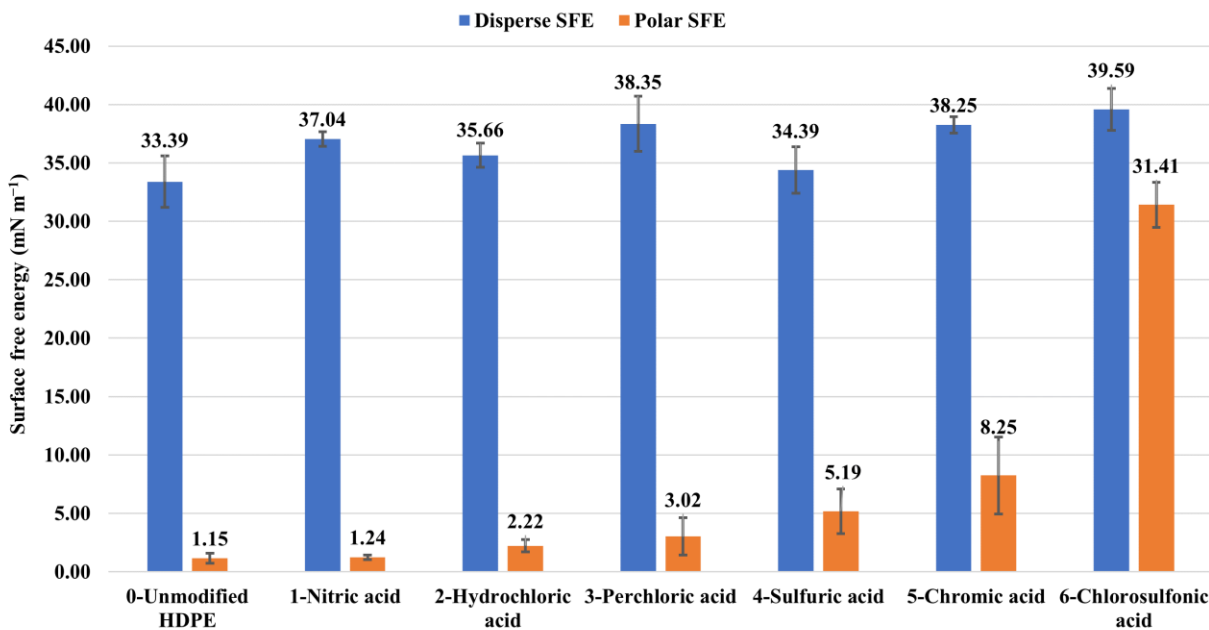

Figure 3. Surface free energy measurements after chemical treatments

3.2. ATR-FTIR

Figure 4 presents the results of ATR-FTIR measurements on unmodified (control) and all modified samples. For all samples, two strong sharp peaks at 2920 cm^{-1} and 2850 cm^{-1} and two moderately sharp peaks at just below 1400 cm^{-1} correspond to the Csp3–H stretching and vibration, respectively. Figure 4.a shows there are no detectable changes on the HDPE surface after chemical treatment with hydrochloric acid and perchloric acid, except for a weak peak at 1090 cm^{-1} that may correspond to C–O stretching, and another weak peak at 3500 cm^{-1} which appeared after using perchloric acid and suggests the presence of the hydroxyl group.

Figure 4.b shows the FTIR results for sample 1 and 4, which were treated with nitric acid and sulfuric acid, respectively. For sample 1, the peak at 1650 cm^{-1} shows the presence of C=O bonds. The broad peak between 3100 cm^{-1} and 3500 cm^{-1} and the peak at 1350 cm^{-1} correspond to O–H bond stretching and bending, respectively. It is worth mentioning that the different shape of the peak between 3100 cm^{-1} and 3500 cm^{-1} for sample 4 compared to samples 5 and 6 may be due to its overlap with the N–H peak as XPS results showed 0.9% nitrogen on the HDPE surface after treatment with nitric acid. Less changes with respect to the control could be detected on sample 4, where the peak at 1060 cm^{-1} indicated the presence of S=O bonds.

Finally, the FTIR results of sample 5 and 6 are presented in Figure 4.c. The changes on the HDPE surface are more noticeable after treatment with chromic acid and chlorosulfonic acid, in comparison to the first four samples. For both samples the broad peak at 3500 cm^{-1} belongs to O–H bond stretching, while the peaks at 1155 cm^{-1} and 1615 cm^{-1} correspond to S=O and C=C bonds. The two peaks at 1220 cm^{-1} and 1040 cm^{-1} show the presence of C–O bonds in carboxylic acid and hydroxyl groups, respectively. According to Zhang et al. treating polyethylene with chromic acid at 75 ⁰C for 1-8 hours creates carbonyl and sulfonic acid functional groups on HDPE's surface.[19] The results presented here show that these changes can be detected after shorter treatment times, even after only 20 minutes. It should be mentioned that for all cases, the peaks are stronger when chlorosulfonic acid was used. The two peaks at 885 cm^{-1} and 820 cm^{-1}, which appeared only for sample 6, may be associated with the presence of C=C and C–Cl bonds on the HDPE surface, respectively.
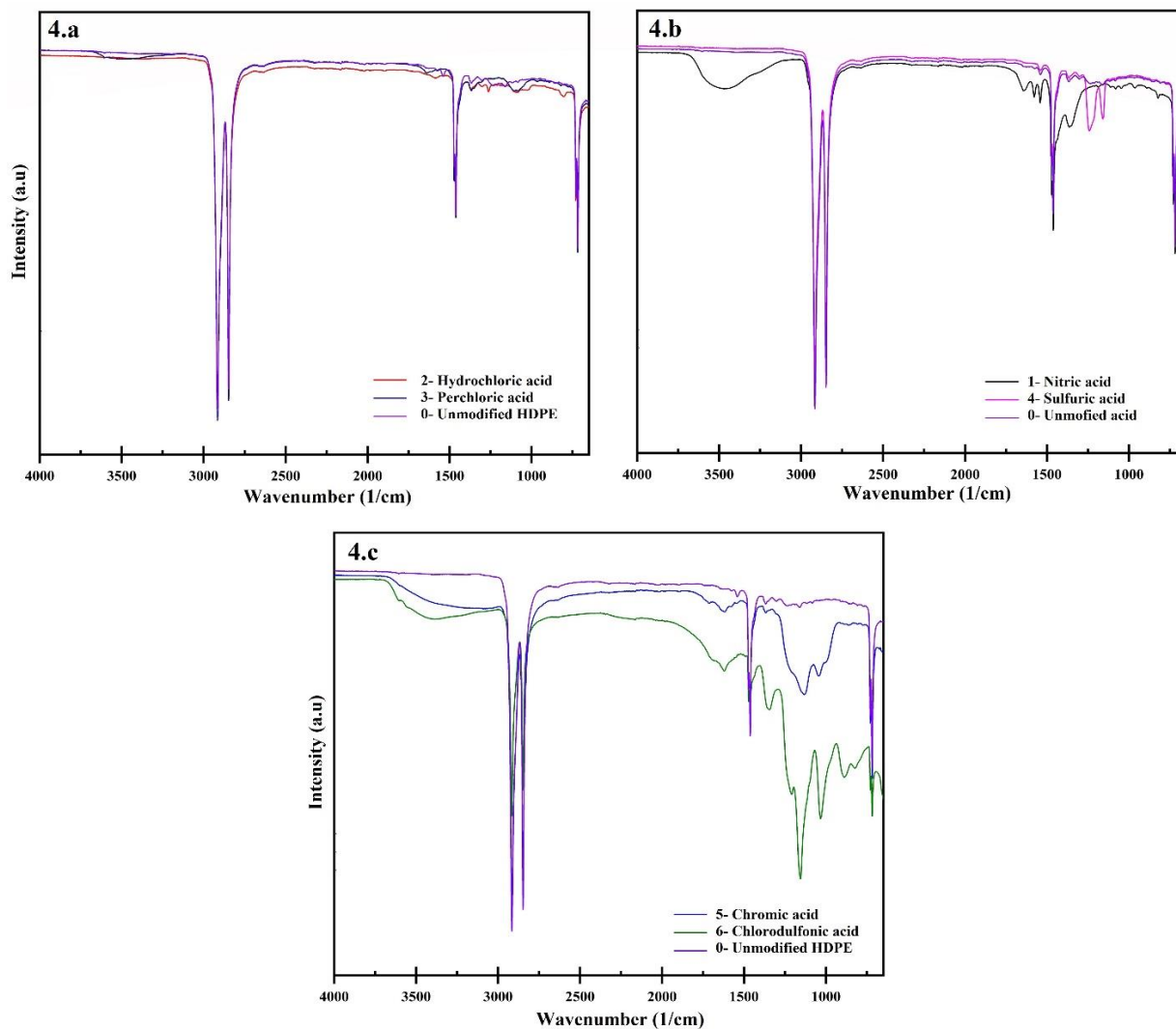
Figure 4. ATR-FTIR results of HDPE before and after chemical treatment

3.3. XPS

IR spectroscopy revealed the formation of various polar functional groups on the surface of samples treated with different acids. However, IR spectroscopy penetrates the surface to a depth of approximately 10 µm [28], which limits its utility in identifying surface functional groups. But XPS, with its near surface penetration, can better detect the functional groups created by surface oxidation. The XPS spectra and the deconvoluted XPS spectra for the C1s peak of unmodified and all modified HDPE samples are shown in **Figure 5** and **Figure 6**, respectively. The oxygen

and sulfur to carbon ratios, binding energies (position), areas, full widths at half maximum (FWHM) and atomic percentage (at%) calculated from the deconvoluted XPS spectra are presented in Table 2. The XPS spectrum of the unmodified HDPE sample indicates a low level of oxygenated species, with oxygen to carbon ratio (O/C) of 4.22% and complete absence of sulfonated species. The detected oxygen on the surface may be attributed to HDPE manufacturing additives and impurities.

Table 2. Oxygen and sulfur to carbon ratios, binding energies, full widths at half maximum (FWHM), peak areas and percent calculated from the deconvoluted XPS spectra for all HDPE samples

NO		C–C, C–H	C–OH	C=O	C=OOH	O/C (%)	S/C (%)
0	Pos	285	286.7	287.7	288.9	4.22	0
	FWHM	0.88	1.23	1.23	1.23		
	Area	10588.0	0	147.4	514		
	Conc %	94.1	0	1.3	4.6		
1	Pos	285	286.5	288	288.9	10.53	0
	FWHM	1.13	1.30	1.3	1.3		
	Area	104964.9	4823.0	809.3	4839.4		
	Conc %	90.9	4.2	0.7	4.2		
2	Pos	285	286.7	287.7	288.9	8.01	0
	FWHM	0.81	1.21	1.21	1.21		
	Area	12097.7	0	122.4	450.3		
	Conc %	95.5	0	1	3.6		
3	Pos	285	286.7	287.7	288.9	13.23	0
	FWHM	0.84	1.22	1.22	1.22		
	Area	11920.9	0	124.8	555.5		
	Conc %	94.6	0	1.0	4.4		
4	Pos	285	286.7	287.7	288.9	21.09	2.72
	FWHM	0.90	1.18	1.18	1.18		
	Area	10900.3	0	124.7	441.2		
	Conc %	95.1	0	1.1	3.8		
5	Pos	285	286.5	288	289.3	31.24	4.99
	FWHM	1.07	1.3	1.3	1.3		
	Area	91138.4	8767.7	1856.8	1551.8		
	Conc %	88.2	8.5	1.8	1.5		
6	Pos	285	286.5	287.7	289.5	37.44	10.90
	FWHM	1.00	1.3	1.3	1.3		
	Area	3086.1	456.6	202.2	45.7		
	Conc %	81.4	12.0	5.3	1.2		

For the first three samples, the O/C ratio on the HDPE surface increased to 10.53%, 8.01% and 13.23% which are almost 2 to 3 times the initial values and, further, since there was no sulfur in the acid used, the sulfur to carbon ratio (S/C) ratio remained zero after the treatment. After using sulfuric acid, however, the concentration of oxygen rose five times and 2.10% sulfur was detected on the HDPE surface. The S/C ratio almost doubled after using chromic acid (which was made with sulfuric acid), compared to when sulfuric acid alone was used. The highest surface level of sulfur was detected after using chlorosulfonic acid which was 10.99%. This confirms the finding from FTIR results which indicated the presence of S=O bonds on samples 4-6. Furthermore, chlorosulfonic acid and chromic acid created the highest amount of oxygen on the HDPE surface with the O/C ratio of 37.44% and 31.44%, respectively. Most noticeable changes on FTIR graphs were detected after using these same two acids.

As it can be seen from **Figure 6** and Table 2, no hydroxyl group was detected on unmodified HDPE or samples that were treated with hydrochloric acid, perchloric acid and sulfuric acid. 4.2% of carbon on sample 1's surface was connected to a hydroxyl group. This number increased to 8.5% and 12.0% after treating with chromic acid and chlorosulfonic acid, respectively. The concentration of carbonyl functional group remained constant or even slightly decreased for the first four samples, increased by 38% for the fifth sample and increased more than 400% after using chlorosulfonic acid. The detected amount of carboxylic acid was about 4% and it did not increase after chemical treatment with different acids.

Based on the results in Table 2 and Figure 3, the changes that the first three oxidants caused on the HDPE surface are less pronounced compared to the other three acids. This result is in line with the surface energy measurements. Perchloric acid, which caused the highest O/C surface ratio among the first three acids, also increased polar and total surface energies of HDPE more

than the other two acids. The level of changes that sulfuric acid caused on the HDPE surface was more than the first three acids and lower than the last two. Although the surface O/C ratio increased almost five times, a considerable amount of these oxygen atoms were bonded to sulfur atoms. The biggest difference on the surface was detected after using chromic and chlorosulfonic acid. The sharp increase in the surface O/C and S/C ratios and hydroxyl and carbonyl functional groups caused the polar surface energy of HDPE to rise significantly, especially for chlorosulfonic acid, which increased from 1.15 $mN\,m^{-1}$ for the unmodified sample to 31.41 $mN\,m^{-1}$ with SD of 1.93 $mN\,m^{-1}$.

The solution of potassium dichromate and sulfuric acid has been used as an oxidizing agent to oxidize various organic compounds. The oxidizing half reaction is shown in equation (5).[36,37]

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad\qquad Equation (5)$$

The FTIR and XPS results verify that this strong oxidizing solution can oxidize HDPE to some degree, creating hydroxyl and carbonyl functional groups on its surface. The presence of a transition metal at its highest oxidation state (VI) and its transformation to a lower oxidation state (III) is the major difference between acid number 5 and the other acids, which makes it a stronger oxidizing agent.

The unique structure of chlorosulfonic acid and the weak S–Cl bond may be the reason behind its strong effects on HDPE's surface. It has been traditionally used for sulfonating various hydrocarbons.[38] It reacts with the carbons in the HDPE chain, $O_3HS^{\delta+}$ replaces the H atom that is bonded to the carbon and $Cl^{\delta-}$ reacts with the H atom creating hydrochloric acid. As a tertiary H can be replaced by $O_3HS^{\delta+}$ easier than a secondary H,[38] there is a higher chance that this reaction would occur where there is a branch on the main chain (carbon atoms that are connected

to three other carbon atoms). This mechanism justifies the high level of sulfur and oxygen that were detected by XPS measurement and also the strong S=O peak that was seen in the FTIR (Figure 4.c).
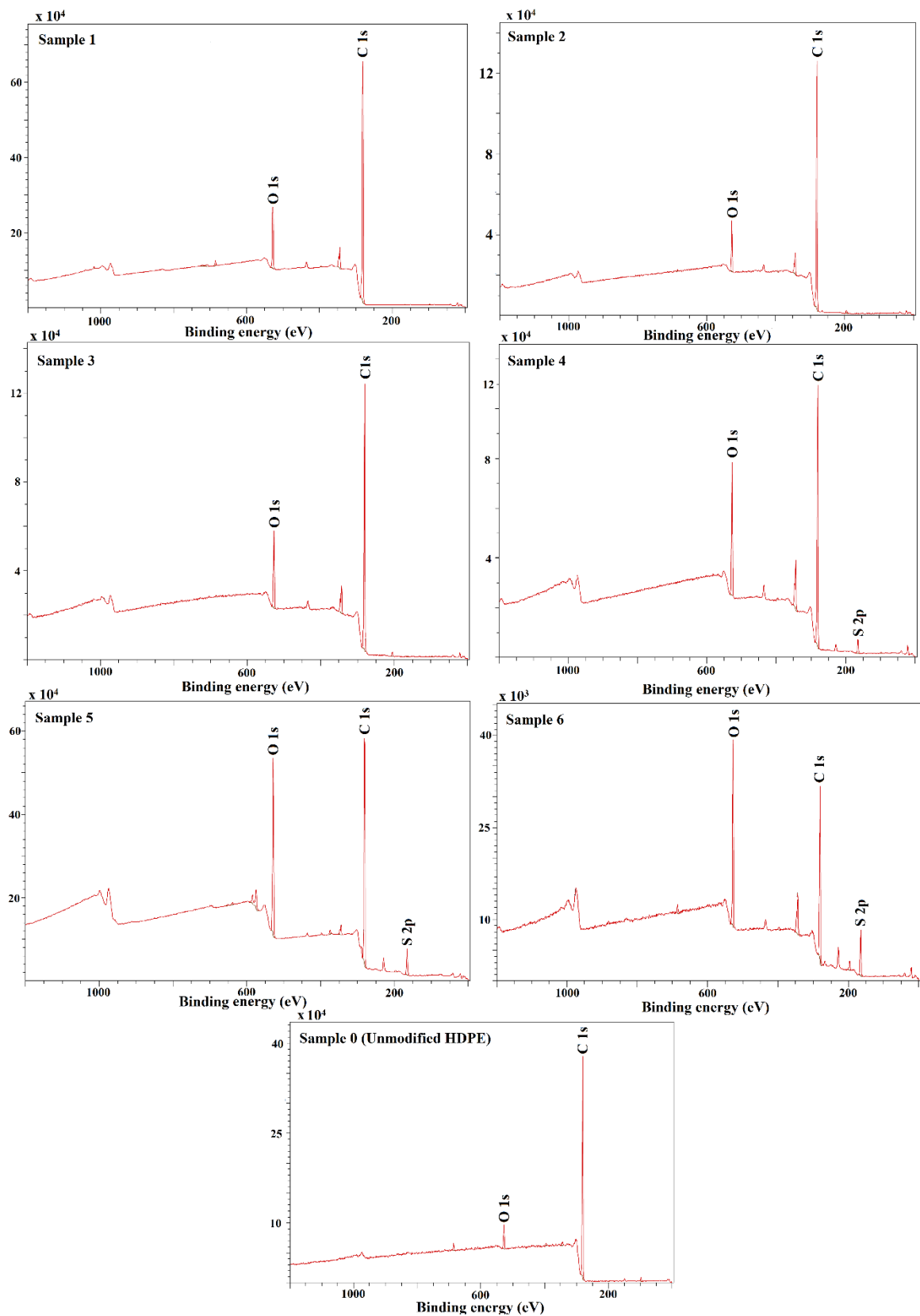
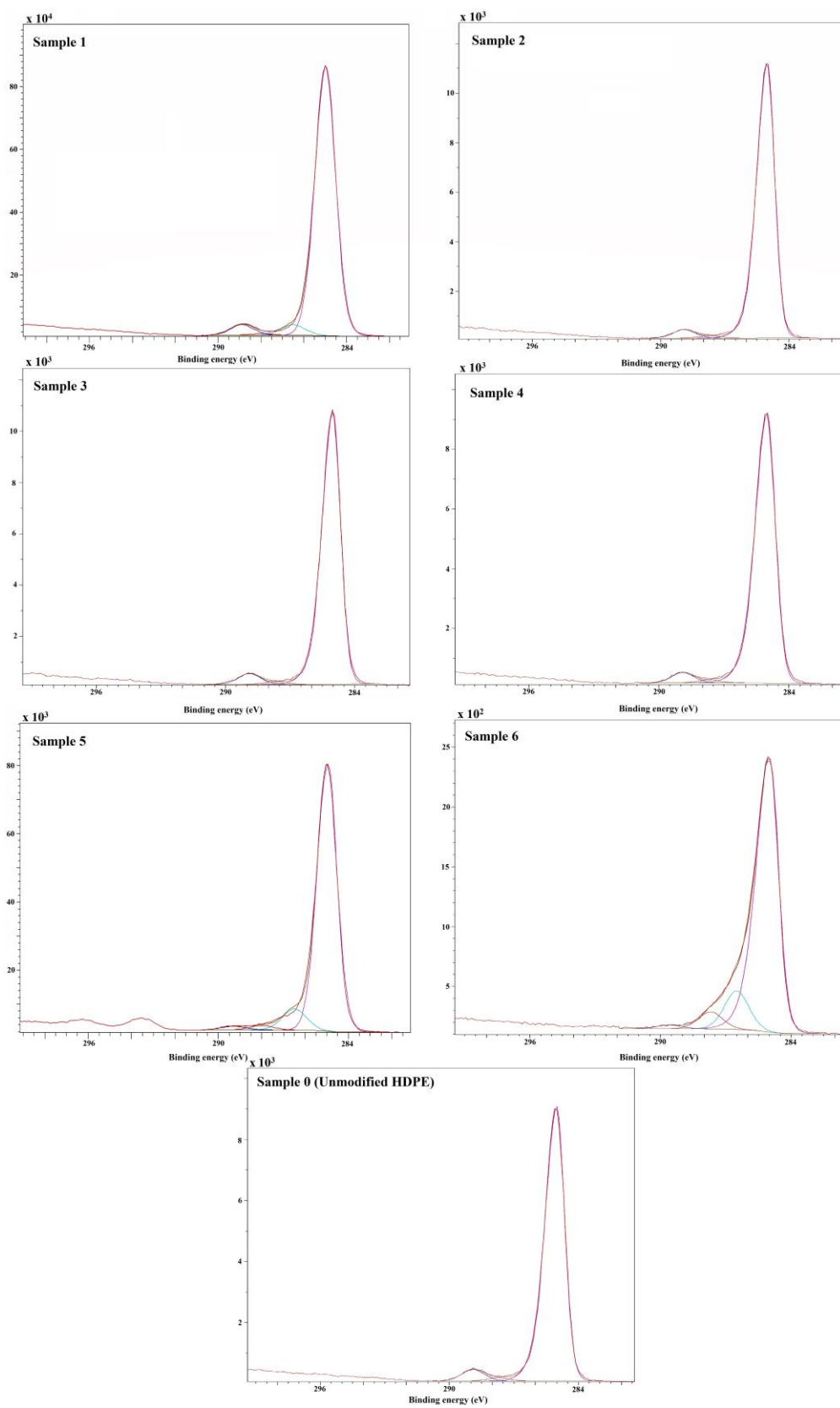Figure 5. XPS Spectra of all modified and unmodified HDPE samples

Figure 6. Deconvoluted XPS spectra of C1s for the all modified and unmodified HDPE samples

3.4. Pull-off strength

The results of pull-off strength tests are presented in **Figure 7**. The adhesion results between modified HDPE and LE are similar for the first three samples, with 45% to 55% improvement compared to the unmodified HDPE. Sulfuric acid had a slightly higher effect on the adhesion value with a 66% improvement. The highest results were obtained after using chromic acid and chlorosulfonic acid with adhesion values which are 2.84 and 4.19 times more than the initial value for the unmodified sample, respectively. This is because these acids, with their strong oxidizing powers, created more polar functional groups on the HDPE surface, which increased its polar-polar interaction with LE and resulted in stronger adhesion and higher pull-off strength values.
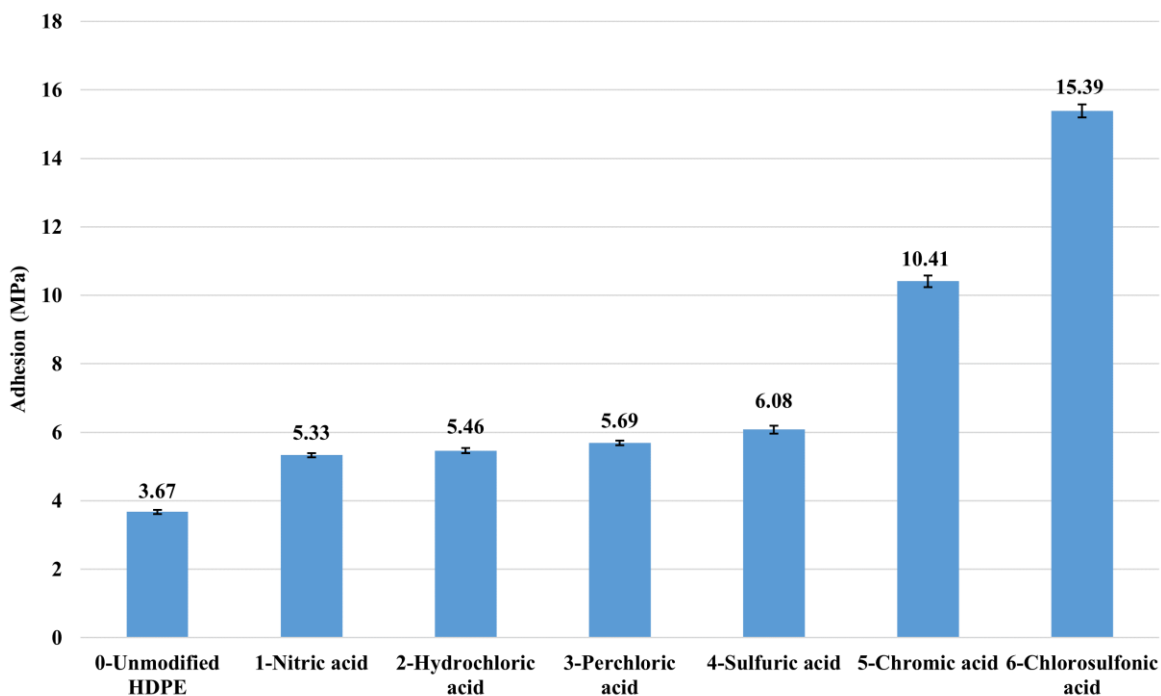

Figure 7. Adhesion results of all samples to LE

The adhesion results confirm the previously discussed surface analysis methods. Sample 5 and 6 which have the highest adhesion values, also had the highest C/O, S/O, carbonyl and hydroxyl

groups. They also had the highest polar and total surface energies compared to all other samples. Furthermore, sample 4, which had lower total surface energy, but higher polarity compared to sample 3, forms a stronger bond to LE.

There has been a disagreement in the literature about the relation between oxygen to carbon ratio and adhesion level.[17,28] The results presented here show that although, in general, it could be said that higher oxygen to carbon values favor higher adhesions, this ratio cannot be used as the only parameter for predicting the adhesion levels of HDPE to polar coatings such as liquid epoxy. Furthermore, these results show that stronger acids (lower pKa) are not necessarily more effective in creating different polar functional groups on HDPE surface and improving its adhesion to LE. As explained in section 3.3, other chemical characteristics of acids, such as the presence of a transition metal in chromic acid or the weak S–Cl bond in chlorosulfonic acid, are also contributing factors to the effects that each acid exerts on HDPE's surface. For example, perchloric acid, which has a lower pKa than chlorosulfonic acid, increases the polar surface energy of HDPE by only 1.87 mN m^{-1} and improves its adhesion to liquid epoxy by only 55%, while these values for the chlorosulfonic acid-treated sample are 30.26 mN m^{-1} and 319%, respectively.

3.5. Work of adhesion

To calculate the work of adhesion according to the OWRK model, the polar and disperse portions of LE's surface tension are required. Using a Kruss-K11 tensiometer with a Wilhelmy plate, the surface tension of LE and the interfacial tension between LE and DI water were measured. Equation 2 and 3 were used to calculate the polar and disperse portion of LE's surface tension. The results are reported in Table 3.

Table 3. LE's measured properties

	Density (g cm^{-3})	Surface tension (mN m^{-1})	Interfacial tension - DI water (mN m^{-1})	Polar surface tension (mN m^{-1})	Disperse surface tension (mN m^{-1})
Liquid epoxy	1.37	34.48	25.33	31.25	3.23

Using the surface tension results reported in Table 3, the surface energy of the unmodified and all modified HDPE samples presented in Figure 2, and employing equation 4, the work of adhesion for all samples were calculated and they are presented in **Figure 8**. Except for sample 4, the trend of work of adhesion improvement is the same as the trend of adhesion improvement which was observed in Figure 7. However, the magnitude of these improvements is not similar, especially with increasing adhesion values for the last two samples.
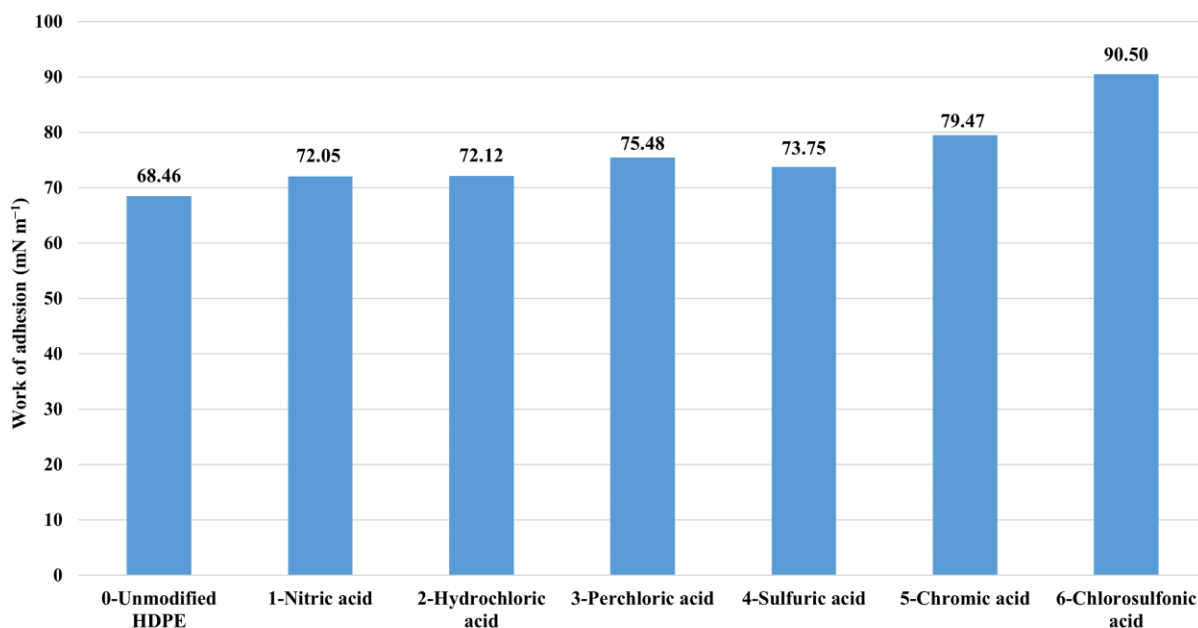

Figure 8. Work of Adhesion between all samples and LE according to the OWRK model

According to the OWRK model, equation 4, for any solid with a specific surface energy the work of adhesion will be the highest if its polarity is equal to the polarity of the adhered liquid.

Moreover, the contribution of polar and disperse forces to the work of adhesion are incorporated into the formula with similar terms. **Figure 9** shows the relative work of adhesion (calculated using equation 4) on the y-axis and the relative adhesion (measured from pull-off) on the x-axis. All numbers are relative to the values of the unmodified HDPE sample. The maximum relative work of adhesion (blue points) is calculated to be 1.32, which means only a 32% improvement compared to the unmodified HDPE. However, for the same sample the relative adhesion is measured to be 4.19, which indicates a 319% improvement.

According to the results of this work, although similar polarities between HDPE and LE are a factor in determining the work of adhesion, the contribution of the polar portion of the surface energy to the work of adhesion is significantly higher when the polarity of HDPE increases upon surface treatment. Modifying the second term in equation 4 and changing it to ($\sigma_{HDPE}^{P} * \sigma_{LE}^{P}$), a modified relative work of adhesion for all samples was calculated and it is also shown in Figure 9 (red points). The maximum relative work of adhesion is calculated to be 3.79 which is very close to the measured adhesion values with pull-off strength method. Furthermore, the contribution of polar forces to the work of adhesion according to the OWRK model, is 2.8%, 6.5% and 22.3% for the unmodified sample, sample 5 and 6, respectively. With the modified formula, the contribution of polar forces to the work of adhesion would be 10.3%, 43.6% and 74.3%.
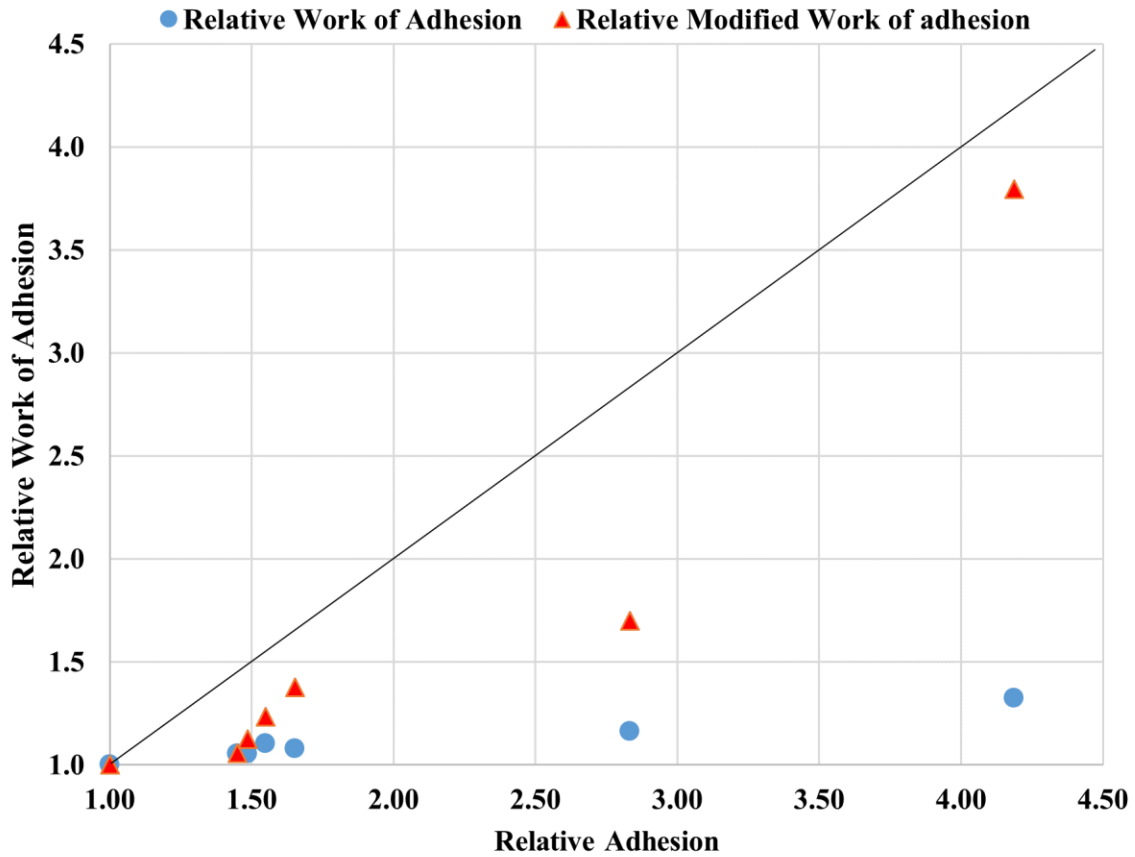
Figure 9. Relative Work of Adhesion (OWRK model, equation 4) and Relative Modified Work of Adhesion *vs.* Relative Adhesion obtained from pull-off tests.

To further illustrate how the modified version of the OWRK model describes the current system more accurately, **Figure 10** shows the relative work of adhesion versus the relative (O+S)/C, which was calculated from XPS results. For sample 4, which was treated with sulfuric acid, XPS results show that the concentration of oxygen and sulfur on the surface increased 6.63 times compared to the unmodified HDPE which resulted in the polar portion of its surface energy increasing to 5.19 mN m^{-1}. According to the OWRK model, the work of adhesion of this sample is less than sample 3, which has considerably lower polar elements on its surface and lower polar surface energy, 3.02 mN m^{-1}. This does not confirm our findings from pull-off strength tests, as the relative adhesion for sample 4 is 1.65 higher than the relative adhesion result for sample 3, which is 1.55. This shows the contribution of polar-polar interactions to the adhesion is

considerably higher than the generic mean of polar surface energy and tension of the solid and liquid and a more suitable model is required, especially for more polar surfaces.

It must be mentioned that the modification that has been made to the OWRK model here is merely to show that when the polarity of HDPE increases, the generic mean of its polar surface energy and polar surface tension of LE do not reflect the magnitude of improved adhesion caused by polar-polar interactions. To offer a comprehensive model for higher polarities more experimental data is needed. Some attempts have been made to develop an empirical model for adhesion of low density polyethylene with polyurethane.[39] However, no inclusive model for work of adhesion could be found that incorporates the polar and disperse surface energies of both solids and liquids, takes into account the higher magnitude of polar-polar interactions compared to disperse forces, and is in agreement with measured adhesion values.
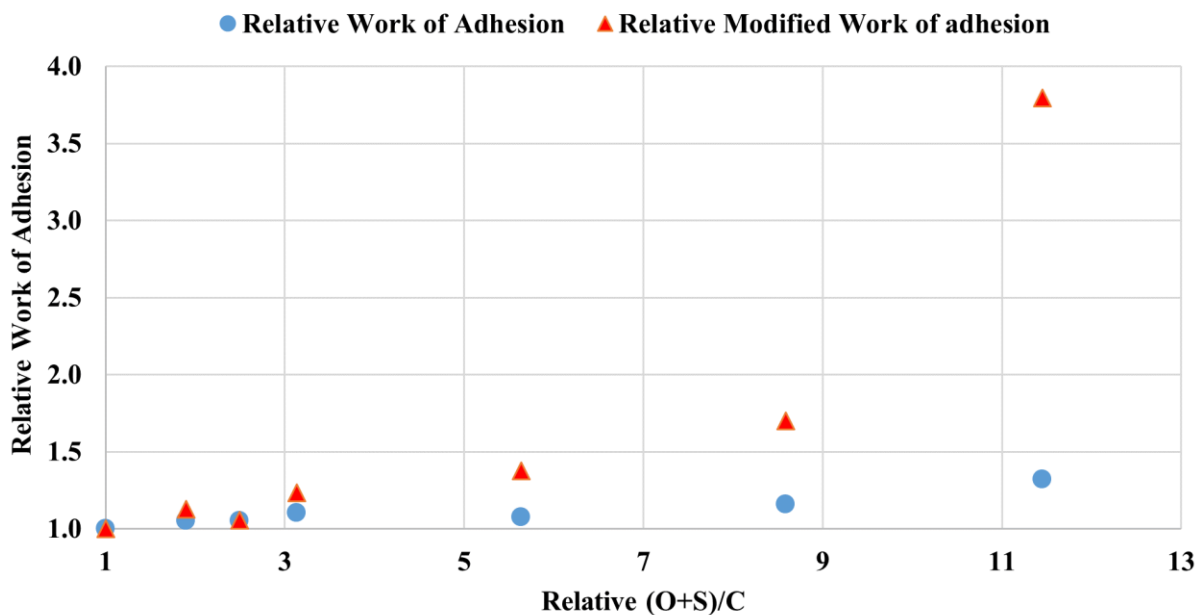

Figure 10. Relative Work of Adhesion and Relative Modified Work of Adhesion Vs Relative (O+S)/C

3.6. Effect of treatment temperature and duration

The above experiments were also conducted at different acid treatment temperatures of 20 ± 1 ºC and 40 ± 1 ºC (as opposed to 60 ± 1 ºC used for the experiments presented above). Additionally, the acid treatment time was changed to 5 minutes and one hour (as supposed to 20 minutes used for experiments presented above). For the sake of brevity, these graphical results have not been presented here, but the results showed that higher temperatures of chemical treatment enhance the functional group formation on HDPE and its subsequent adhesion to LE. However, for chlorosulfonic acid there were noticeable changes on the HDPE surface even at 20 ± 1 ºC and after just 5 minutes. For the first four acids, surface changes are minimal when the temperature is 40 ± 1 ºC and 20 ± 1 ºC or the time only 5 minutes. Furthermore, most of the functional groups were created during the first 20 minutes as prolonging the exposure time to one hour did not result in any noticeable changes on the surface energy, surface functionality and adhesion.

4. Conclusion

4.1. Among the six acids tried here, each acid increases both the polar and disperse surface energies of HDPE to a different extent; but this is not necessarily a function of the acid strength and depends on the unique chemical structure of each oxidant.

4.2. Chlorosulfonic acid and chromic acid were the most effective acids for surface modification of HDPE. According to ATR-FTIR and XPS results, they increased the O/C ratio by 8.87 and 7.4 times vs. the initial value and created hydroxyl, carbonyl and sulfonyl functional groups on the HDPE surface.

4.3. Pull-off strength test results show that chemical treatment can improve the adhesion of HDPE to LE by more than 400%, which proves its suitability for surface modification of HDPE.

4.4. Both disperse and polar surface energies of HDPE change during chemical treatment. However, most changes occur to the polar surface energy. The highest change of the polar surface energy was 30.26 mN m^{-1}, while the highest improvement for disperse surface energy was only 6.2 mN m^{-1}.

4.5. A comparison between adhesion results and work of adhesion clearly showed that the contribution of polar-polar interactions to the adhesion is considerably higher than what the OWRK model predicts, especially when the polarity of HDPE increases.

4.6. To develop a more inclusive model between the adhesion of more polar polymers and polar liquids, further research is required. The effect of various combinations of peroxides and transition metals on the HDPE surface should be studied to obtain a wide variety of surfaces with different polar and disperse surface energies. Then, after analysing their surface and measuring their adhesion to epoxies with different polarities, enough data could be obtained to modify the current work of adhesion models. Furthermore, the possible effects of surface treatment on HDPE's crystallinity, surface morphology and thermal stability should be investigated in a separate work.

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