DEVELOPMENT OF A COATING TECHNOLOGY FOR WOOD PLASTIC COMPOSITES

By

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A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN MATERIALS SCIENCE AND ENGINEERING

WASHINGTON STATE UNIVERSITY
School of Mechanical and Materials Engineering

December 2006

To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of BARUN SHANKAR GUPTA find it satisfactory and recommend that it be accepted.

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Chair

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ACKNOWLEDGMENT

I would like to thank my advisor Dr. Marie-Pierre G. Laborie for giving me the opportunity to work on this wonderful project. I will never forget her exceptional help and assistance during my project work that kept me dedicated and rewarded to the project. Secondly, I would like to thank my committee members Dr. Michael Wolcott, Dr. Kerry Hipps and Dr. Armando McDonald for assisting me during hours of my need.

I would like to thank the Office of Naval Research whose funding provided financial support for my research. I would also like to thank Drew Paints, Inc. and Specialty Polymers for providing us the coating materials and other technical details.

I would like to extend my thanks to the staffs of Wood Materials and Engineering Laboratory. Our director Dr. Don Bender has always spared time for helping me analyze data and provided the necessary enthusiasm for me to push forward. In addition, my special thanks go to Judy Edmister, Patricia Smith, Janet Duncan, Bob Duncan, and Scott Lewis whose cooperative nature endured throughout my work in WMEL. Dr. Karl Englund has been especially helpful providing resources throughout my work on this project. Dr. Patrick Pedrow from the EECS helped me to carry out the plasma treatments in his lab. Dr. Charles Knaack and Dr. Louis Scudiero helped me to perform the X-ray analyses. Lastly, I want to acknowledge the help by my friends, office mates, and other colleagues.

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Abstract

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December 2006

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Wood plastic composites (WPCs) are gaining increasing popularity in exterior applications. However, the weatherability of WPCs drives the need for developing surface finishes that would offer both protection and aestheticism. Developing a suitable coating system for WPCs requires a thorough understanding of the surface properties, surface chemistry and wettability in particular, since these properties directly relate to paint adhesion to WPCs. The first objective of this thesis is therefore to understand the surface properties of WPCs and their relationship to the adhesion of a standard coating. The adhesion of coatings to plastics is greatly improved by surface treatments. The second objective of this research is then to evaluate the impact of common plastic surface treatments on the surface properties of WPCs and on the adhesion of a standard coating to WPCs. In performing these objectives, 8 WPC formulations are manufactured according to a 2^3 full-factorial, so that the effect of formulations on the surface chemistry, wettability and primer adhesion can be determined. Surface chemistry and wettability are evaluated using attenuated-total-reflection FTIR (ATR-FTIR) spectroscopic

measurements and dynamic contact angle analysis with water. Primer adhesion to WPC is determined from an 180° Peel test.

Untreated WPCs showed high contact angle (95-105°) with water and low surface energy (31.5 mJ/m^2) similar to neat polyolefins. As a result, the primer adhesion to untreated WPCs (177-309 N/m) is intermediate to that of neat polyolefins (126-48 N/m) and neat wood (526 N/m). The primer adhesion is linearly related to WPC surface roughness and heterogeneity as determined from contact angle hysteresis.

Moreover, the four surface treatments implemented, oxygen plasma, flame, ultraviolet (UV)-Benzophenone (BP) and chromic acid increase the primer adhesion to WPCs by 1.5-2.5 fold. The chromic acid treated (637 $\pm$ 88 N/m) and oxygen plasma treated (516 $\pm$ 116 N/m) WPCs show the highest primer adhesion, greater than that with neat wood. Surface analyses further suggest that different adhesion mechanisms are responsible for the enhancement in coating adhesion. In the case of plasma treated WPCs, surface oxidation and therefore primary bonding and secondary interactions likely play an important role. On the other hand, chromic acid treatment increases surface roughness significantly resulting in greater interfacial contact for adhesion mechanisms,

Finally, to validate the results obtained on bulk WPCs, the extruded 'skin' surface and the bulk 'core' material of WPCs is compared. Concentration of lubricants and plastic in the 'skin' compared to the core yield lower peel load (135 $\pm$ 24 N/m)

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Dedication

This thesis is dedicated to my mother and father.

CHAPTER ONE

1.1 Introduction, Problem Statement, Rationale and Objective

Wood thermoplastic polymer composites (WPCs) have had a continued annual 20% increase in market demand (Kent 2005, Clemons 2002). WPCs typically contain 45– 60 percent of wood flour, 35 – 50 percent of a thermoplastic polymer such as high density polyethylene (HDPE), isotactic polypropylene (i-PP) and poly(vinyl chloride) (PVC) (Clemons 2002). Apart from these main components, processing additives like lubricants are often added in small amounts (1-5%) to reduce friction between die and melt (Li and Wolcott 2004). Coupling agents and performance enhancing components can also be added in some formulations (Wolcott et al 2001). WPCs are mainly manufactured by profile extrusion. In this process, wood, the polymer, and additives are passed through a heated barrel and mixed by rotating screws. The final shape of the composite is given by a die attached to the end of the barrel. Other common processing technologies include injection molding and compression molding (Clemons 2002).

WPCs have been traditionally sold as low maintenance materials. As a result, much of the research on WPCs has been dedicated to improving the mechanical performance while the protection of WPCs from biodegradation and weathering has been scarcely addressed (Hristov and Vasileva 2003). Recent conferences (Forest Products Society 2001, 8th International Conference on WPCs, Ma, 2005) have underscored the need to improve the durability and resistance of WPCs against degradation and weathering. The simplest method to protect WPCs from weathering is to apply a protective coating. Although coating technologies are available for neat wood and

polyolefins, no coating technology is currently available for WPCs. The overall objective of this research is to provide the knowledge required for designing an optimum coating technology for WPCs. In order to design an optimum coating system, the surface properties of WPCs should be well-known. A thorough study of the physical and chemical properties of WPC surface is therefore needed. In addition, recent research has suggested that adhesion of coatings to WPCs can be improved by selected surface pretreatments. Yet, a comprehensive assessment of all the potential surface treatments has not been performed to date. Furthermore, a fundamental understanding of the adhesion mechanisms involved in the coating of WPCs is lacking. Finally WPC surface and adhesive properties are likely depend on the formulations. A comprehensive understanding of possible formulations and their subsequent impact on surface behavior of WPCs is also needed. From this perspective, the specific objectives of this research are to:

1) Characterize the physical (wettability) and chemical properties of WPC surfaces and their corresponding dependence on specific and varying formulations.
2) Evaluate the adhesion of a standard coating on WPCs and its dependence on the formulations.
3) Evaluate the efficacy of potential surface treatments for improving paint adhesion properties to WPCs.
4) Provide insight on the adhesive mechanisms in action between a standard acrylic coating and WPC surfaces with and without surface treatment.

1.2 Literature Review

In this section, the general practices for coating neat wood and plastic surfaces will be reviewed. While wood can be readily coated because of its polar and porous surface, plastics require pretreatments to activate the surface. This literature review will therefore place particular emphasis on the common pretreatment techniques available for use with polyolefins, while providing a basis in selecting potential surface treatments for WPCs. In fact, a few studies have evaluated the effect of surface treatment on adhesion to WPCs; these will be reviewed last.

1.2.1 Coating of Wood

Industrial settings routinely use wood coating technology as a standard process and have performed so for well over 100 years. Currently, water borne coatings that have a low volatile organic compound (VOC) content have dominated wood coatings. Indeed, Hammerton (2005) reported 8.1×10^6 gal of waterborne coatings was used against 1.08×10^6 gal of solvent borne coatings. Hardboard, plywood, particleboard and strand board commonly use polyvinyl acetate (PVA) and acrylic paints. Additionally, common coatings for wood consist of solvent-borne acrylic, alkyd, nitrocellulose and polyurethanes. Regardless of the coating selected, sanding or planing is performed first to refresh the surface of wood in lieu of chemical processing

1.2.2 Coating of Plastics

Acrylics, polyurethane, polyvinylacetate, melamine, polyester as resins and water, butyl-alcohol, isopropyl alcohol, propylene glycol methyl ether as solvents dominate the

coating of plastics (Ryntz 1998). In 2000, solvent based coatings accounted for 43% of the total consumption, while water based coatings and powder coatings accounted for 26% and 12% respectively (Ryntz 1998). In general, the coating of a plastic substrate is broadly divided into three parts – primer (25 μ), basecoat (13 - 45 μ) and topcoat (45 – 51 μ). The substrate surface is first coated with a primer which acts as an adhesion promoter, eliminates surface defect, reduces porosity and improves surface quality (Ryntz 1998). A base coat is then applied on the primer to hide the primer / substrate color (Ryntz 1998). Finally a clear coat is applied over base coats for protecting the substrate from UV degradation, chemical resistance, chip mark and scratch resistances, etc (Ryntz 1998).

Polyolefins are low surface energy polymers and have no polar component; it is therefore difficult to paint such plastic surfaces. Lindberg (1976) measured adhesion of different paints to plastics and concluded that surfaces with higher free energy (>35mN/m) were easier to paint and there was no correlation established between the adhesion value and thermodynamic properties of the paint media. Bikerman (1959) first suggested that adhesion problems associated with polyethylene may be due to the weak boundary layer (WBL). Schonhorn (1966) and co-workers have put forward evidence in favor of weak boundary concept using polyethylene as a substrate. Moreover, they suggested that surface treatments act primarily by eliminating the WBL.

Schonhorn's research subsequently established a trend, based upon the WBL, which consequently led to a number of pretreatment techniques applied on plastic substrate before application of a coating. Common treatments include flame, cold-plasma, corona, acid etching, UV, electron beam, ion-beam, excimer laser and other

reactive gas treatments. Paint needs to be applied immediately after surface treatment to avoid the loss in surface activity.

The treatments that are most efficient for polyolefins are reviewed next, as they may be evaluated as part of the development of a coating technology for WPCs.

1.2.2.1 Flame treatment

Ryntz (1998) compared several pretreatment methods that included Flame, Chromic acid, Plasma and UV photographing. Ryntz noted flame and chromic acid treatments as having high oxygen content and subsequent total oxidation species (Table 1.1).

Table 1.1: Comparison of Technologies for bonding of low surface energy polymers (Ryntz, 1998)

Pretreatment method	***XPS percentage Total Oxygen content***		***XPS/ATR wt % Total Oxidation Species***		
	Before wiping off	After wiping off	C-O	C=O	COO
Flame Treatment	16.5	6.0	14.2	5.0	1.0
Chromic Acid Treatment	16.5	8.0	--	---	---
Plasma Treatment	14.5	4.0	10.3	6.0	2.0
UV/Benzophenone	21.0	15.0	6.3	9.4	3.1

Flame is a subsonic wave supported through combustion produced by a burner which is held approximately an inch away from the substrate (DiGiacomo 1998). The critical parameters of the treatment include the gas-air ratio, equivalence ratio, and the contact time between the flame and the polyolefin. Flame plasma treatment removes the contamination from the substrate surface and performs a surface activation that leads to the introduction of functional groups and cross linking between chains. The typical

temperature of a flame zone is around 1850°C (DiGiacomo 1998). This high temperature causes the oxygen to form activated mix of ions, electrons, atoms and molecules known as flame-plasma-treatment. The activated species impregnate the hydrocarbon surface, replacing the hydrogen atoms, causing free radicals and introducing oxygen functionalities.

Strobel et al (2001) suggested gas and air naturally cause an occurrence of alkoxy, peroxy and hydroperoxy groups with polyolefins (RH) in a free radical pathway and that this causes the formation of ROOH or ROH groups which increases the polar component of the polyolefins. Thus, Papirer et al (1993) observed that the flamed PE has higher oxygen content (19.4%) as compared to the flamed PP (17.6%) after 10 passes. Additionally, more numerous carbon-carbon chain scissions in PE result in a higher amount of low molecular weight oxidized material (LMWOM) on PE surface as compared to the PP surface. Papirer reported that following a flame treatment of PE and PP, the treated polyolefins were assembled with a styrene-butadiene-rubber (SBR) piece. The 180° peel strength of SBR on treated PE had considerably higher peel adhesion strength of 1600 J/m^2 while the peel strength of SBR on treated PP was 500 J/m^2. The researchers presumed that the LMWOM has favored the bondability for PE while hindered adhesion for PP.

1.2.2.2 Cold Plasma treatment

Ryntz (1998) described cold plasma treatment in presence of oxygen, ammonia, fluorine, nitrogen, argon and other materials (silanes, siloxanes, vinyl etc) performed in a vacuum chamber. If the treatment is performed in presence of inert gases, it is referred as

CASING (Cross-linking with Activated Species of Inert Gases). It is a mix of activated species comprising of ions, electrons, atoms, molecules and excited-state molecules (Ryntz 1998). Electromagnetic energy is imparted by frequency or by coupling type model which creates the glow with the objects being placed in the middle. The rate of modification of substrate depends on a number of parameters including the reactor-design, distance of the objects from the electrodes, reaction time, aging, gas flow, pressure and power. The efficiency of the reaction is determined by the rate of deposition of the species. For inert polymers, functional groups can be incorporated into the surface. The disadvantage is that, due to high crosslinking, the substrate surface may behave mechanically incoherent to the bulk material. Oxygen plasma interacts with PE via chain scission and creation of oxygenated polar functionalities of C-O, C=O, COOH groups (Drnovska et al, 2003). On the other hand, PP undergoes hydrophilic modification at primary carbon atom followed by cross linking at the tertiary carbon atom (Bhat and Upadhyay 2002). Morra M et al (1990) stated that the time dependant aging of the plasma treated surface is quite common and the hydrophobic recovery of contact angle of PE is much less than PP, and that this was probably due to cross-linking induced by plasma in PE. With epoxy adhesive, the untreated HDPE and PP exhibited lap shear strength of 2.1 MPa and 2.55 MPa respectively while plasma treated HDPE and PP exhibits shear strength of 24 MPa and 21 MPa respectively (Ryntz 1998).

1.2.2.3 UV treatment

UV lamps operating between 250 – 400 nm are widely used to alter the surface property of polymer surfaces (Ryntz 1998). It is generally performed in presence of

oxygen, ozone, and in the presence or absence of another photoinitiator. The energy carrier, photon, activates the chemical species which then displaces a hydrogen atom from the polymer chain; thereby, creating free radicals. Cross-linking and fragmentation are the two paths followed by the species. Benzophenone (BP) is the most commonly used photoinitiator since it absorbs UV light at 340-360 nm and excitation occurs rapidly in singlet and triplet state discharging hydrogen from the polymer substrate to generate free radical (Ranby 1999). The free radical reacts with the applied coatings to impart enhanced adhesion.

Castell et al (2004) studied the effect of different concentrations of BP on PP substrate and observed an increase in substrate surface free energy from 26 mN/m to 34 mN/m for substrates treated by solutions containing BP more than 1wt%. The increase in surface energy was produced during first 100sec of irradiation and after that it became constant. Similarly, Yang and Ranby (1997) observed 98% of grafting efficiency for methyl-acrylate on PE treated with 2 wt% of BP and irradiated for 60sec.

1.2.2.4 Chromic Acid treatment

Chromic acid etching and oxidization is a well known method for modifying the polymer surfaces. The acid solution (ASTM D 2093) is generally prepared by mixing the dichromate and the sulfuric acid at room temperature. The polyolefin is then dipped into the solution for a given period of time. The treatment temperature can be varied to obtain optimum output. It functionalizes the polymer surface by incorporating sulphate, carboxylic and carbonyl groups. The mechanism of reaction is believed to be cross linking and chain scission. Apart from the environmental regulations, the disadvantage

from of the method includes the higher amount of chain scission which can cause uncontrollable etching of the surface which washes away during the process of treatment.

Blais et al (1973) did thorough study on chromic etching and suggested that the rate of surface removal enhances with higher temperature and increased reaction time. Mechanistically, chromium VI from the chromic acid forms chromium IV ester with the polymer intermediate - leading to polymer chain scission and incorporation of oxygen moieties, like CO, COOH, OH groups. Briggs et al (1976) studied the effect of etching time on PP and PE and suggested additional presence of SO_3H group on polymer surface. In fact, with epoxy resin, untreated PE and PP exhibited lap shear strength of 0.55 MN/m^2 and 0.28 MN/m^2 while treated PE (6hr/70^oC) and treated PP (6hr/70^oC) exhibited lap shear strength of 6.96 MN/m^2 and 11.2 MN/m^2 respectively. The researchers concluded that the difference in the shear strength exhibited by PE and PP were due to the difference in etching rates on the surface. Moreover, they observed that the lap shear strength increases with increase in etching time.

1.2.2.5 Other treatments

Corona, excimer laser, ion-beam, mechanical abrasion and solvent wiping are other common treatment techniques used in the plastic industry. The corona treatment involves an electric-discharge on a moving substrate over a dielectric covered roll. The discharge causes the gas to ionize and introduce polar functionalities on the inert polyolefin surface (Novak and Florian 2001). The extent of oxidation depends on the parameters of net power, voltage, frequency, electrode geometry, air-gap and the film speed. Additionally, improvements of wettability and adhesion occur in conjunction with

laser treatment. Photons of energy between 5eV to 10eV generates from sources like fluorine (157nm), KrF (248 nm) and Argon (308nm) (Fushinobu et al 1999). Ions beam treatment includes energetic species with high momentum. They have low mean free path and thus can be targeted either to sputter off a species or to alter the surface composition. Ion-implantation and ion-deposition are carried out in vacuum. This method, however, is limited to some specialized application and academic investigations.

Grazing the substrate surface with abrasives to improve adhesion through surface roughening is an old practice (Ryntz 1994). The process removes surface contaminants and weak boundary layers thereby exposing the fresh bulk material for bonding. Solvent wiping with chemicals, like acetone, and cotton cloth is also an old practice. It is used for materials where retaining of surface topography is important. The chemicals cause the surface contaminant and some amount of WBL to dissolve and be wiped away. Chlorinated polyolefins (CPOs) are also used as 'tie coat' to assist adhesion to the subsequent topcoats (Ryntz 1994). A variety of CPOs is commercially available to the coatings industry, however these are expensive.

1.2.3 Coating of Wood Plastic Composites (WPCs)

A few studies have been conducted on surface characteristics of WPCs. Clemons et al (1999) reported the occurrence of composite skin-core morphology in injection molded and extruded composites. For injection molded composites, fibers in the core layer were found to be oriented perpendicular to flow direction and the fibers in skin layers were oriented parallel to flow (Clemons et al 1999). In addition, fiber volume fraction was found to be higher in the core layer as compared to the skin layer (Clemons

et al 1999). Processing parameters also affects the skin-core morphology. Low temperature-slow speed processing leads to thick skin while high temperature-high speed processing leads to thin skin (Fu et al 1999).

Similarly extrusion processing also leads to skin-core morphology and differences in moisture absorption properties. The extruded surface shows higher density and more fiber alignment as compared to the core (Barbosa and Kenny, 2000). Moreover, Stark et al (2004) found that the planed WPC composites have much higher wood content in comparison to extruded and injection molded composites. In all, the nature of WPCs, therefore, appears to be dependant on processing conditions, sampling depth and specimen preparation method.

A comprehensive study on the adhesion and durability of latex paint on wood fiber reinforced polyethylene (WFRP) was performed by Akhtarkhavari et al (2004). The researchers compounded 50% by weight of WFRP in a kinetic mixer. They prepared small specimens (7.0 cm x 12.0 cm) under two conditions, hot and cold-molded conditions. For cold-molded (CM) samples, material discharged from the kinetic mixer was immediately compression molded with 256 MPa pressure in a 20°C steel mold mounted in a 50t press with water chilled platens. For, hot molded specimens the discharged material was held at 185°C and then transferred to a convection oven set to a specific temperature. Consequently, the specimens were subjected to three pretreatment methods. One group was sanded by emery cloth with grit sizes 50, 80, 150 and 220 to completely remove the top surface. A second group was subjected to wheat starch blasting in front of a 6.3 x 38 mm^2 blasting nozzle, 90 cm/min table speed, 207 kPa pressure, 20° nozzle angle and 5.5 kg/min mass flow. And, lastly, a third group was

subjected to a corona treatment by a lab-scale 10,000V treater, 100 mm/min speed, 375mA input current and at a distance of 5 mm from surface. Consequently, the untreated and treated specimens were spray coated with water based white acrylic primer and subjected to scratch test, peel test and durability test to ascertain the level of modification. The scratch test was performed as per ASTM D-3359. Peel test was conducted at room temperature on a computer-controlled screw driven Sintech 20 tensile testing machine, 20 mm/min cross head speed, 5kN load cell and at an angle of 45°. Durability test was conducted by immersing the specimens in water at $40\pm1^{o}C$ in a convection oven. The wetted specimens were immediately removed after 10, 20, 30, 60, 120, 150 and 180 days of immersion and tested for swelling and blistering of paint. The authors reported that the surfaces of the WFRP are process dependent. The HM surface was smooth and glossy confirming the melting and flow of polymers on the surface. In contrast, the CM surface exhibited significant roughness due to exposed wood-fibers (WF) indicating solidification of matrix before flow. Moreover, they found that the surface free energy of CM specimens as 38.8 ± 5.4 mJ/m^2 and HM specimens as 31.3 ± 2.2 mJ/m^2 in comparison to the surface energy of wood (41.8 ± 2.9 mJ/m^2) and PE (30.1 ± 1.8 mJ/m^2). In addition, HM-WPCs revealed lower durability in water immersion than the CM-WPCs.

The authors also studied the effect of aging on corona treated WPCs and found 20% reduction in surface tension within seven days. Furthermore, scratch adhesion performance of the painted HM-WPCs increased from 1.0 to a maximum of 3.75 after sanding and to a maximum of 5.0 after corona treatment. In addition, peel adhesion force increased from 0.5 N/mm to 1.25 N/mm for sanded HM-WPCs and increased from 2.0

N/mm to 10.0 N/mm for corona treated CM-WPCs. Consequently, the researchers concluded that the fiber content on surface is process dependent and has an effect on wettability, durability, and adhesion value. A similar study was conducted by Yang et al (2005) and they observed an increase in surface energy with increasing fiber content in WPC formulation.

Gardner et al (2005) studied the shear strength of epoxy adhesives (90lbs/MSGL) on WPCs as per ASTM D905. The researchers extruded four different WPC formulations with PP, HDPE, PS and PVC polymer matrix. The natural, planed and sanded PP WPCs exhibited dry shear strength of 2.49 MPa, 7.65 MPa and 9.96 MPa respectively. After flame treatment, the same PP composites exhibited adhesive shear strength of 10.52 MPa, 10.43 MPa and 10.05 MPa, respectively. The natural-flamed, planed-flamed, sanded-flamed HDPE composites exhibited much smaller dry adhesive shear strength of 5.25 MPa, 6.25 MPa and 5.65 MPa, respectively. The natural-flamed, planed-flamed and sanded-flamed PS composites, however, exhibited high dry shear strength of 10.17 MPa, 10.79 MPa and 10.12 MPa respectively. On the other hand, the PVC composites exhibited dry shear strength of 4.93 MPa, 7.21 MPa and 5.68 MPa for natural-flamed, planed-flamed and sanded-flamed conditions. Moreover, the researchers reported composite material failure of 0-100% for PP composites, 100% for HDPE composites, 100% for PS composites and 47-92% for PVC composites. Consequently, the researchers concluded that flame treatment was beneficial in increasing adhesive bonding with WPCs.

Overall, the wood plastic composites have great market potential in industrial and domestic sectors. The improvement of its surface properties for better adhesion,

however, will widen its applicability. Specifically, the common surface pre treatment technique proves to be a promising methodology to improve adhesion between WPCs and paints and/or adhesives.

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CHAPTER TWO

SURFACE CHARACTERIZATION AND COATINGS OF WOOD PLASTIC COMPOSITES (WPCS)

2.1 Abstract:

Wood thermoplastic composites (WPCs) are widely used for exterior and interior applications. Exterior usages, like waterfront applications, are demanding protective coatings on WPCs. However, lack of knowledge on surface properties of WPCs is a challenge to the development of a suitable coating system. Moreover, change in WPC components leads to different formulations which may affect the surface properties and consequently paint adhesion to WPCs. A 2^3 factorial design was employed to extrude eight different formulations of WPCs with two polymers, two wood species and two coupling agent conditions. High density polyethylene (HDPE) and polypropylene (PP) were used as the polymer matrix; maple (*Acer spp.*) and pine (*Pinus spp.*) wood flour were used as reinforcements. Maleated polypropylene (MAPP) was used as coupling agent. Surface wood content was measured from the Fourier transform infrared spectroscopic analysis (ATR-FTIR). Wettability and topographical parameters were evaluated from the dynamic contact angle analysis (DCA). An 180° peel test was performed to measure the adhesive interaction between a water based primer and WPCs. The study revealed heterogeneous and low energy surface for WPCs. Consequently, the primer adhesion strength to WPCs (168-309 N/m) was measured to be intermediate to that of neat polyolefins (48-126 N/m) and wood (524 N/m). Moreover, analysis of

variance (ANOVA) revealed significant effect of wood species, polymer type and coupling agent condition on the surface chemistry, wettability and primer adhesion strength. Furthermore, the adhesion of the primer on WPCs depended on the amount of surface wood content and surface roughness.

2.2 Introduction

Wood plastic composites (WPCs) are getting increasing importance in fencing, decking, railing, siding, paneling, boardwalk, patio, picnic table, automotive interiors, profile making and other applications since early 1900s(Clemons 2002, Morton 2003). The market is forecasted to grow at an average annual growth rate of 18% in Northern America and 14% in Western Europe (Morton 2003). The low cost of wood and natural fiber fillers, renewable resources and recycled resins are the major driving forces for the manufacturing of wide range of formulations (Rajan 2005). However, the weatherability of WPCs is an issue of concern for the consumers. One way to protect WPCs from environmental degradation is by applying a protective coating on WPC surface (Forest Products Society, 8th International Conference on WPCs, Ma, 2005). Additionally, a coating increases the aesthetic beauty and provides soft touch to the product. The major problem to develop a coating system is that it requires thorough understanding of the substrate surface properties. However, only a few researches have been performed so far on the surface characteristics and paint adhesion to WPCs. For instance, Stark et al (2004) studied the surface chemical composition for 50% wood flour-polyethylene composites using Fourier-transform-infrared spectroscopy (ATR-FTIR). The researchers observed higher amount of wood on the extruded composites as compared to the injection molded composites. Additionally, the researchers found higher amount of wood component on planed extruded surface as compared to the naturally extruded surface. Stark and Matuana (2004) conducted another study on the weatherability of WPCs with

the ATR-FTIR and found significant increases in carbonyl and vinyl group content on the surface during artificial weathering. On the other hand, Akhtarkhavari et al (2004) studied the acrylic paint adhesion to compression molded WPCs with two different processing temperature conditions. The researchers observed dissimilarities in surface fiber content, contact angle and paint adhesion properties between the cold molded (CM) and hot molded (HM) composites. Specifically, the CM composites exhibited high surface fiber content, low contact angle and consequently high paint adhesion (2.2 N/mm) as compared to the HM composites (0.49 N/mm). Moreover, the researchers observed better coating durability for the CM composites compared to the HM composites. The differences in coating durability were explained by the fact that the CM composites surfaces had higher amount of wood fiber which consequently increased the adhesion with the paint and enhanced the durability.

The problem with all of these studies is that the surface properties of WPCs were evaluated in ways which were different in each research. Moreover, the results were stated quantitatively while the fundamental knowledge is ignored to interpret the results. Consequently, a comprehensive study on the coating aspects of WPCs with respect to formulation, chemistry, wettability and adhesion is required. The specific objectives of this research are to

1. Characterize the physical (wettability) and chemical properties of WPC surfaces and their dependence on formulation.
2. Evaluate the adhesion of a standard coating on WPCs and its dependence on formulations

3. Provide insight on the adhesion mechanisms in action between a standard acrylic coating and WPC surfaces.

2.3 Experimental

Materials: The raw materials for WPCs were wood flour, thermoplastic polyolefins, maleic anhydride grafted polypropylene (MAPP), talc and lubricant. The 60 mesh pine (*Pinus spp*) wood-flour and maple (*Acer spp*.) wood-flour were obtained from American Wood Fibers. The high density polyethylene (HDPE, LB0100, melt index 0.40 g/10min, density 0.95 g/ml), polypropylene (PP, H04F00, melt index 4.0 g/10min at 230°C, density 0.90g/ml) and MAPP (950P, density 0.93g/ml, free maleic anhydride content <0.9%) were obtained from Innovene Inc., Equistar Chemicals and Honeywell respectively. The ester-stearate lubricant (OP100) and talc (Nicron 403) were obtained from Honeywell and Luzenac America Inc respectively. A water based white acrylic primer (Raykote 2000, sp. gravity 10.57 and coating VOC 132.67) was used as supplied by Drew Paints, Inc for testing the paint adhesion to WPCs. The dried wood flour, polymer, talc, lubricant and coupling agent (when used) were dry blended prior to extrusion and fed into the extruder.

Extrusion processing: A 2^3 factorial design was employed to formulate eight different WPC formulations. The components of different formulations are given in Table 2.1. Extrusion was conducted on a 35 mm intermeshing twin screw extruder (Cincinnati Milacron) operating at a 5-8 rpm screw speed and 3.45-5.52 MPa melt pressure. The

barrel temperature and die temperature for the HDPE formulations were 163°C and 171°C respectively. Similarly the barrel temperature and die temperature for the PP formulations were 185-193°C and 185°C respectively. A rectangular die (38mm x 10mm) set up was used to extrude the WPC sections. The hot extruded components were spray-cooled in a water bath and stored in a dry shade before converting into small specimens.

Table 2.1: Formulations for PP and HDPE wood composites

Formulation No.	Wood Flour		Polyolefin		Lubricant	MAPP	Talc
	Type	Wt (%)	Type	Wt (%)	Wt (%)	Wt (%)	Wt (%)
1	Pine	59	HDPE	33.8	1	2.3	4
2	Maple	59	HDPE	33.8	1	2.3	4
3	Pine	59	PP	33.8	1	2.3	4
4	Maple	59	PP	33.8	1	2.3	4
5	Pine	59	HDPE	36.1	1	0.0	4
6	Maple	59	HDPE	36.1	1	0.0	4
7	Pine	59	PP	36.1	1	0.0	4
8	Maple	59	PP	36.1	1	0.0	4

Specimen preparation: Small specimens were sliced from the extruded WPC sections perpendicular to the flow direction to yield rectangular thin pieces. The thin specimens bore rough surface and polymer rich skin layer. Consequently, the specimens were milled by approximately 1 mm all around the surface to remove the polymer rich skin to represent a thin uniform dimensioned (36x9x1 mm^3) homogeneous material. ASTM D 2093 was followed in preparation of the specimens. The specimens were first sanded with 320 grit sandpaper, wiped with lint free cotton cloths, washed in acetone to remove the dust and stirred in acetone for 10 minutes to remove the surface contaminants. Specimens thus prepared were then dried for 1 hour period at 40°C and conditioned in

desiccators with drierite (W.A. Hammond Drierite Company, OH) overnight for next day testing and analysis. The surface of the bulk material was thus tested for chemical, wettability and adhesion tests. For each characterization and adhesion test, 4 replicates were chosen to represent the material property.

ATR-FTIR: The surface chemistry of the 8 WPCs formulations (Table 2.1) and the neat plastic and wood were characterized by an attenuated total reflection-FTIR (ATR-FTIR) spectrometer (Thermo Nicolet Continuum model, MCT-A detector, 45 $\pm$ 5 ^{o} incident angle, 560 scans, 4 cm $^{-1}$ resolution) with ZnSe crystal and Omnic 5.0 software. An index for surface cellulosic hydroxyl groups was measured by normalizing the cellulosic hydroxyl peak intensity at 1023 cm^{-1}(Fig 2.1), with respect to the polyolefinic νC-H stretching peak intensity at 2912 cm $^{-1}$ (Stark 2004).

$$Index_{OH/C-H} = \frac{I_{1023}}{I_{2912}} \quad (1)$$

Contact angle analysis was performed immediately after surface characterization.

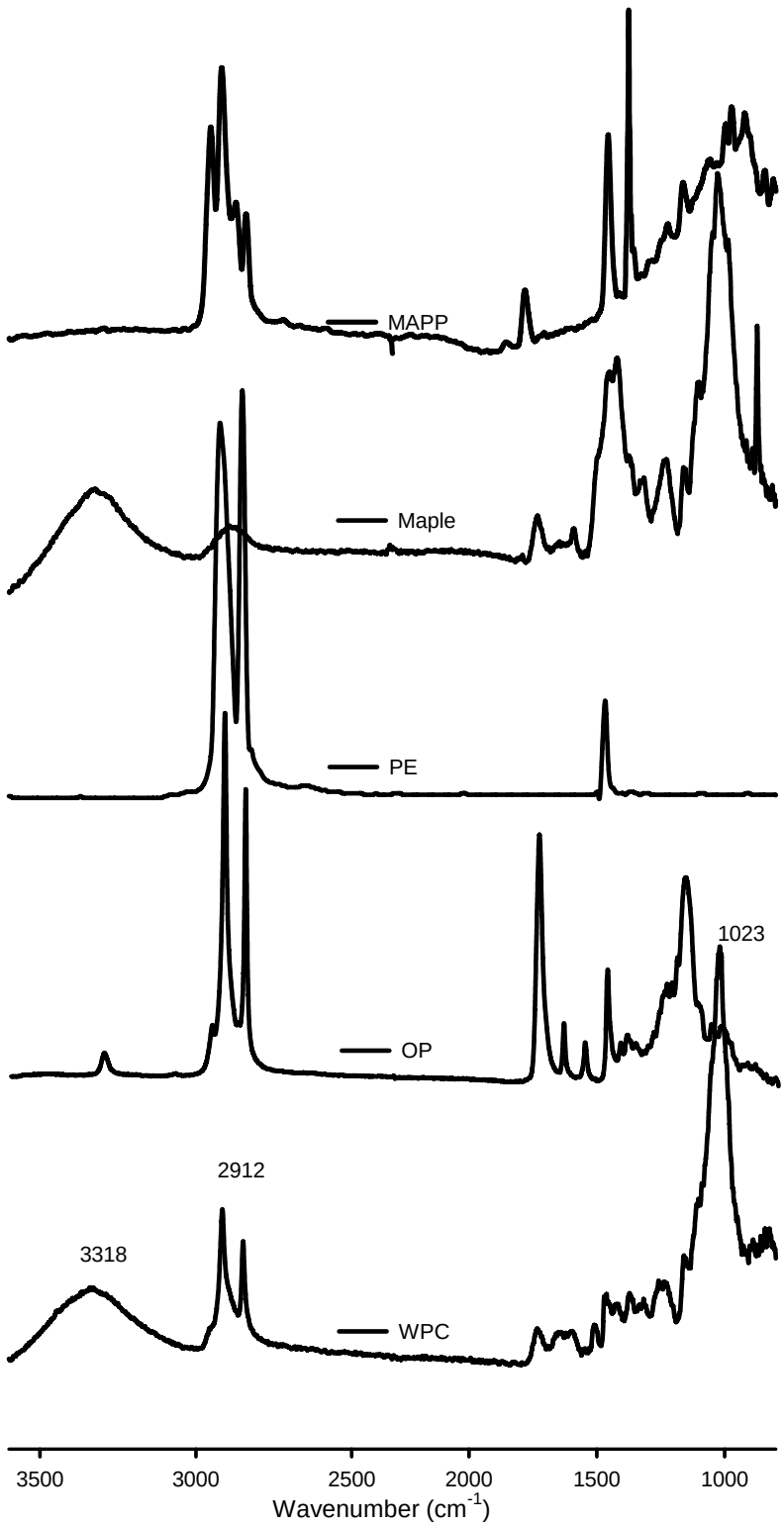

Figure 2.1: Absorbance spectra (ATR-FTIR) for WPC, OP-100, polyethylene, wood and MAPP

DCA: The surface wettability of eight formulations of WPCs was measured by a dynamic contact angle analyzer (DCA Cahn 322) in water (72.8 mJ/m^2) at room temperature. Contact angle was obtained by Wilhelmy plate technique (194 μm /s) at an air-water-sample interface described by the following equation (Walinder and Johansson 2001) –

$$F = \gamma_l p \cos\theta - Ah\rho g \quad (2)$$

Where, γ_L - liquid surface tension, θ - contact angle, A - sample area of immersion, ρ - liquid density , p - wetted perimeter of sample and h denotes the depth of immersion of the specimen in water. Consequently, the linear integration of the force versus stage displacement curve revealed the advancing (θ_a) and receding contact angles (θ_r). θ_a was used to describe the wettability of the dry surface. The contact angle hysteresis was measured from the relative difference between the θ_a and θ_r (Chen et al 1991).

$$\Delta W = \gamma_L (\cos\theta_r - \cos\theta_a) \quad (3)$$

The critical surface tensions (γ_C) of the WPC surfaces were obtained from Zisman plot analysis. The $\cos\theta_a$ of WPCs were measured against the surface tension (γ_L) of 40%, 50%, 60% and 80% solutions of acetic acid and water (Gardner et al 1991). Glass slide was used to measure γ_L. The intersection of the extrapolated line in the plot of $\cos\theta_a$ versus γ_L at θ_a=0 yielded γ_C for the solid surfaces (Adamson 1982). A separate set of specimens were used to evaluate the primer adhesion to WPCs.

180° Peel test: An acrylate primer was applied (0.28-0.41 mm) onto the 8 WPCs formulations, Maple wood and neat PP and HDPE with the help of a wire wound draw down bar (#32, Diversified Enterprises) to test the adhesion strength by peel test. Wet

film thickness was measured by a thickness gauge (S. G. Pinney & Ass. Inc.). A substrate-coating-cloth assembly was prepared following the procedures of ASTM D 6083. A strip of cheese cloth (9 mm wide) was adhered to the uncured coated surface of WPCs. Consequently, the assembly was cured at room temperature (23°C) for 1 hr and a second layer of primer was applied and cured for 48 hrs. Before peeling, the free end of the cloth was wrapped with a mask tape (3M 250) to prevent elongation of the cotton cloth. 180° peel test was performed with an Instron tensile grip (model 4426) at a crosshead speed of 2.0 cm/min (Ranby 1995).

Statistical analyses: Analysis of variance (ANOVA) was performed (SAS software, 2002) to determine the significance (α level of 0.5) of formulations on OH/CH, θ_a, relative hysteresis and peel adhesion strength of WPCs. Sigma plot software (2002) was used for the graphical analysis.

2.4 Results and Discussion:

The surface chemistry of WPCs is quantified by measuring the relative amount of surface wood content (OH/CH) on WPCs by ATR-FTIR. The specific interest on the OH/CH index is related to the fact that the polar O-H bond implies the possibility of bonding with the polar acrylate primer. Moreover, the effect of formulations on the OH/CH index is assessed.

OH/CH ratio: Table 2.2 shows the OH/CH ratio for different formulations of WPCs obtained from the ATR-FTIR spectra. WPCs yield an OH/CH ratio between1.20±0.24 and 2.80±0.01. The OH/CH ratio of Maple is 3.88±0.77 while PE and PP shows 0.0. Thus, there are higher amount of wood component over the polyolefins which agrees well with the WPCs composition (60% wood versus 33% polyolefins). The effects of different WPC components on the OH/CH ratio are summarized in Table 2.3. The choice of the thermoplastic polymer formulations (p=0.0246) have a significant effect on the OH/CH ratio. Specifically, PP formulations have a higher OH/CH ratio (2.37±0.81) than the HDPE formulations (1.83±0.65). Considering the fact that neither PP nor HDPE possesses hydroxyl groups, the variation in OH/CH ratio for the polymer formulations may be explained due to the differences in amount of wood component in surface. Additionally, the choice of wood species have a significant effect on the OH/CH ratio (p= 0.0131). Specifically, formulations with hardwood Maple show higher OH/CH ratio (2.41±0.83) than formulations with softwood Pine (1.81±0.60) which may have resulted due to the differences in their chemical composition (Wise and Jahn 1952). Moreover, the two factor interaction between the choice of MAPP and wood selection is significant (p = 0.041). Introduction of MAPP may have influenced this chemical complexion. Overall, the surface chemistry of WPCs is depended on the extrusion formulations. However, apart from surface chemistry, the adhesion depends on the wetting of the substrate. Wetting of a dry surface is defined by the advancing contact angle. Low contact angle indicates better wetting and consequently better adhesion.

Table 2.2: Surface characteristics of typical WPCs formulations and adhesion of an acrylate coating on WPCs.

Formulation	OH/CH	θ_a (^{o})	Wetting Hysterisis (mJ/m^2)	Peel Load (N/m)
HDPE / Pine/ MAPP	2.32 ± 0.15	95 ± 5	67 ± 15	177 ± 21
HDPE /Maple/ MAPP	1.52 ± 0.05	95 ± 5	63 ± 9	168 ± 13
PP/ Pine/ MAPP	1.90 ± 0.03	102 ± 6	82 ± 16	232 ± 9
PP/ Maple/ MAPP	2.56 ± 0.08	101 ± 4	80 ± 8	249 ± 9
HDPE / Pine	1.20 ± 0.24	99 ± 3	79 ± 2	218 ± 16
HDPE / Maple	2.75 ± 0.04	98 ± 3	78 ± 3	217 ± 23
PP / Pine	2.18 ± 0.26	99 ± 2	85 ± 12	290 ± 24
PP / Maple	2.80 ± 0.01	105 ± 1	90 ± 2	309 ± 20
Maple	3.88 ± 0.77	75[a]	-	524 ± 64
PP	0.0	95 [b]	-	126 ± 35
HDPE	0.0	87 [c]	-	48 ± 1

[a] Zieglar et al, J. Adhesion Sci. Tech, 18, 6 (2004)
[b] Morra et al.: Journal of Adhesión, 33 (1990), pp 77-88
[c] Drnovska H. et al: Colloid Polymer Science, 281 (2003), pp 1025-1033

Table 2.3: The p-value obtained from ANOVA (α level of 0.05) to evaluate the effect of formulation and component interactions on properties of WPCs.

Factors	OH/CH	θ_a (^{o})	Wetting Hysteresis (mJ/m^2)	Peel Load (N/m)
MAPP	0.4575	0.7047	**0.0017**	**0.0004**
Wood	**0.0246**	0.2744	0.8689	0.6114
Polymer	**0.0131**	**0.0104**	**0.0096**	**0.0001**
MAPP*Wood	**0.0410**	0.1909	0.5939	0.8448
MAPP* Polymer	0.4401	0.8145	0.3770	0.5864
Wood*Polymer	0.4018	0.5837	0.5043	0.3714

Wettability: Table 2.2 shows the water contact angle behavior for the eight formulations of WPCs. The contact angle for WPCs ranges from 95 ± 5° to 102 ± 6°, which is similar to that of pure plastics (Morra et al 1990). Previous researches have shown that Maple and Pine yield water contact angle of 75° and 46° respectively (Zieglar et al 2004). This indicates that WPCs have wetting characteristics similar to neat polyolefins. Figure 2.2 shows the Zisman plot for the formulations containing Maple/HDPE/MAPP and Pine/MAPP/PP. WPCs have critical surface tension of 31.5 mJ/m^2, similar to that of polyethylene at 31.0 mJ/m^2 (Ryntz 1998) and less than Maple at 46.6 mJ/m^2 (Zieglar et al 2004) and Pine 58.5 mJ/m^2 (Zieglar et al 2004). This confirms that WPCs possess low energy surfaces like polyolefins. The effect of different components on wettability of WPCs is given in Table 2.3. The choice of polymer has a significant effect on the θ_a of WPC formulations ($p=0.0104$). PP formulations have higher θ_a ($103^{o} \pm 6^{o}$) than HDPE formulations ($97^{o} \pm 6^{o}$). However, while statistically significant, the practical difference in θ_a between the two formulations is not high. Nevertheless, the results are consistent with a higher water contact angle for PP at 95° compared to PE at 87° (Morra et al 1990, Drnovska et al 2003). Additionally, this indicates that the surface energy of WPCs is dominated by the plastic polymer.

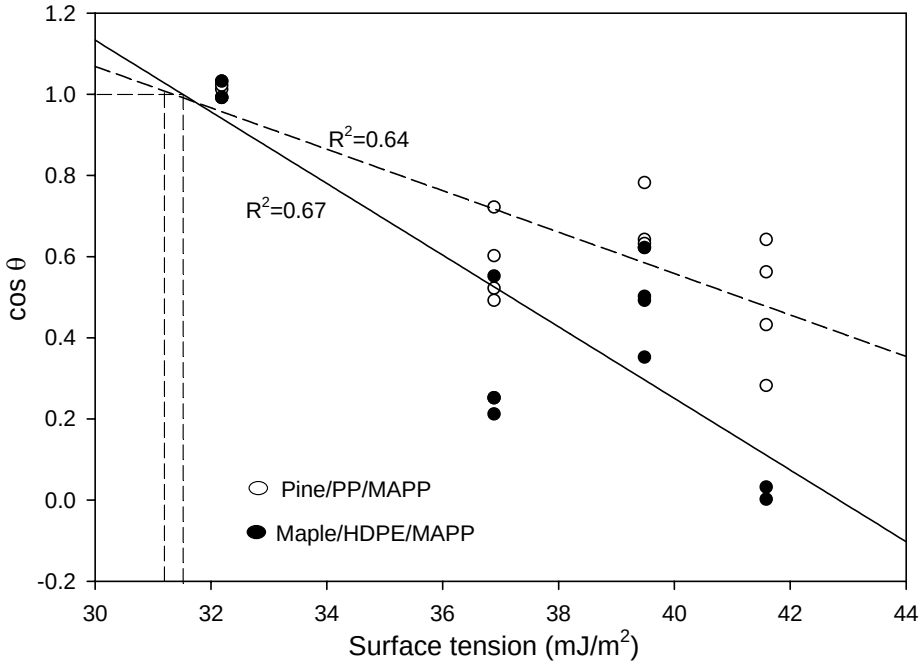

Figure 2.3: Zisman plot of WPCs (Maple/HDPE/MAPP and Pine/PP/MAPP)

Wetting hysteresis: Table 2.2 shows the wetting hysteresis of WPCs. The hysteresis is an indication of surface heterogeneity and roughness. WPCs show wetting hysteresis range from 63 $\pm$ 7 mJ/m^2 to 90 $\pm$ 2 mJ/m^2 (Figure 2.3). This indicates that WPCs have heterogeneous surface. The hysteresis may have resulted due to the intrinsic mechanical and chemical irreversibility due to the combined presence of wood and plastics. Table 2.3 gives the effect of different formulations on the wetting hysteresis. The choice of MAPP condition has a significant effect on the wetting hysteresis (p=0.0096). The formulations without MAPP have a higher hysteresis (83 $\pm$ 8 mJ/m^2) than those with MAPP (73 $\pm$ 14 mJ/m^2). This indicates that formulations without MAPP have higher heterogeneity than those with MAPP. In addition, choice of polymers has a significant effect on the wetting hysteresis (p=0.0017). PP formulations show higher hysteresis (85 $\pm$11 mJ/m^2) than the HDPE formulations (72 $\pm$ 11 mJ/m^2). This suggests that

formulations containing PP are more heterogeneous than formulations containing HDPE. In general, the WPCs have heterogeneous surface and have wetting behaviors similar to the neat polyolefins. Moreover, the surface chemistry, wettability, heterogeneity and roughness combine to define the work of adhesion. Consequently, the WPC surface is coated with a water-based acrylate primer and the adhesion between the primers with different formulations of WPCs is evaluated.

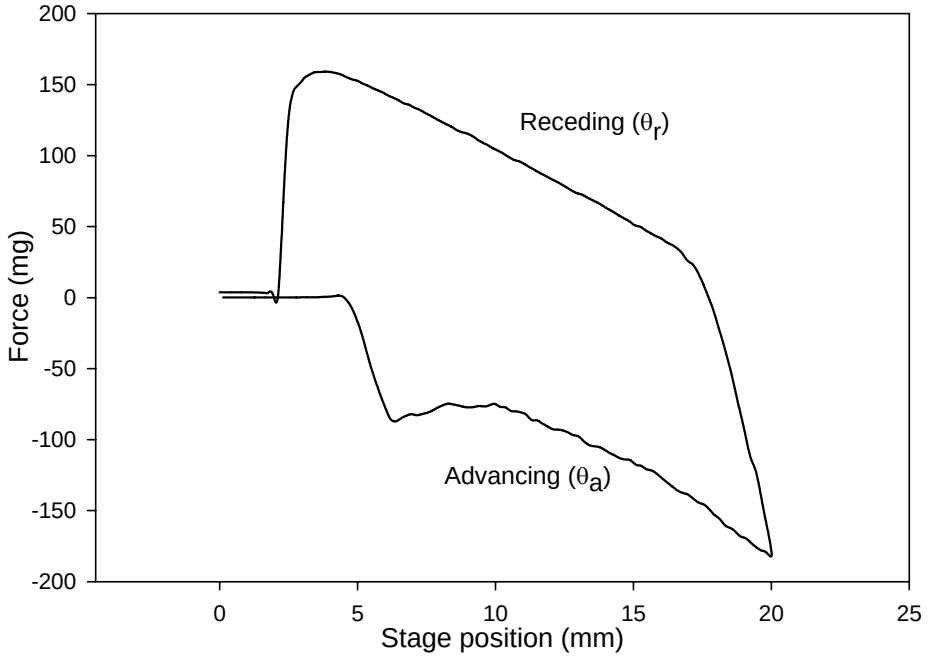

Figure 2.3: DCA analysis of WPCs.

Acrylate primer adhesion strength: Table 2.2 shows the adhesion strength of the acrylate primer to different formulations of WPCs. The peel strength ranges from 168±13 N/m to 308±20 N/m which is greater than the peel strength exhibited by neat PP (126±35 N/m), HDPE (48±1 N/m) and less than that of wood (524±64 N/m). The presence of polyolefins in WPC formulations reduces primer adhesion with the WPCs

which is consistent to the fact that PP and HDPE have low surface activity (OH/CH) and wettability as compared to wood. Previous works on acrylic coated hot molded and cold molded WPCs have reported peel strength (45^0 peel test) of 0.49 N/mm and 2.2 N/mm respectively (Akhtarkhavari et al 2004). Therefore the adhesion characteristics of the acrylic coating to extruded WPCs is comparable to the previous research conducted with another acrylic coating on compression molded WPCs.

Table 2.3 shows the effect of different components on the primer peel adhesion strength of WPCs. The choice of polymers (p=0.0001) has a significant effect on the primer adhesion of WPCs. The PP formulations show higher peel load (270$\pm$45 N/m) than the HDPE formulations (195$\pm$37 N/m). However, the PP formulations have shown higher advancing contact angle which indicates less wettability. From this observation, one would expect adhesion to PP formulation to be lower than adhesion to HDPE formulations, which is not the case. This discrepancy may be due to the fact that albeit significant, the difference in wettability is practically small. The effect of wettability on the adhesion is not detected in this case. However, PP formulations have higher hysteresis and higher hysteresis results from chemical heterogeneity and / or roughness. Consequently, the increase in peel load may be assigned to the fact that PP formulations have higher surface roughness which is expected to lead to better adhesion due to greater surface area. Furthermore, the surface chemistry evaluation have shown greater OH/CH ratio for PP formulations. Higher OH/CH ratio indicates additional presence of wood on the surface and hence greater adhesion. Additionally, neat PP shows superior acrylate primer adhesion strength than neat HDPE which may have occurred due to their chemical

or stereo-chemical differences. Thus, surface chemistry and surface heterogeneity have positively affected in improving the adhesion strength of acrylate primer to PP formulations in comparison to HDPE formulations

Additionally, Table 2.3 reveals significant effect (p=0.0004) of the presence of MAPP in the WPC formulations on the peel adhesion strength of an acrylate coating. Non-MAPP formulations demonstrate higher peel load (258 $\pm$ 54 N/m) than the formulations containing MAPP (207$\pm$ 44 N/m). This may be contributed to the previous observation that formulations without MAPP have demonstrated hysteresis greater than the MAPP formulations. Heterogeneity and surface roughness may have contributed to the hysteresis. Again, higher surface roughness in MAPP-free formulations meant greater surface area and better adhesion to a primer. Thus, it may be concluded that the practical work of adhesion for the two formulations having differences in coupling agent conditions depends on the difference in their surface heterogeneity. This is expected since an increase in surface roughness indicates greater surface coverage for the acrylate primer and consequently better chance of inter-diffusion and chemical bonding with the substrate.

In general, the surface chemistry, wettability and roughness have considerable effect on the peel adhesion strength of WPCs. However, the basic mechanism of adhesion is still to be evaluated and is conducted by studying the relationship between the peel load versus OH/CH, θ_a and relative hysteresis. The coefficient of determination (R^2) is used to predict the linearity between the variables.

Surface chemistry and peel load: The plot of peel load versus OH/CH ratio is shown in Figure 2.4. It appears that the peel load increases with increasing OH/CH ratio. This suggests that the adhesion between the acrylate primer and WPCs increases with an increase in wood content on the surface. The upward trend indicates that there may be an interfacial interaction, most possibly adsorption and penetration of the acrylate coating into wood (Meijer 2003) which leads to other surface specific interactions. The fact, that chemistry is not the only governing factor to adhesive interaction, suggests approaches in studying the effect of surface wettability on peel load.

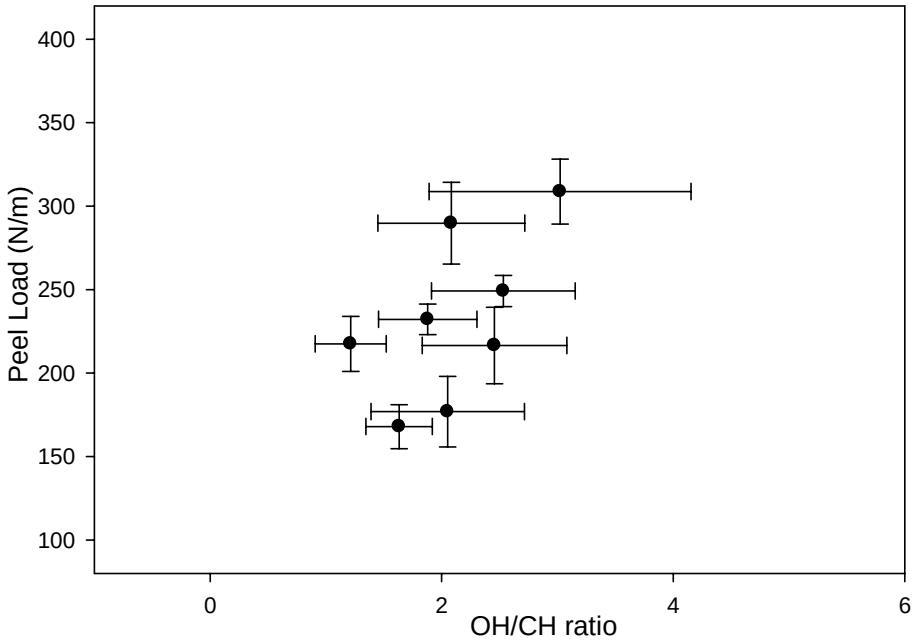

Figure 2.4: Plot of peel load against OH/CH ratio

Surface wettability and peel load: The plot of peel load versus advancing contact angle is shown in Figure 2.5. In general, the peel load increases with an increase in advancing contact angle (R^2=0.54) which is inconsistent with the fact that increasing contact angle

indicates a decrease in wettability and consequently a decrease in adhesion. However, previous researches have shown that the advancing contact angle increases with increasing surface roughness (Adamson 1982, Morra et al 1990). Thus surface roughness may have influenced the contact angle and peel load. Figure 2.6 shows the plot of peel load versus relative hysteresis. In general, peel load increases with an increase in wetting hysteresis as shown by the positive linear relationship between peel load and hysteresis (R^2=0.89). This is consistent with the fact that surface roughness is one of the main reasons of hysteresis and roughness indicates an increase in geometric area of the substrate. Thus in accordance with Kendall (2001) the increase in peel load with hysteresis may be explained due to an increase in geometric area of the substrate leading to greater adhesive interaction between the applied primer and the substrate. Mechanical interlocking between the cured primer and the rough surface may also be a contributing factor to increase the adhesive strength.

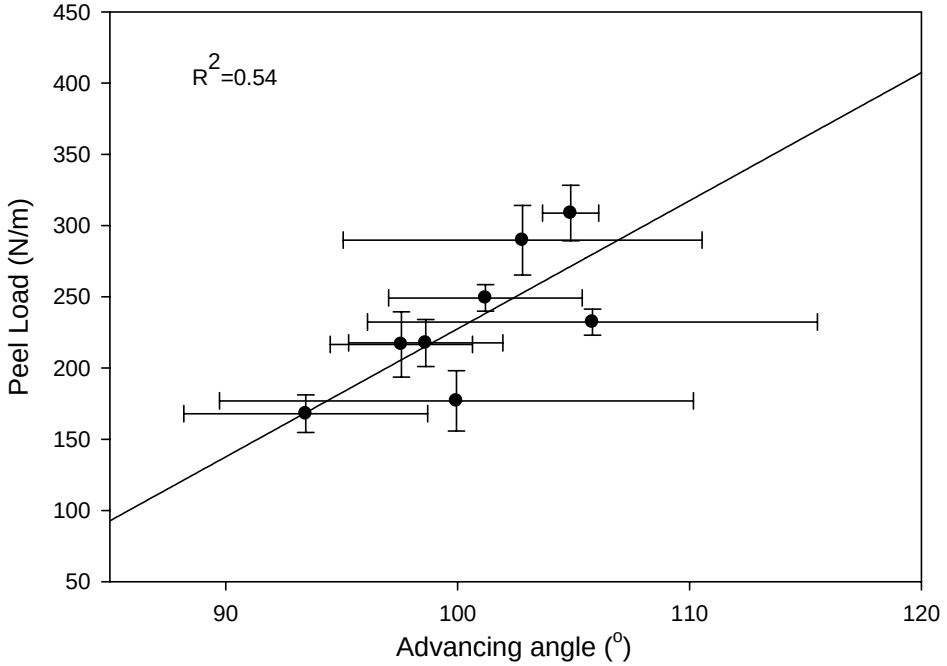

Figure 2.5: Plot showing the dependence of peel load on advancing contact angle

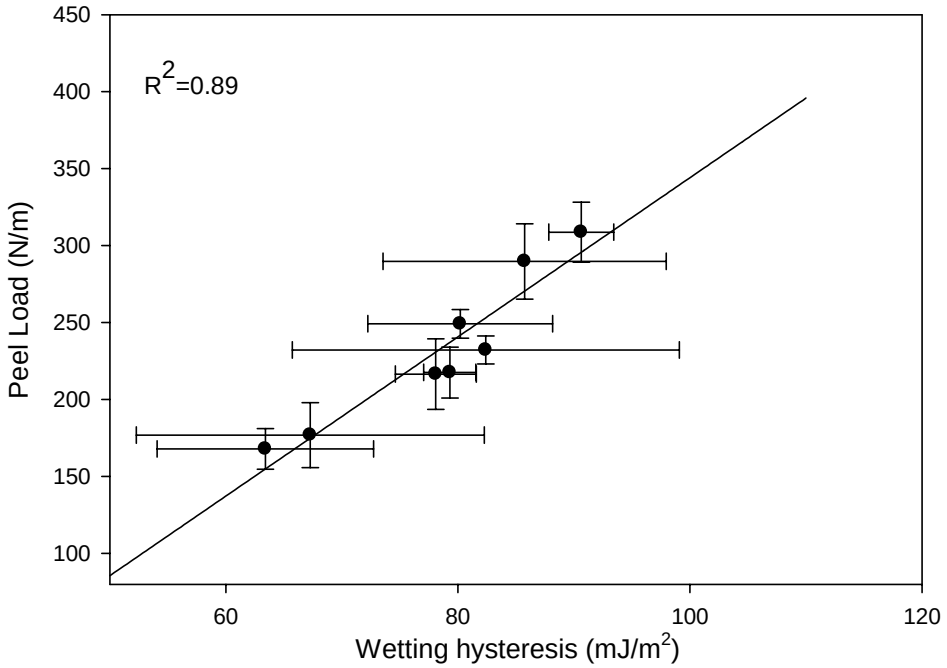

Figure 2.6: Plot showing the dependence of peel load on wetting hysteresis

2.5 Conclusion

The surface chemistry, wettability and acrylate primer adhesion was measured for the eight formulations of WPCs. Surface chemistry was evaluated from the ATR-FTIR spectral interpretation. Relative wood content was measured by calculating the ratio of wood OH peak intensity versus polyolefinic CH peak intensity (OH/CH). The OH/CH ratio of WPCs (1.33-2.77) compared well with the wood flour (59%) versus polyolefin (36%) ratio in the WPC formulations. Additionally, significant effect of components was obtained for the surface chemistry of WPCs. Maple formulations and polypropylene (PP) formulations have significantly high OH/CH as compared to the Pine and polyethylene (HDPE) formulations. Furthermore, the two factor interaction between the maleated polypropylene (MAPP) condition and the choice of wood species on the OH/CH ratio was significant.

The wettability of the WPCs was measured by dynamic contact angle analysis. The contact angle of WPCs with water was high (95-105°) as compared to the literature value of pure wood; however, it was similar to the contact angle values of neat polyolefins. Additionally, the WPCs have high wetting hysteresis which possibly has resulted due to chemical and mechanical heterogeneity. Significant effect of the choice of polymers and MAPP conditions was found on the contact angle and hysteresis. PP formulations have higher contact angle and greater hysteresis than the HDPE formulations. Additionally, formulations without MAPP have greater hysteresis than the

MAPP formulations. Zisman plot analysis confirmed low surface energy (31.5 mJ/m^2) behavior of WPCs similar to neat polyolefins.

The WPC surface was coated with an acrylate primer to measure the adhesion strength to WPCs by an 180° peel test. Results showed higher peel strength (177-309 N/m) as compared to neat polyolefins (126-48 N/m). However, the peel adhesion strength to WPCs was less as compared to wood (526 N/m). The primer adhesion depended on the choice of polymers and the condition of MAPP. The PP formulations exhibited higher primer adhesion as compared to the HDPE formulations which compared well with the high OH/CH and high hysteresis. Similarly, non-MAPP formulations demonstrated greater peel strength as compared to the MAPP formulations. The surface specific interactions, penetration of liquid coating into the WPCs and mechanical interlocking are the main cause of adhesion. Overall, surface chemistry, formulations, wettability and surface topography have significant effect on the primer adhesion to WPCs.

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CHAPTER THREE

SCREENING OF DIFFERENT SURFACE ACTIVATION METHODS TO IMPROVE PAINT ADHESION TO WOOD PLASTIC COMPOSITES (WPC)

3.1 Abstract:

The low priced wood plastic composites (WPCs) are gaining increasing popularity in exterior as well as interior purposes mainly for building, decking, paneling and furniture applications in place of the traditional wood items. WPCs are manufactured by reinforcing wood fibers or wood flours into the plastic matrix. The presence of surface inactive plastic imparts low paint adhesion to the WPCs as compared to the wood. Generally, the neat plastic surfaces are activated before paint application by various pretreatments to increase the paint adhesion. The pretreatment technique enhances the adhesion to wood too. However, the application of the surface treatment for improving the coating adhesion to WPCs is scarcely addressed. Four treatments, namely, oxygen plasma, chromic acid, flame and ultra-violet/Benzophenone treatments were performed on the WPC surface to determine the best pretreatment technique in terms of paint adhesion. Surface chemistry was measured by Fourier transform infrared spectroscopy (ATR-FTIR) and surface wettability was measured by dynamic contact angle (DCA) analysis. An acrylate primer was applied to the untreated and treated surfaces of WPCs to measure the 180° peel adhesion strength. Statistical analysis was performed to assess the effect of treatments on the surface properties. Treatment conditions had significant effect on the surface chemistry, wettability and primer

adhesion to WPCs. Moreover, the chromic acid treatment (637 $\pm$ 88 N/m) and the oxygen plasma treatment (516 $\pm$ 116 N/m) were the best surface activation methods to enhance acrylate primer adhesion to WPCs. The UV/BP (466 $\pm$ 107 N/m) and flame treatment (381 $\pm$ 94 N/m) followed the rank accordingly. Additionally, the primer adhesion to WPCs depended on the substrate surface area and the amount of surface oxidation. In particular, chromic acid treatment increased the surface roughness while oxygen plasma treatment increased the surface polarity. Surface wood content had little effect in defining the mechanism of adhesion to treated WPCs.

3.2 Introduction

Wood plastic composites (WPCs) are new generation, light weight composites gaining increasing popularity in building, joineries and furniture sectors. Generally, the WPCs have 30-65% of wood as reinforcements (Maine 2004) in the polyolefin matrix. The economic issue of replacing the high cost polyolefins with low cost wood fillers is the major attraction for the companies (Rajan 2005) to enter into the $775 million WPC market (Morton 2003). Despite enjoying the economic advantages, recent conferences have addressed the weathering of WPCs thereby raising concern over the durability features (Forest Products Society, 8th International Conference on WPCs, Ma, 2005). One of the easiest ways to enhance the durability and aesthetic value of WPCs is by application of a coating on the surface. Though, fundamental knowledge exists on the coating adhesion to wood (Back 1991) and polyolefins (Ryntz 1998) there is currently little information on the coating adhesion to WPCs. In fact, Gupta and Laborie (2006) observed low acrylate adhesion to WPCs (168-309 N/m) as compared to the acrylate adhesion to wood (524 N/m). Particularly, the presence of surface inactive polyethylene (PE) and polypropylene (PP) creates surface heterogeneity and insufficient paint adhesion to WPCs (Gupta and Laborie 2006). Definitely, the activity of the polyolefins is enhanced by priming or pretreating the surface with flame, chromic acid etching, ultra-violet (UV) radiation and oxygen plasma treatments (Ryntz 1998). The pretreatments oxidize the substrate surface and increase the polarity and surface energy. Specifically, the oxygen plasma causes carbon-carbon chain scission in PE (Drnovska 2003) and crosslinking in PP (Bhat et al 2002) to incorporate oxygen moieties. Flame treatment

generates alkoxy, peroxy and hydroperoxy groups to react with the polyolefins in a free radical pathway thereby forming reactive substrates (Strobel et al 2001). Benzophenone (BP), however, gets photo-excited to high energy states in UV radiation and undergoes reactive collision with the polymer substrates to create active polyolefins (Ranby et al 1999). Similarly, the esterification in the wet process of chromic acid etching leads to chain cleavage and formation of polar groups on the polyolefins (Blais et al 1974). Furthermore, wood also exhibits enhancement in surface polarity and adhesion with the corona, flame, ozone, oxygen plasma and acid pretreatments (Back 1991, Nussbaum 1993, Mahlberg et al 1999, Podgorski et al 2000). Nevertheless, each of these surface treatments has limited lifetime and requires rapid coating of the activated surface (Yasuda 1985, Brewis and Mathieson 2002).

Thus, it is not surprising that the paint adhesion to WPCs can be improved by the surface activation methods aforementioned. In fact, Akhtarkhavari et al (2004) reported improvement in paint adhesion after pretreating the compression molded WPCs surface with sanding, wheat-starch blasting and corona treatment. The authors observed significant process dependency of WPCs resulting to fiber-rich surface for the cold-molded (CM) WPCs and fiber-lean surfaces for the hot-molded (HM) WPCs. Moreover, compared to the sanding and wheat starch blasting, the corona treatment was found to be superior in terms of acrylate paint adhesion. Similarly, Gardner et al (2005) studied the epoxy adhesive shear strength with the extruded WPCs and reported increase in dry and wet adhesive shear strength after sanding and flame treatment. Specifically, the dry

adhesive shear strength of the PP-composite (2.50 MPa) was increased to 9.96 MPa after sanding and 10.05 MPa after sanding and flaming.

To date, however, there has been little systematic assessment of the potential surface activation techniques on the adhesion of coatings on WPCs. Consequently, within the broader view to develop the optimum coating technology for the WPCs, this study has two objectives:

1. Determine the best surface pretreatment technique to develop strong adhesion between WPCs and an acrylate coating.
2. Determine the effect of the treatments on the surface properties (chemistry, wettability and topography) of WPCs and get insight on the adhesion mechanisms.

3.3 Experimental

8 formulations of WPCs were extruded with two polymers, two wood species and two coupling agent conditions. Four treatments, namely, oxygen plasma, chromic acid, UV/BP and flame treatment were performed on the eight formulations of WPCs.

Materials: The raw materials for WPCs were wood flour, thermoplastic polyolefins, maleic anhydride grafted polypropylene (MAPP), talc and lubricant. The 60 mesh Pine (*Pinus spp*) wood-flour and Maple (*Acer spp.*) wood-flour were obtained from the

American Wood Fibers. The high density polyethylene (HDPE, LB0100, melt index 0.40 g/10min, density 0.95 g/ml), polypropylene (PP, H04F00, melt index 4.0 g/10min at 230°C, density 0.90g/ml) and MAPP (950P, density 0.93g/ml, free maleic anhydride content <0.9%) were obtained from Innovene Inc., Equistar Chemicals and Honeywell respectively. The ester-stearate lubricant (OP100) and talc (Nicron 403) were obtained from Honeywell and Luzenac America Inc respectively. A water based white acrylic primer (Raykote 2000, sp. gravity 10.57 and coating VOC 132.67) was used as supplied by Drew Paints, Inc for testing the paint adhesion to WPCs. The dried wood flour, polymer, talc, lubricant and coupling agent (when used) were dry blended prior to the extrusion and fed into the extruder.

Extrusion processing: A 2^3 factorial design was employed to formulate eight different WPC formulations. The components of different formulations are given in Table 3.1. Extrusion was conducted on a 35 mm intermeshing twin screw extruder (Cincinnati Milacron) operating at a 5-8 rpm screw speed and 3.45 – 5.52 MPa melt pressure. The barrel temperature and die temperature for the HDPE formulations were 163°C and 171°C respectively. Similarly the barrel temperature and die temperature for the PP formulations were 185-193°C and 185°C respectively. A rectangular die (38mm x 10mm) set up was used to extrude the WPC sections. The hot extruded components were spray-cooled in a water bath and stored in a dry shade before converting into small specimens.

Table 3.1: Extruded formulations of PP and HDPE wood flour composites

Formulation No.	Wood Flour		Polyolefin		Lubricant	MAPP	Talc
	Type	Wt (%)	Type	Wt (%)	Wt (%)	Wt (%)	Wt (%)
1	Pine	59	HDPE	33.8	1	2.3	4
2	Maple	59	HDPE	33.8	1	2.3	4
3	Pine	59	PP	33.8	1	2.3	4
4	Maple	59	PP	33.8	1	2.3	4
5	Pine	59	HDPE	36.1	1	0.0	4
6	Maple	59	HDPE	36.1	1	0.0	4
7	Pine	59	PP	36.1	1	0.0	4
8	Maple	59	PP	36.1	1	0.0	4

Specimen Preparation: Small specimens were cut from the extruded WPC lumbers perpendicular to the flow direction to yield rectangular thin pieces. However, this specimen contained polymer rich skin layer and polymer-lean core material. In order to have homogeneous surface, the specimens were milled by approximately 1 mm around the sides to remove the skin to represent a thin uniform dimensioned specimen of 36x9x1 mm^3. ASTM D 2093 was followed in preparation of specimens. The specimens were first sanded with 320 grit sandpaper (wet and dry type), wiped with lint free cotton cloth, washed in acetone to remove the dust and then stirred in acetone for 10 minutes to remove any surface contaminants. Specimens thus prepared were then dried for 1 hour period at 40^oC and placed in desiccators with drierite overnight for next day testing and analysis. The surface of the bulk material was thus tested for chemical, wettability and adhesion tests. 4 replicates were chosen for each surface treatment and adhesion test.

3.3.1 Surface Treatments

a.) Oxygen plasma treatment: Plasma was generated in a cylindrical reactor with a radio frequency (13.56MHz, ASTM D 6105-04) coil, at room temperature, 100 watt power and $0.2x10^{-6}$-$2.1x10^{-6}$ MPa base pressure. The design of the reactor is given elsewhere (Shepsis et al 2001). All four replicates were treated in a single run. The specimens were firmly end-attached on a double sided scotch tape wrapped on a steel rod running through the middle of the reactor (along the horizontal axis). HDPE formulations were treated at $0.013x10^{-3}$ MPa pressure, 52sccm oxygen flow rate and 30min treatment period (Drnovska et al 2003). PP formulations were treated at $0.011x10^{-3}$ MPa pressure, 10sccm oxygen flow rate and 10min treatment period (Bhat and Upadhyay 2002). To avoid contamination and aging, treated specimens were transported in clean glass vials and characterized within 150min of treatment.

b.) Chromic acid treatment: A chromic acid solution was prepared as per ASTM D-2093. The specimens were immersed in fresh chromic solution under constant stirring at 70°C for 2min (Rasmussen et al 1977). The specimens were subsequently washed in distilled water for 20min, dried in oven at 40°C for 1 hr, conditioned in desiccators overnight and carried in glass vials for characterization within 24 hrs.

c.) Flame treatment: Air (2.9 kPa) and natural gas (3.7scfm) were mixed in a venturi-tube to generate flame from a 'T' type utility ribbon burner (Ensign Ribbon Burners LLC, NY). The burner was packed with four layers of corrugated sheets to produce

uniform flame cones. Specimens were placed side-by-side on a steel plate at a distance of 12mm from burner-edge (Park et al 2003) and manually moved at a speed of ~0.3m/s in flame.

d.) UV/ BP treatment: Test specimens were dipped into an Acetone / Benzophenone (BP) solution (5% by wt) (Castell et al 2004) for 1 minute and let the solvent evaporate at room temperature. A thin film of BP was thus deposited on the WPC surface. BP coated specimens were irradiated for 2min, each side, under metal halogenide lamp (Heraeus 380 watt) at 20cm substrate-to-source distance (Castell et al 2004). Exposed specimens were washed with acetone (to remove extra BP) and kept in glass vials wrapped with aluminum foils for overnight.

3.3.2 Characterization Methods

Untreated and treated specimens were first characterized by the Attenuated-total-reflection-Fourier-transform-infrared-radiation (ATR-FTIR) and immediately evaluated for the dynamic contact angle analysis (DCA). SigmaPlot and SAS software were used to perform the graphical representation and statistical analysis respectively.

a.) ATR-FTIR analysis: The surface chemistry of the 8 formulations of WPCs was characterized by the ATR-FTIR (Thermo Nicolet Continuum model, MCT-A detector, 45 $\pm$ 5 ^{o} incident angle, 560 scans, 4 cm^{-1} resolution, ZnSe crystal and Omnic 5.0 software) after treatment by flame, chromic, UV/BP and O_2 plasma and also without treatment.

These treatments are expected to oxidize WPC surface and therefore increase surface polarity. In particular, most pretreatment techniques are expected to modify the surface by incorporating the C=O groups (Strobel et al 1995). In addition, in a previous study (Gupta and Laborie 2006) a positive correlation was found between the surface OH content in WPCs and adhesion to an acrylate coating. Therefore ATR-FTIR was used to monitor possible chemical changes. Two parameters were evaluated to quantify the surface oxidation and cellulosic content respectively (a) O=C/C-H and (b) cellulosic O-H / polyolefinic C-H.

The surface O=C/C-H ratio was determined by normalizing the band area at 1530-1840 cm^{-1} with the area at 1410-1530 cm^{-1}(Fig 3.1) (Strobel et al 1995). The bands are selected in close proximity in order to minimize the variation within the sampling depth and the amount of contact with the ZnSe crystal. The region of 1530-1840 cm^{-1} was specifically selected as it represents the presence of C=O moieties in COOH, CHO, esters and anhydride groups which is easily detected by the ATR (Brewis and Briggs 1981). The O=C/C-H in untreated WPCs is assigned to the carbonyl groups present in the cellulose, lignin, hemicellulose and / or extractives (Moore and Owen 2001, Hristov and Vasileva 2003). Minor absorbance by the MAPP (2.3% by weight) and OP (1% by weight) will be masked by the strong absorbance from the wood carbonyl groups (59% by weight). The region of 1410-1530 cm^{-1} represents the C-H bending and scissoring motion which is expected to be least affected during the treatment.

$$OC/CH = \frac{A_{1530-1840}}{A_{1410-1530}} \quad (1)$$

However, there is a possibility that the surface oxidation process may change the C-H bonds appearing in the band 1410-1530 cm^{-1}. Consequently, an intensity ratio was performed with the surface cellulosic hydroxyl group by normalizing the cellulosic hydroxyl peak intensity at 1023 cm^{-1} with respect to the polyolefinic νC-H stretching peak intensity. The C-H stretching peak intensity is selected at 2912 cm^{-1} for the HDPE formulations and 2918 cm^{-1} for the PP formulations (fig 3.1). A change in the concentration of surface polymers or wood would indicate a change in OH/C-H ratio.

$$Index_{OH/C-H} = \frac{I_{1023}}{I_{2912}} \qquad (2)$$

Contact angle analysis was performed immediately after surface characterization.

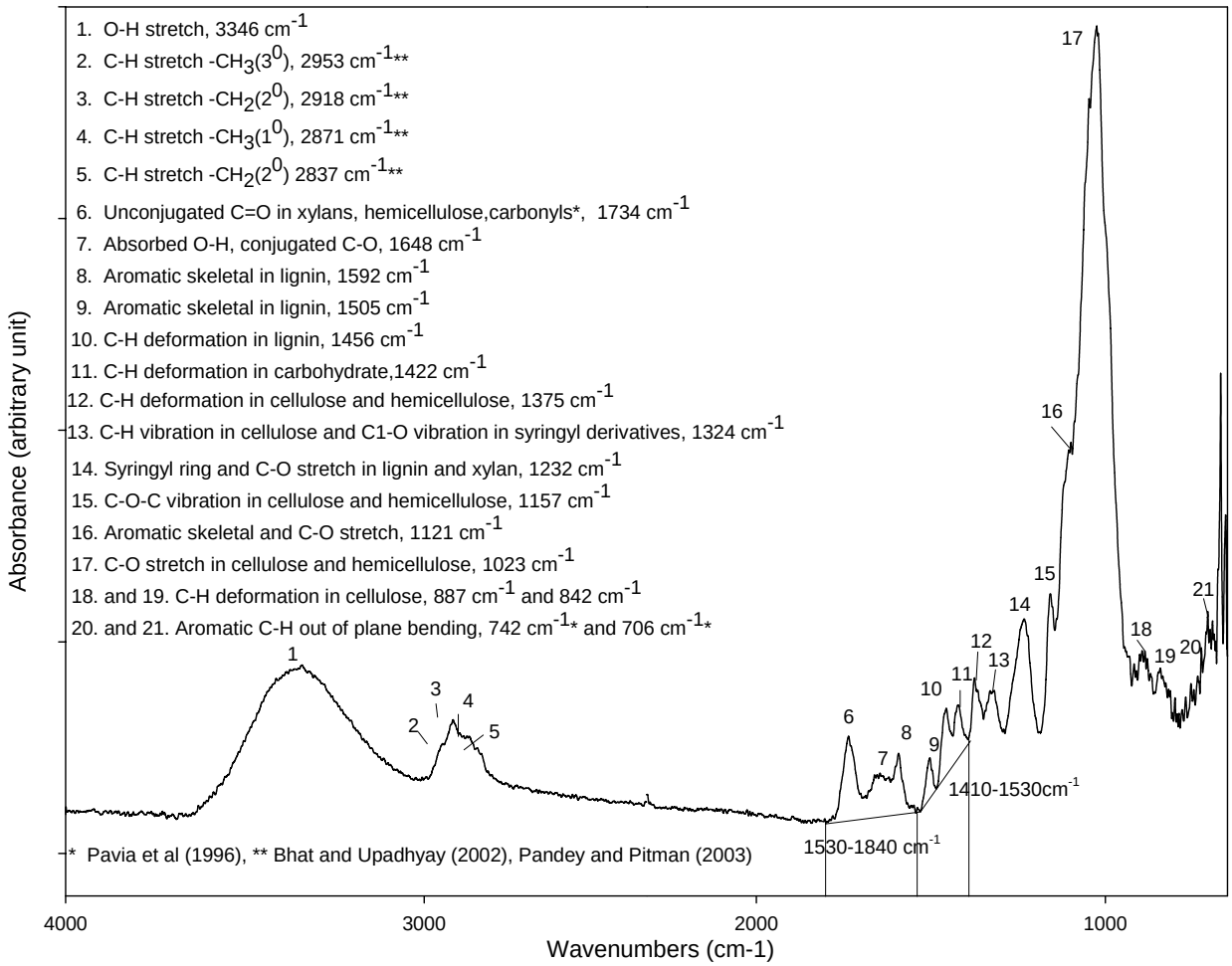

Figure 3.1: ATR-FTIR spectra of PP/Maple/MAPP formulation.

b.) DCA analysis: The surface wettability of the eight formulations of WPCs was measured by a dynamic contact angle analyzer (DCA Cahn 322) in water (72.8 mJ/m^2) at room temperature. Contact angle was obtained by Wilhelmy plate technique (194 μm /s) at an air-water-sample interface described by the following equation (Walinder and Johansson 2001) –

$$F = \gamma_l p \cos\theta - Ah\rho g \qquad (2)$$

Where, γ_L - liquid surface tension, θ - contact angle, A - sample area of immersion, ρ - liquid density , p - wetted perimeter of sample and h denotes the depth of immersion of the specimen in water. Consequently, the linear integration of the force versus stage displacement curve revealed the advancing (θ_a) and receding contact angles (θ_r). θ_a was used to describe the wettability of the dry surface. The wetting hysteresis was measured from the relative difference between the θ_a and θ_r (Chen et al 1991).

$$\Delta W = \gamma_L (\cos\theta_r - \cos\theta_a) \qquad (3)$$

c.) XRD: Polymer crystallinity and morphology may also be affected by the treatment. Therefore X-ray diffraction (XRD) was used to further monitor changes in polymer morphology. A sample survey was performed on the formulation HDPE/Pine/MAPP. Presence of crystallinity in the composite formulation was evaluated from the X-Ray diffractometric measurements (Kristalloflex Diffractometer, D 500, Siemens Daco MP) using Cu-Kα radiation and scanning from 5.0 to 25.0 of 2θ with a step size of 0.01.

d.) Profilometer: Surface roughness was qualitatively measured (SPN Technology Inc.) by pressing the specimen surface against a diamond stylus (12.5 µm radius). A sample survey was performed for the untreated and treated HDPE/Pine/MAPP formulation to assess the effect of treatments on surface topography. 35 mm of the surface was scanned at a rate of 0.4 mm/sec with an application force of 10 mgF. Root mean square (RMS) roughness was measured by Intelligent Profiler software (Version Stress 8.10, 1993).

e.) Scanning Electron Microscopy: Surface structure of the untreated and treated WPCs were characterized by SEM technique by gold coating with a Hitachi SEM (20kV).

3.3.3 Adhesion test

An acrylate primer was applied (0.28-0.41 mm) onto the 8 WPCs formulations of treated WPCs with the help of a wire wound draw down bar (#32, Diversified Enterprises) to test the adhesion strength by the peel test. Wet film thickness was measured by a thickness gauge (S. G. Pinney & Ass. Inc.). A substrate-coating-cloth assembly was prepared following the procedures of ASTM D 6083. A strip of cheese cloth (9 mm wide) was adhered to the uncured coated surface of WPCs. Consequently, the assembly was cured at room temperature (~23°C) for 1 hr and a second layer of primer was applied and cured for 48 hrs. Before peeling, the free end of the cloth was wrapped with a mask tape (3M 250, flat stock paper backing, rubber adhesive, adhesion to steel 89N/100mm width) to prevent elongation of the cotton cloth. 180° peel test was

performed with an Instron tensile grip (model 4426) at a crosshead speed of 2.0 cm/min (Ranby 1995). Peel load (N) was reported against 10^3mm specimen width.

Statistical analyses: To evaluate the effect of the surface treatments on each oxygen ratio, the data were analyzed in a randomized complete block design (CBD). The measured oxygen ratios, OH/CH, θ_a, relative hysteresis and peel load of a particular treatment were confounded in a single block and the treatment effects were investigated. A one-way analysis of variance (ANOVA) was performed to detect the significance of differences ($\alpha = 0.05$) in the ratios among the treated and control WPCs. Further analysis with Duncan's multiple range test (MRT) was performed to compare ($\alpha = 0.05$) the effects of the 5 conditions.

3.4 Results and Discussion:

The effect of surface treatments are first evaluated on the surface chemistry, namely O=C/C-H and O-H/C-H and then on the surface morphology or crystallinity of the thermoplastic polymer in the WPCs.

O=C/C-H: Table 3.2 and Figure 3.2 show the O=C/C-H ratios for all the formulations and all the treatments. In general, there is a good reproducibility in the measured ratio, albeit some cases display a large variation (Table 3.2). The variability in the measurement may arise from heterogeneities in the sample and also in the surface treatment. In addition, the FTIR measurement is local (20μ). For each treatment, the

O=C/C-H ratio generally varies from simple to double with different formulations. Table 3.3 shows the results of the ANOVA and Duncan test to evaluate and compare the effect of the treatments on surface properties. Regardless of the WPC formulations, there is a significant effect of surface treatment on WPC O=C/C-H content ($p=0.0021$). Specifically, the oxygen plasma treated WPCs have significantly higher surface C=O content (3.14 ± 1.73) than WPC surfaces that are either untreated (2.06 ± 0.70) or have been subjected to other surface treatments. The oxygen plasma treatment therefore significantly oxidizes WPC surfaces. This result is consistent with the previous observations showing incorporation of oxygen moieties as C=O groups after plasma treatment on neat polyolefins (Ryntz 1998) and on cellulosics (Mahlberg et al 1999). However, the flame (1.83 ± 1.06), chromic (1.63 ± 1.6) and UV/BP (1.89 ± 1.8) treatments do not significantly affect the measured C=O content of WPCs compared to the untreated WPC (2.06 ± 0.70). In other words, surface oxidation with those treatments is not evident at least from the O=C /C-H ratio. This result is somewhat surprising, since all the three treatments are expected to oxidize the surface of WPCs. However this result does not preclude that chemical oxidation has occurred as a result of the treatment especially for the polyolefin fraction. Surface composition of the WPC may also have changed as a function of the treatment, thus obscuring the effect of oxidation.

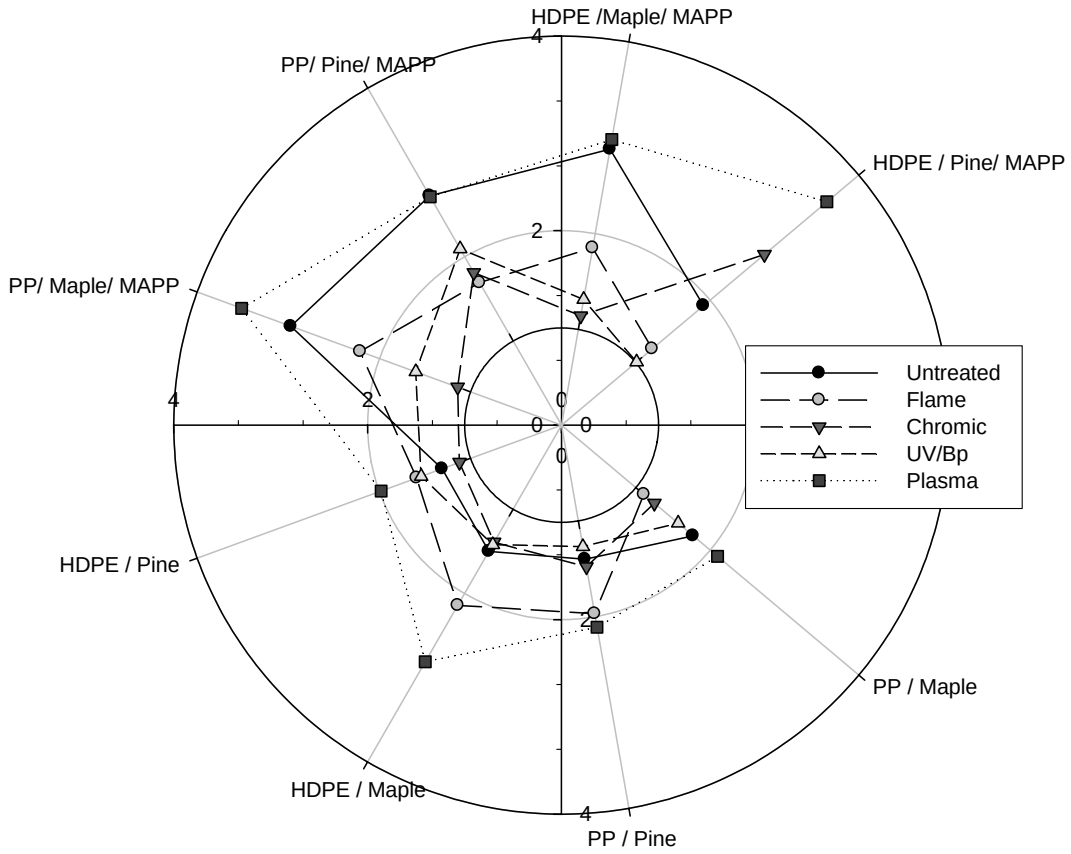

Figure 3.2: Polar plot of O=C/C-H for different formulations of untreated and treated WPCs

Table 3.2: C=O/C-H and cellulosic O-H/polyolefinic C-H ratio for the untreated and treated WPC formulations.

Formulation	Untreated		O_2 Plasma		Flame		Chromic		UV/BP	
	C=O / CH	OH / CH	C=O / CH	OH / CH	C=O / CH	OH / CH	C=O / CH	OH / CH	C=O / CH	OH / CH
Pine / HDPE / MAPP	2.32 ± 0.15	1.91 ± 0.29	2.43 ± 0.93	3.57 ± 0.31	1.72 ± 0.51	1.22 ± 0.30	0.73 ± 0.33	2.73 ± 0.09	0.97 ± 0.55	1.01 ± 0.05
Maple/ HDPE / MAPP	1.52 ± 0.05	2.88 ± 0.21	1.42 ± 0.38	2.98± 0.31	1.35 ± 0.90	1.85 ± 0.49	0.59 ± 0.18	1.14 ± 0.34	1.04 ± 0.54	1.31 ± 0.39
Pine / PP / MAPP	1.90 ± 0.03	2.72 ± 0.31	2.85 ± 0.91	2.71 ± 0.42	2.21 ± 0.75	1.69 ± 0.38	1.08 ± 0.64	1.81 ± 0.07	2.16 ± 0.76	2.09 ± 0.47
Maple/ PP / MAPP	2.56 ± 0.08	2.97 ± 0.17	1.16 ± 0.54	3.51 ± 0.73	1.43 ± 0.32	2.21 ± 0.48	1.24 ± 0.14	1.14 ± 0.53	1.23 ± 0.74	1.60 ± 0.09
Pine/ HDPE	1.20 ± 0.24	1.31 ± 0.18	1.43 ± 0.49	1.98 ± 0.26	1.64 ± 0.83	1.59 ± 0.45	1.14 ± 0.38	1.12 ± 0.50	1.04 ± 0.66	1.54 ± 0.35
Maple/ HDPE	2.75 + 0.04	1.50 ± 0.30	1.22 ± 0.45	2.81 ± 0.16	1.70 ± 0.39	2.14 ± 0.23	0.93 ± 0.41	1.39 ± 0.47	1.25 ± 0.62	1.42 ± 0.26
Pine / PP	2.18 ± 0.26	1.40 ± 0.33	2.53 ± 0.76	2.11 ± 0.33	1.92 ± 0.12	1.97 ± 0.21	1.17 ± 0.52	1.48 ± 0.61	1.13 ± 0.65	1.27 ± 0.47
Maple / PP	2.80 ± 0.01	1.77 ± 0.34	2.73 ± 0.74	2.10 ± 0.14	1.74 ± 0.10	1.11 ± 0.02	1.27 ± 0.39	2.73 ± 0.09	0.83 ± 0.17	1.57 ± 0.43
Mean	2.06 ± 0.70	2.11 ± 0.77	3.14 ± 1.73	1.97 ± 0.91	1.83 ± 1.06	1.70 ± 0.56	1.63 ± 1.6	1.01 ± 0.46	1.89 ± 1.8	1.25 ± 0.69

Table 3.3: Comparison of the surface properties and coating adhesion to WPCs surfaces subjected to various pretreatments: A denotes the higher value while E denotes the smallest value for a surface property

Treatment	O=C/C-H	O-H/C-H	θ_a(°)	Wetting Hysteresis (mJ/m^2)	R.M.S. Roughness (Å)	Peel Load (N/m)
Untreated	2.06 ± 0.70 (B)	2.11 ± 0.77(A)	100 ± 7 (C)	78 ± 12 (D)	1.74 ± 0.2 (C)	232 ± 56 (E)
Flame	1.83 ± 1.06 (B)	1.70 ± 0.56(B)	104 ± 14 (C)	90 ± 17 (C)	3.4 ± 1.9 (B)	381 ± 94 (D)
Chromic	1.63 ± 1.6 (B)	1.01 ± 0.46 (C)	120 ± 19 (B)	107 ± 20 (B)	5.22 ± 2.3 (A)	637 ± 88 (A)
UV/BP	1.89 ± 1.8 (B)	1.25 ± 0.69(C)	140 ± 10 (A)	128 ± 8 (A)	2.48 ± 0.6 (C)	466 ± 107 (C)
O_2 Plasma	3.14 ± 1.73 (A)	1.97 ± 0.91 (A)	35 ± 14 (D)	71 ± 11 (E)	1.99 ± 0.6 (C)	516 ± 116 (B)
P value	0.0021	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

O-H/C-H: For the OH/CH ratio, similar reproducibility is observed than for the C=O ratio (Table 3.2). Figure 3.3 shows the OH/CH for different formulations of treated and untreated WPCs. In particular, there is no general trend in the OH/CH for a treatment condition. Regardless of the formulations, there is a significant difference ($p<0.0001$) between the O-H/C-H ratios of the WPCs that have received different treatments (Table 3.3). However, untreated WPCs (2.11 ± 0.77) and oxygen plasma treated WPCs (1.97 ± 0.91) have the highest OH/CH ratio. The chromic (1.01 ± 0.46) and UV/BP (1.25 ± 0.69) treated WPCs have the smallest OH/CH ratio. The flame treated WPCs ranks in between the two extremities (1.70 ± 0.56). Therefore, while the plasma treatment does not significantly modifies the surface composition of WPCs, the chromic acid and UV/BP treatments and to a lesser extent the flame treatment appear to increase the concentration of plastic on the surface or to decrease the concentration of wood on the surface. In these treatments, migration of the polyolefin towards the surface may have occurred owing to the high temperatures involved. Importantly, this observation is consistent with the findings of the O=C/C-H ratio. Indeed, Figure 3.4 shows that there is an upward trend of OH/CH with O=C/C-H. In addition, the OH/CH vs O=C/C-H plot yields better fitting

(R^2=0.77) by omitting the plasma treatment result (Inset). Specifically, it confirms that the flame, UV/BP and the chromic treated WPCs have similar O=C/C-H ratio as the untreated WPCs, not just because oxidation has not occurred but also likely owing to the higher concentration of the polyolefin (C-H) on the surface. In fact, the inverted plot of surface oxidation, i.e., the plot of surface polymer content of (C-H/O=C) vs (C-H/O-H) gives good correlation (R^2=0.63) showing increase in C-H content on the surface (fig 3.5) for the chromic, UV/BP and flame treated WPCs.

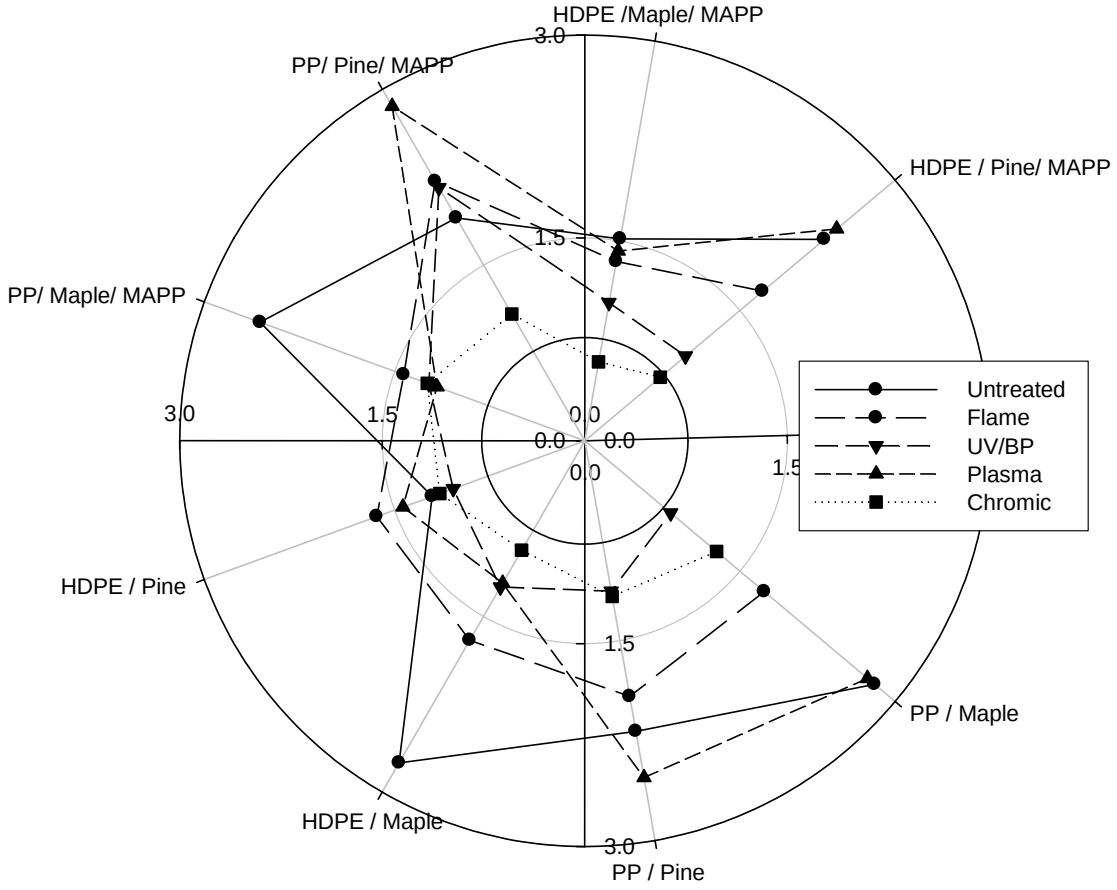

Figure 3.3: Polar plot of O-H/C-H for different formulations of untreated and treated WPCs

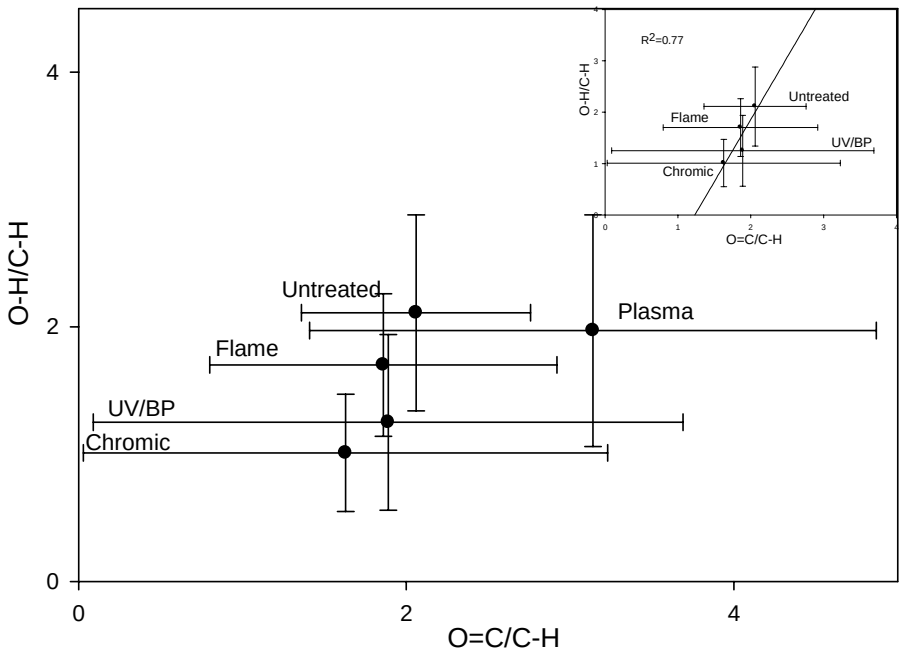

Figure 3.4: Relationship between the O=C/C-H and O-H/C-H showing the amount of surface polarity for the untreated and all treated WPCs. Inset: Relationship between the O=C/C-H and O-H/C-H showing the amount of surface polarity for the untreated, flame treated, UV/BP treated and chromic treated WPCs (R^2=0.77)

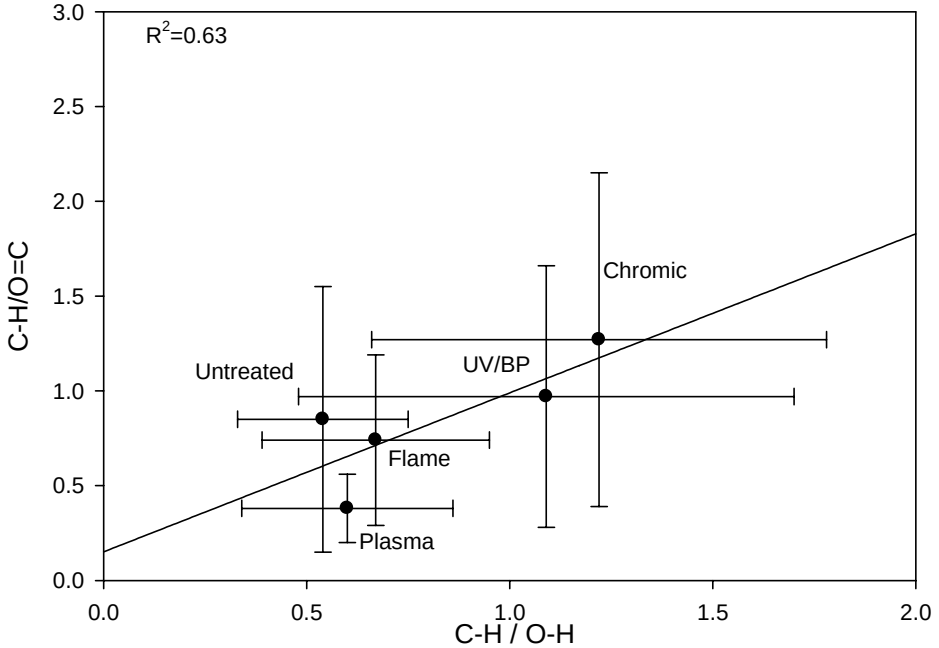

Figure 3.5: Relationship between C-H/C=O and C-H/O-H showing surface polymer content on the untreated and treated WPC surface.

Morphology: In the second part, the effect of the different treatments on the morphology of the thermoplastic polymer is evaluated. Figure 3.6 shows the XRD traces for wood, HDPE and WPCs. Wood have three α-cellulosic peaks at (a) $2\theta \sim 15^0$ for (101) reflection, (b) $2\theta \sim 16^0$ for $(10\bar{1})$ reflection and (c) $2\theta \sim 22^0$ for (002) reflections in accordance with the previous research by Zhang and Kamdem (2000). Similarly, the untreated orthorhombic-HDPE (Li et al 2003) have two peaks at (d) $2\theta \sim 22^0$ for (110) reflection and (e) $2\theta \sim 24^0$ for (200) reflections in agreement with the research by Murthy et al (2000). Untreated WPCs shows the combination of wood peaks (a, b, c) and HDPE peaks (d, e). In addition, distinct peaks are observed at - (f) $2\theta \sim 9^0$ and (g) $2\theta \sim 19^0$ for (002) and (004) reflections of the talc (Obata et al 2001). Looking at the effect of surface treatments, it is clear that the chromic treated, UV/BP treated and plasma treated WPCs show traces

similar to the untreated WPCs. These surface treatments do not modify the crystalline structures of the polyolefin or the wood polymers. However, in the flame treated WPCs additional peaks at $2\theta \sim 14^{o}$, 17°, 19°, 20° and 21° are apparent. This suggests crystalline modification of the polymer matrix in the presence of wood. This is understandable as the flame zone has very high temperature which may have provided enough energy to change the polymer crystal patterns and / or there may be doping or deposition of new elements on the polymer crystals thereby creating new peaks.

Altogether, compared to the untreated WPCs, only oxygen plasma causes an obvious oxidation of WPCs as monitored from the surface carbonyl ratio. The other treatments may also cause surface oxidation, however it is obscured by the changes in surface composition where polyolefins migrate to the surface. In addition, in the case of flame treatment the polyolefin undergoes crystalline modifications. However, apart from the surface polarity, the adhesion of a coating depends on the wettability of the surface. The surface wettability is best defined by the contact angle.

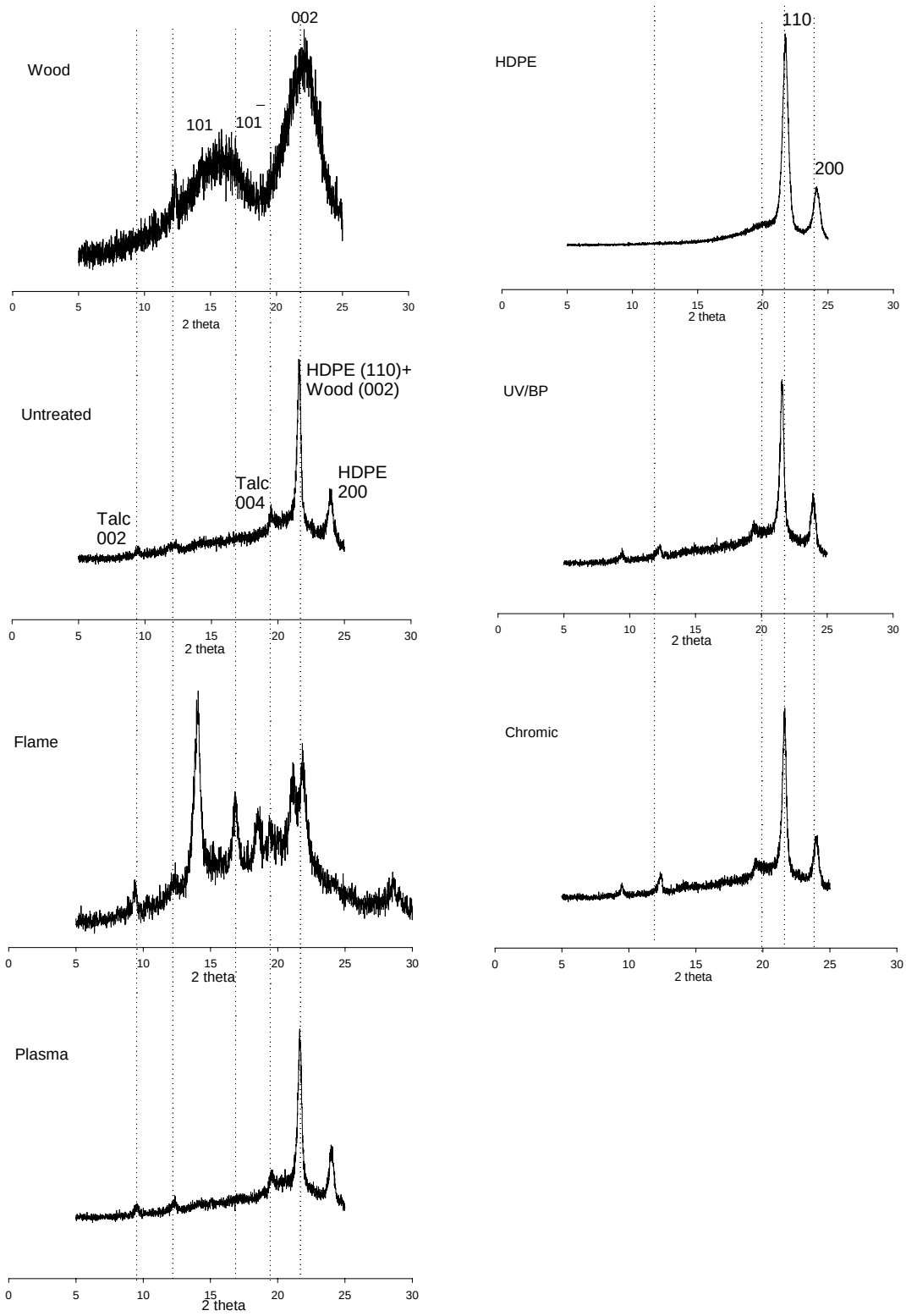

Figure 3.6: XRD trace of neat wood, HDPE, and neat and treated HDPE/Pine/MAPP WPC.

Wettability: Figure 3.7 shows typical advancing and receding force curves for the wetting of the treated and untreated WPCs. There are clear differences in the curves. The flame treated WPCs exhibit force curves very similar to the untreated WPCs. Likewise the chromic acid and UV/BP treated WPCs exhibit similar force curves, that are shifted to lower forces compared to the untreated WPCs. Note also that irrespective of the surface treatments, WPCs have different advancing and receding force curves. This indicates that the untreated and treated WPCs surfaces are heterogeneous. Figure 3.8 shows the advancing contact angle (θ_a) for the different formulations of treated and untreated WPCs. In general, the θ_a of the WPCs have a wide variation of 2-8° indicating heterogeneity of the surface.

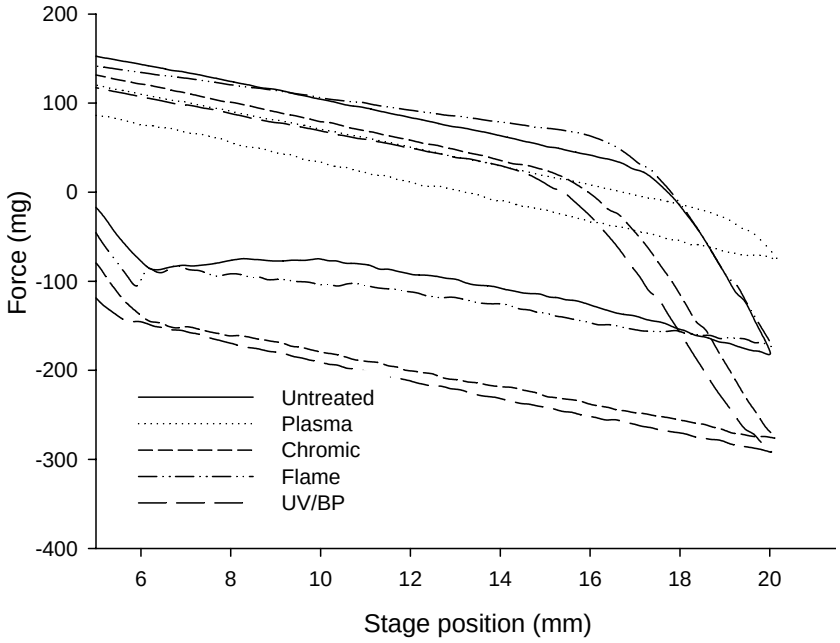

Figure 3.7: Plot showing the wetting behavior of the untreated and treated WPCs during dynamic contact angle analysis

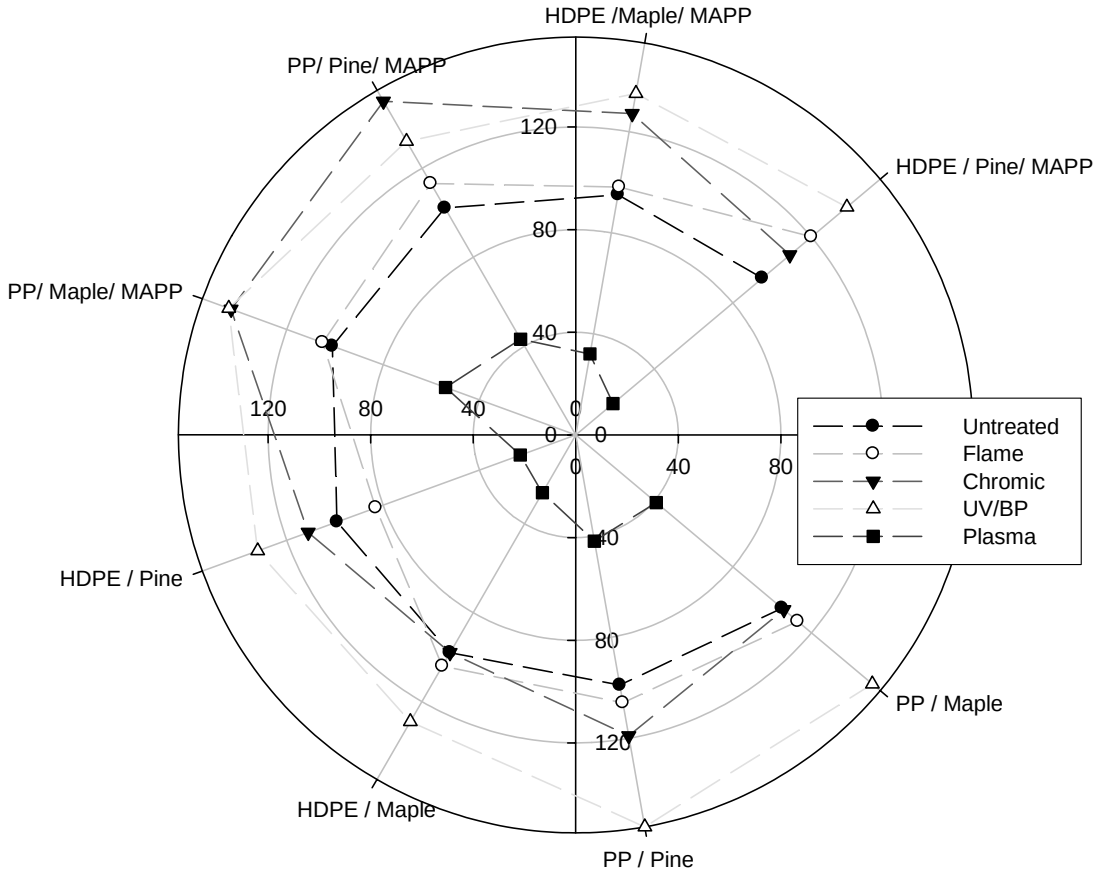

Figure 3.8: Polar plot showing the θ_a for different formulations of untreated and treated WPCs

Table 3.3 summarizes the significant differences in the θ_a of the WPC surfaces considered (p=0.0001). First, as suggested by the force curve, the flame treatment does not significantly impact the θ_a (104 $\pm$ 14 ^{o}) of WPCs. Its θ_a is the same as that of the untreated WPCs (100 $\pm$ 7 ^{o}). On the other hand, the plasma treatment significantly decreases the θ_a (35 $\pm$ 14 ^{o}) and also to a large amount (50-70°) compared to the untreated surfaces. Hence oxygen plasma improves the wettability of WPCs to water. This result is expected owing to the enhanced polarity imparted by the oxygen plasma treatment. This is in contrast to the effect of UV/BP (140 $\pm$ 10 ^{o}) and chromic treatments (120 $\pm$ 19 ^{o}), which actually increases the θ_a compared to the untreated WPCs. This result suggests that the UV/BP and chromic treatment have decreased the wettability of WPCs surface to water, possibly as a result of increased polyolefin content on the surface and therefore increased hydrophobicity or may be due to the increased surface roughness and heterogeneity (Adamson 1982; Briggs et al 1976). Indeed, for this series of WPC, the θ_a largely depends on the surface polarity as is evidenced from Figure 3.9. The θ_a decreases linearly with the increase in O=C/C-H (R^2=0.85) and O-H/C-H (R^2=0.44).

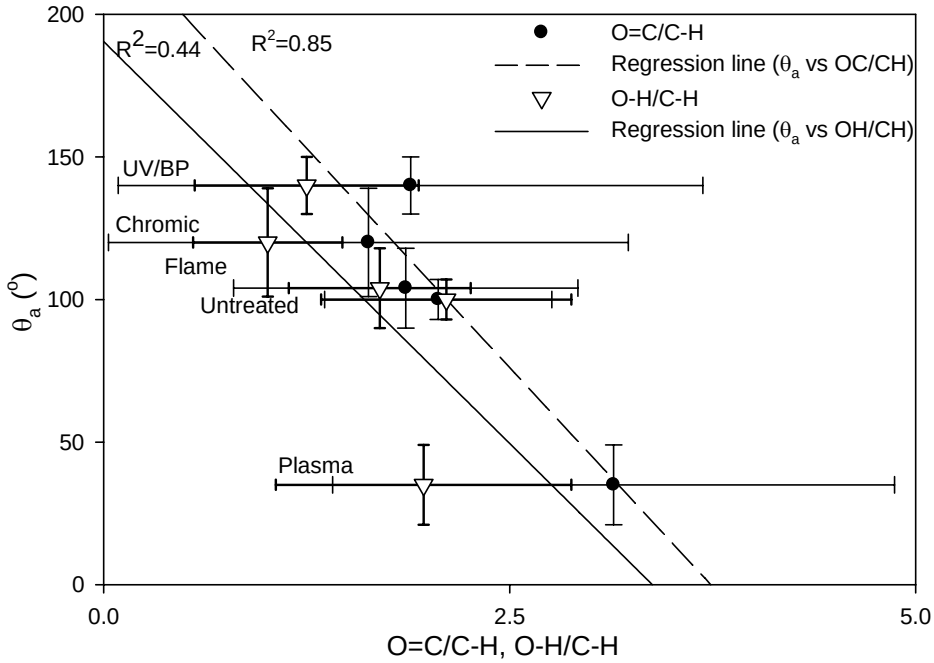

Figure 3.9: Relationship between the surface oxidation (O=C/C-H), surface wood content (O-H/C-H) and advancing contact angle (θ_a) for the untreated and treated WPCs

Hysteresis: Wetting hysteresis is an indication of surface heterogeneity and roughness. In general, the wetting hysteresis values vary from 8 mJ/m^2 to 20 mJ/m^2 of the average value (fig 3.10). All treatments significantly increase ($p<0.001$) the contact angle hysteresis of WPC with water compared to the untreated WPC (78 $\pm$ 12 mJ/m^2) (Table 3.3). The plasma treatment (71 $\pm$ 11 mJ/m^2) decreases the hysteresis to a lower extent. The flame (90 $\pm$ 17 mJ/m^2), chromic acid (107 $\pm$ 20 mJ/m^2) and UV/BP treatments (128 $\pm$ 8 mJ/m^2) increases the hysteresis. The results show that altogether there is an increase in the surface chemical heterogeneity and or roughness of WPCs. To further test the hypothesis of enhanced roughness following surface treatments, the topography of the treated and the untreated WPC surfaces are compared (Fig. 3.11). Chromic treated WPCs clearly display larger variations in topography i.e. higher surface roughness than all the

other WPC surfaces. This is expected from the oxidative etching process (Briggs et al 1976). UV/BP treated and plasma treated WPCs have a similar topography than the untreated WPCs while the flame treated WPCs show smoother topographical profiles. Therefore the increase in hysteresis observed with all the treated surfaces results from the roughness increase in the case of the chromic acid treated WPC and surface chemical heterogeneity increase in the case of the plasma, UV/BP and flame treatments. Table 3.3 shows the roughness for all the treated formulations. Chromic acid treatment causes maximum roughness (5.22 $\pm$ 2.3Å), followed by flame treatment (3.4 $\pm$ 1.9Å), UV/BP treatment (2.48 $\pm$ 0.6Å), oxygen plasma treatment (1.99 $\pm$ 0.6Å) and untreated WPCs (1.74 $\pm$ 0.2Å).

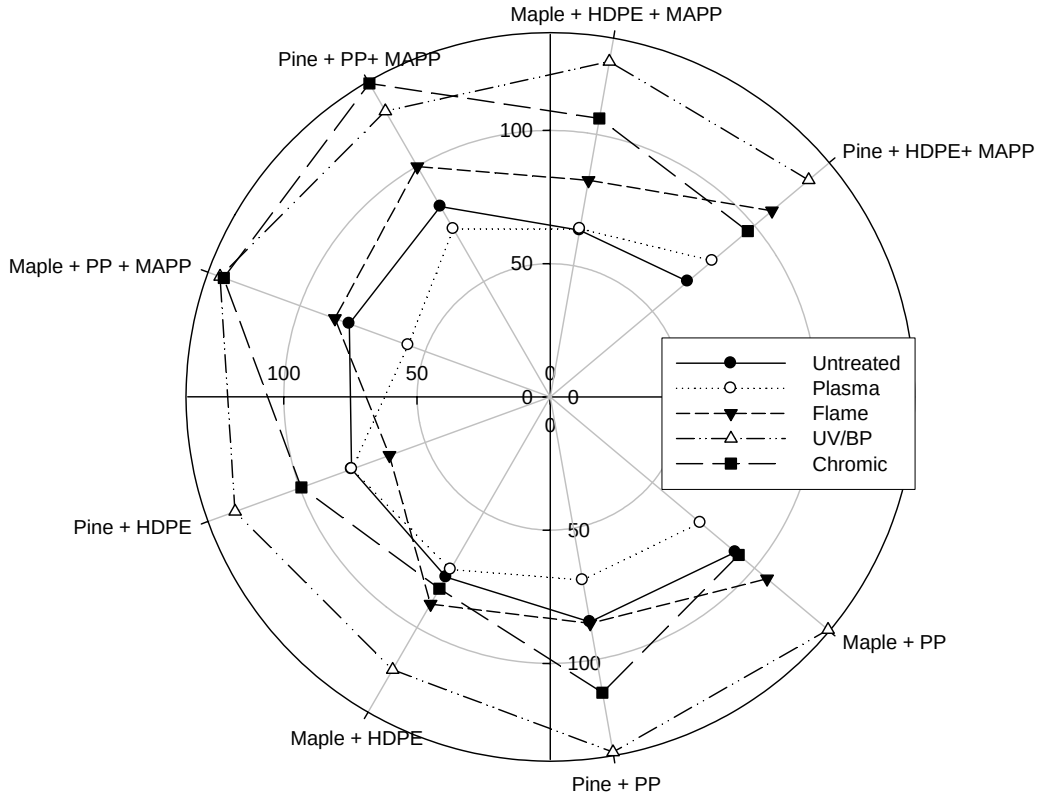

Figure 3.10: Polar plot showing the wetting hysteresis (mJ/m^2) for the untreated and treated formulations of WPCs

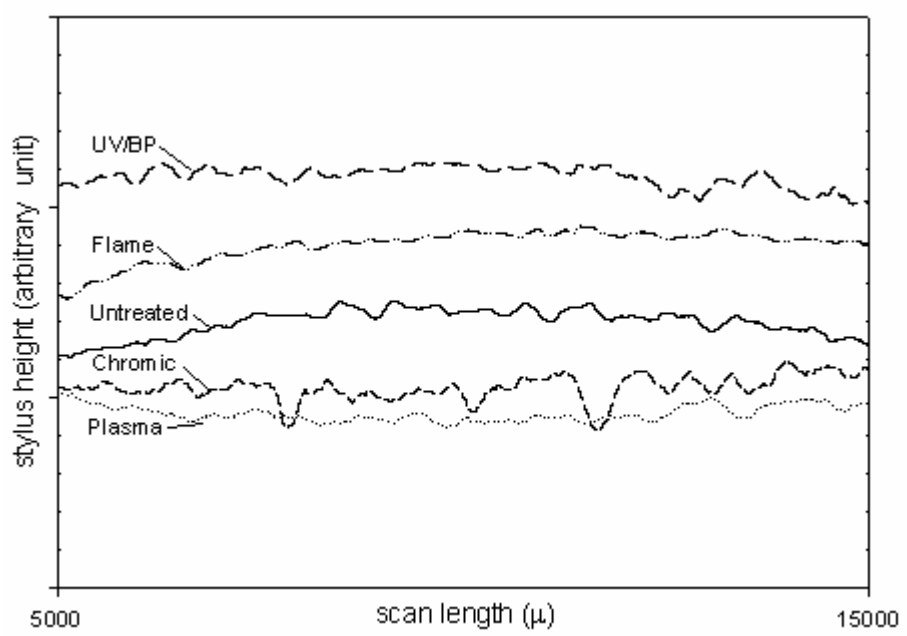

Figure 3.11: Profilometric scanning of the surface topography for the untreated and treated HDPE/Pine/MAPP formulations

Figure 3.12 – 3.16 shows the SEM micrograph of wood and WPCs. The porous structure of wood (Figure 3.12) is clearly distinguished. The untreated WPC surface (Figure 3.13) shows layered plastic structure. The chromic treated WPCs (Figure 3.14) have etched surface. While the flame treated (Figure 3.15), UV/BP treated (Figure 3.16) and plasma treated WPCs (Figure 3.14) have similar surface characteristics like untreated WPCs. Thus the previous findings of the hysteresis may be related to the microscopic observations. The typical surface characteristics of the untreated WPCs probably have created thermodynamically metastable states which in turn generated energy barriers to be surmounted by the wetting liquid. This may be a reason of wetting hysteresis. Additionally, the surface shows considerable amount of unevenness which is also confirmed by the profilometric study. Thus, roughness is also a contributing factor to the wetting hysteresis. Consequently, the high roughness demonstrated by chromic acid

etched surface (Table 3.3) may be related to the microscopic observation of surface fissures and / or crevices.

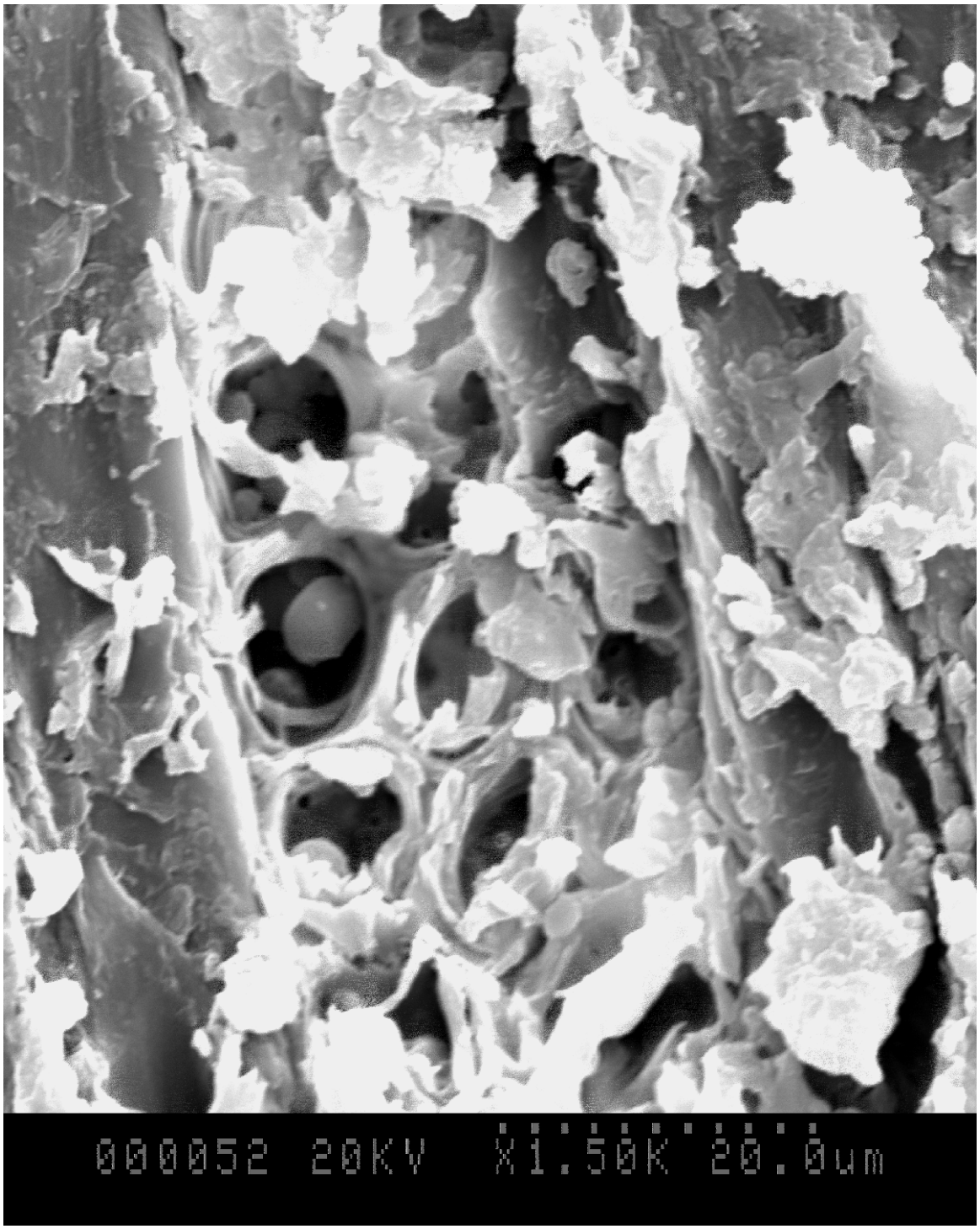

Figure 3.12: SEM micrograph of maple (*Acer spp*) wood

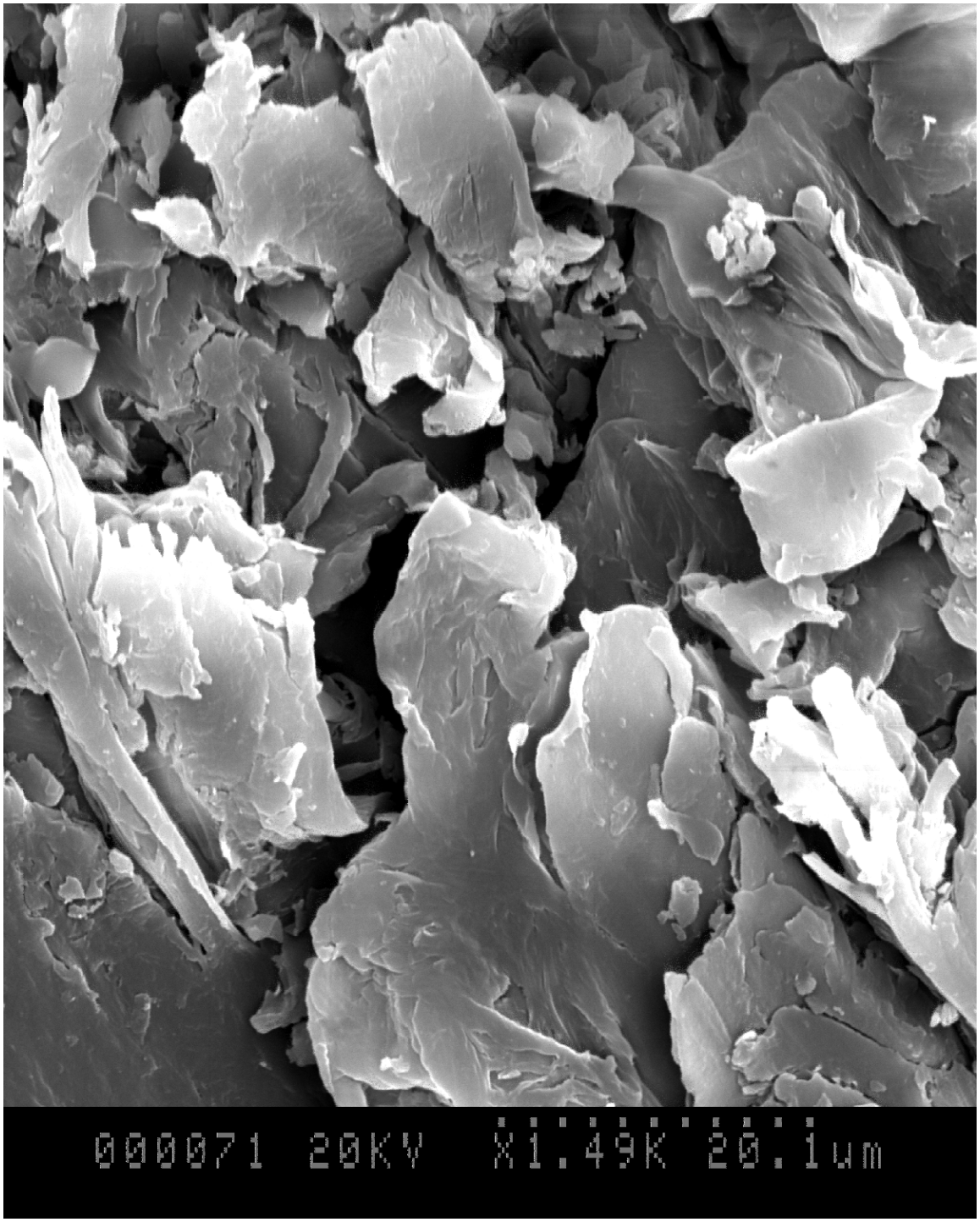

Figure 3.13: SEM micrograph of untreated WPCs

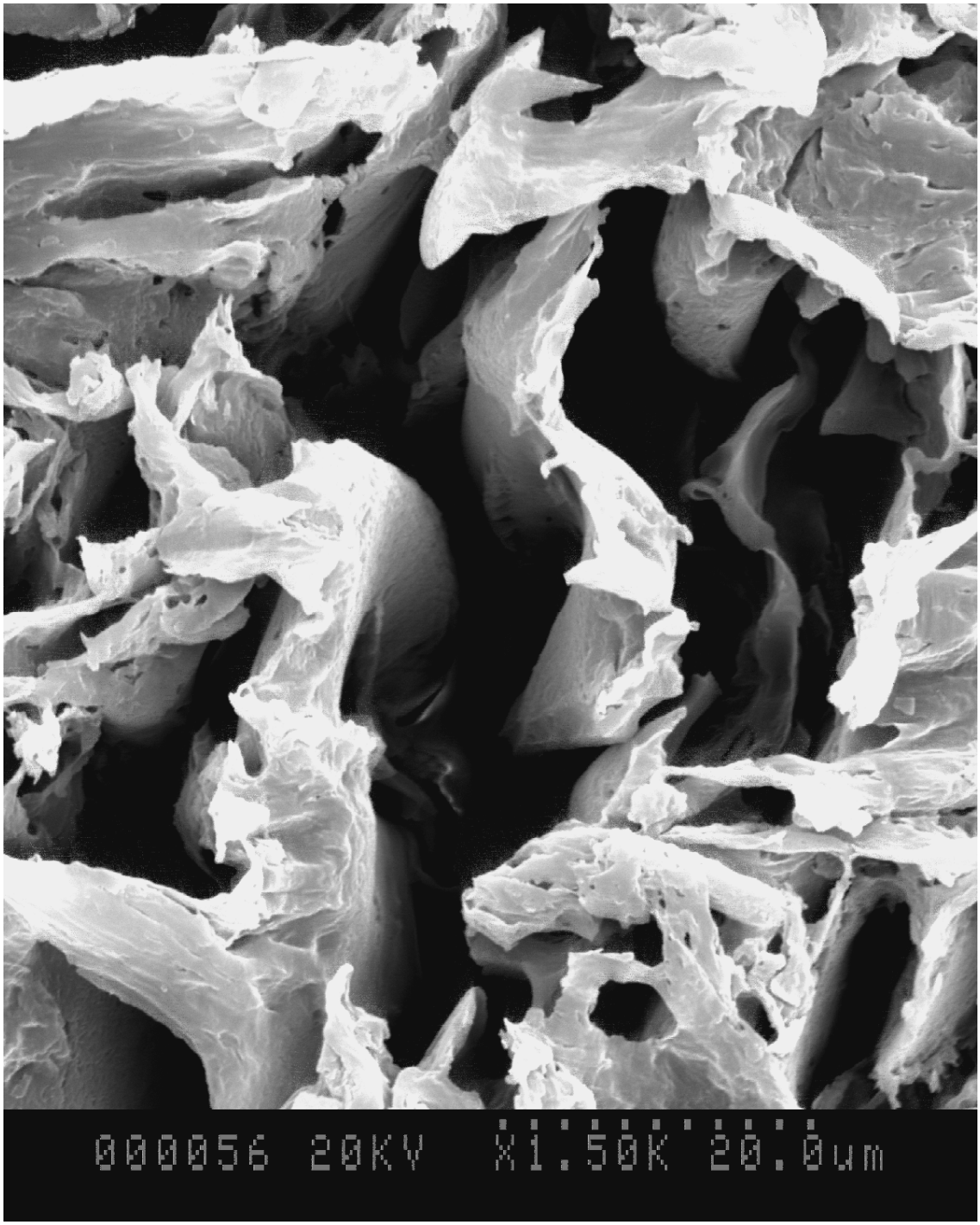

Figure 3.14: SEM micrograph of chromic acid treated WPCs

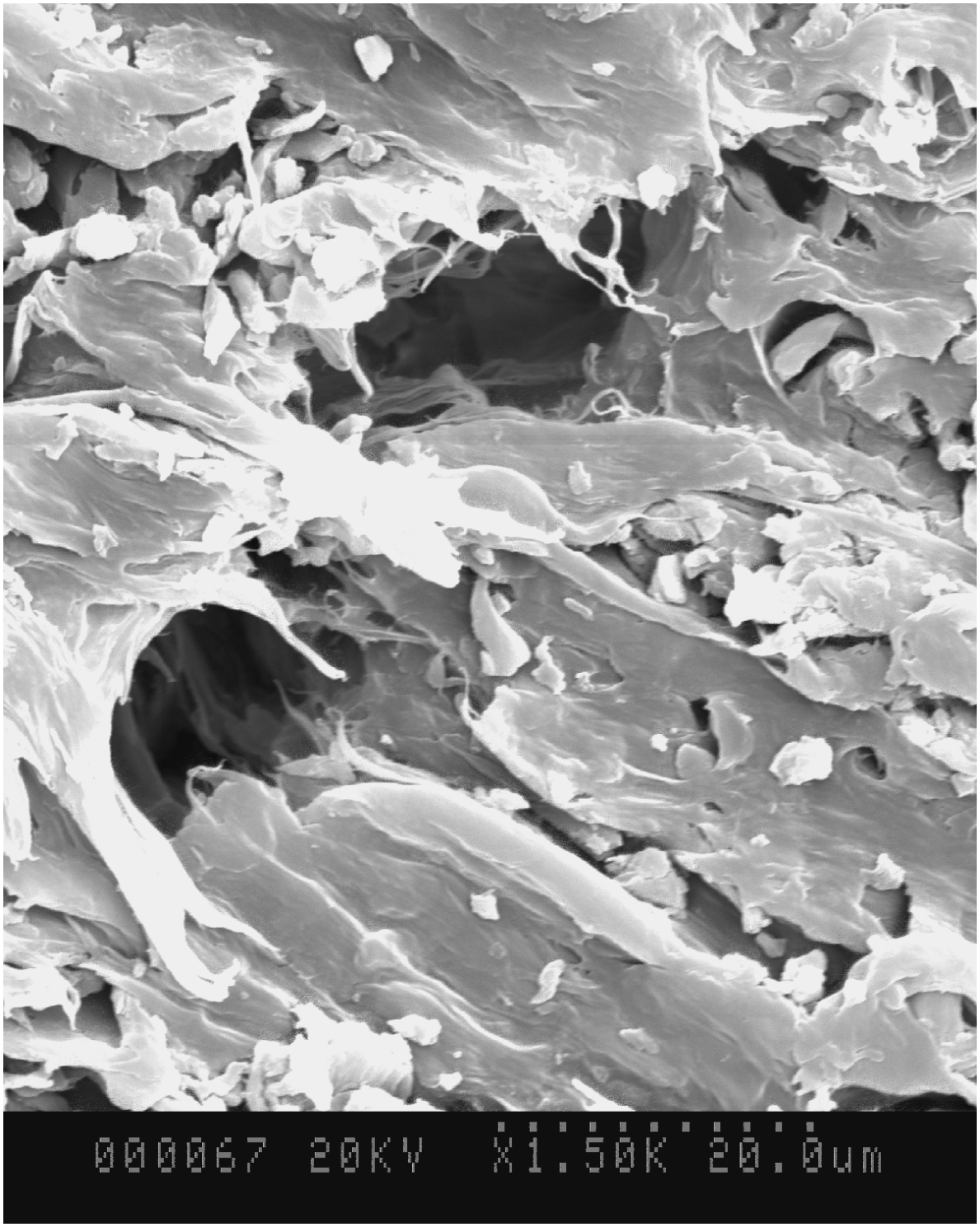

Figure 3.15: SEM micrograph of flame treated WPCs

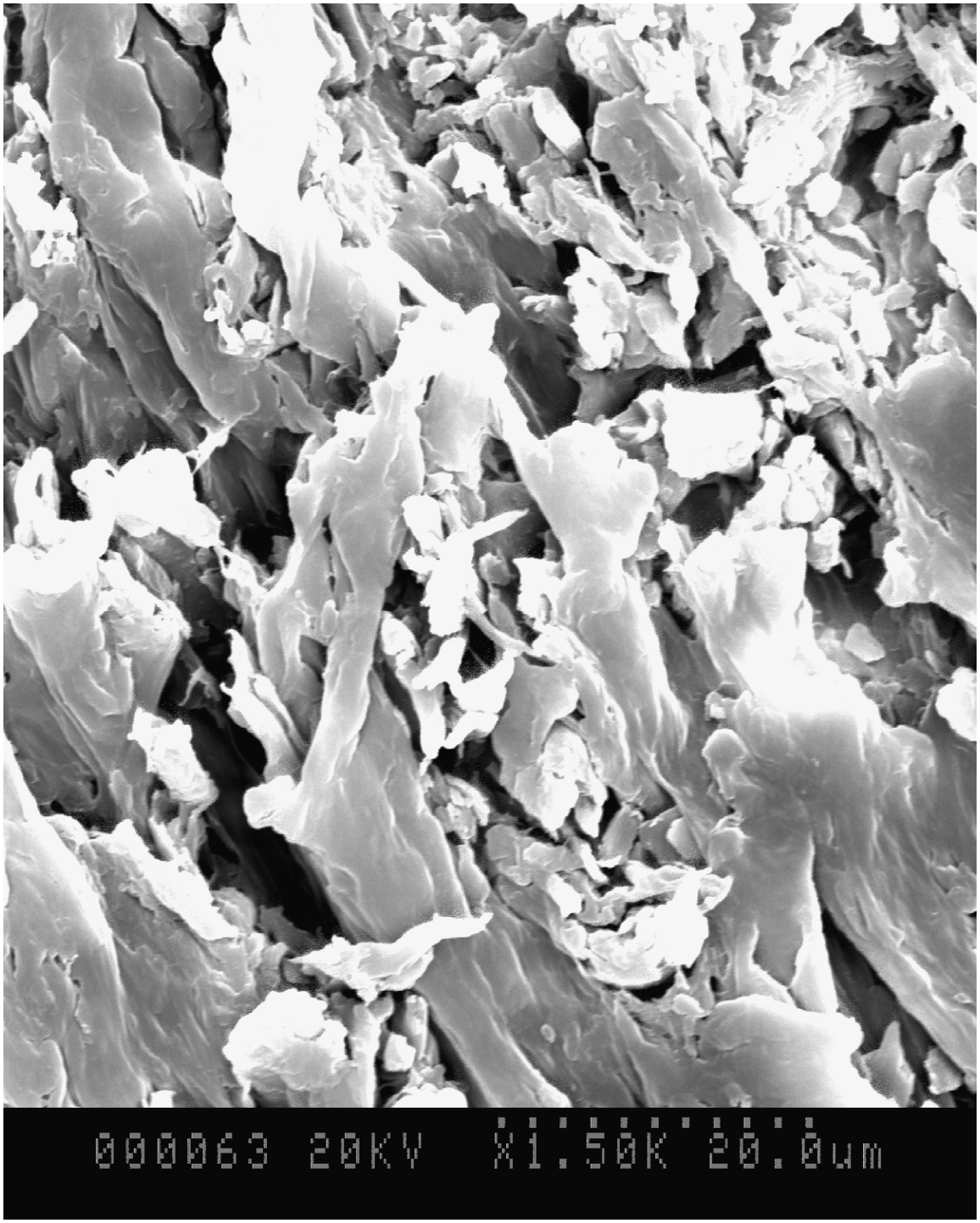

Figure 3.16: SEM micrograph of UV/BP treated WPCs

Fig 3.17: SEM micrograph of plasma treated WPCs

Overall, the contact angle analysis shows that only the oxygen plasma treatment dramatically improves WPCs wettability with water. The other treatments are either ineffective or detrimental to surface wettability. The variation in wettability is to a large extent explained by surface oxidation, as demonstrated by a strong inverse relationship (R^2= 0.85) between contact angle and C=O ratio. On the other hand, all the surface treatments increase the wetting hysteresis either as a result of higher surface roughness or higher chemical heterogeneity as is also observed by Morra et al (1990). Consequently, the WPC surface is coated with a water-based acrylate primer and the adhesion between the primers with different formulations of WPCs is evaluated.

Primer adhesion strength: Figure 3.18 summarizes the peel load for the treated and untreated formulations of WPCs. There is a rather large variation in peel load, owing to the small sample size and also the sample heterogeneity. The treatments have a significant effect ($p<0.0001$) on the peel load of the acrylate coating on WPCs (Table 3.3). All four treatments improve the adhesion of the acrylate coating to WPCs, albeit to a different extent. The chromic acid treatment is the most efficient (637 $\pm$ 88 N/m) followed by the oxygen plasma treatment (516 $\pm$ 116 N/m), the UV/BP (466 $\pm$ 107 N/m) and flame treatment (381 $\pm$ 94 N/m). Except for the flame treatment, the treatments more than double the adhesion strength of the acrylate coating as compared to the primer adhesion to untreated WPCs (232 $\pm$ 56 N/m). Moreover, note that the coating adhesion to chromic acid or plasma treated WPC is in the same range as that to neat wood (524 $\pm$ 64 N/m) and well above that of neat plastic (48-126 N/m) (Gupta and Laborie 2006).

However, albeit the effects of surface treatments are quantified the basic mechanism of adhesion is still to be evaluated. Consequently, the relationship between the peel load versus OC/CH, OH/CH, θ_a and relative hysteresis are evaluated. The coefficient of determination (R^2) is used to predict the linearity between the variables.

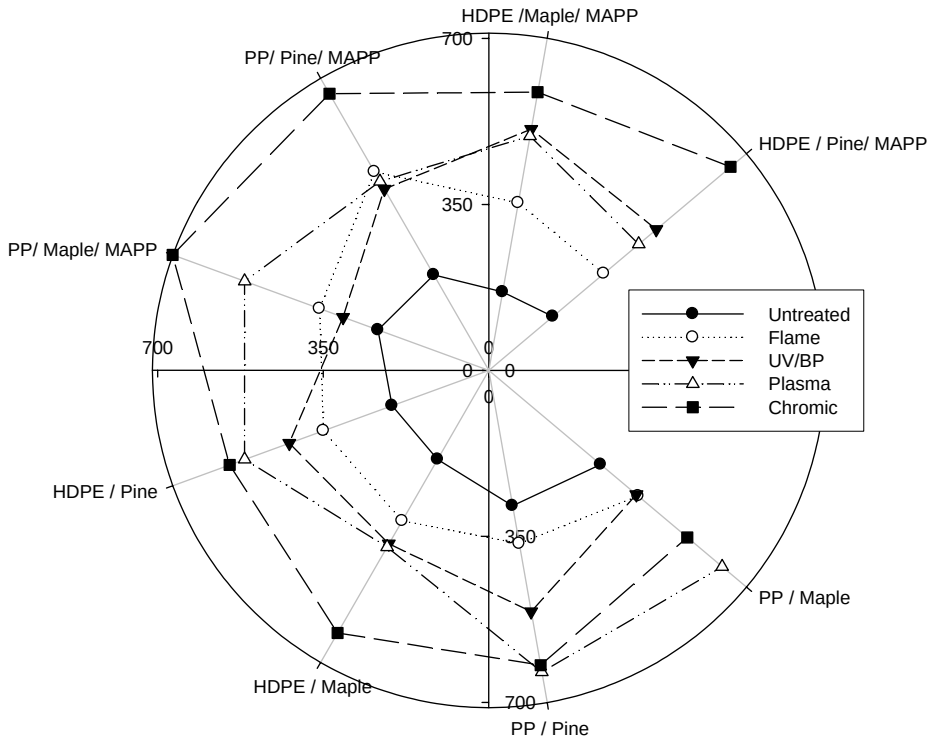

Figure 3.18: Polar plot showing the distribution of peel load for different formulations of untreated and treated WPCs

Factors affecting adhesion mechanism: The chromic acid and the plasma treatments are both very efficient at improving the adhesion of an acrylate coating on WPCs. With the chromic acid treatment, the surface roughness of WPC was found to greatly increase. Surface roughness causes higher interfacial area for bonding and possibly greater energy dissipation mechanisms for plastics. These may be the main adhesion mechanisms in place in the case of chromic acid treated WPC. In the case of plasma treated WPCs, a

significant increase in surface oxidation and related increase in wettability were observed. Higher surface polarity and greater wettability would explain the high efficacy of plasma treatments on WPCs.

However, to comprehend the adhesion mechanisms that may be taking place in the system in greater detail, relationships between the peel load and the surface properties, namely, surface oxidation (O=C/C-H), surface wood content (O-H/C-H), contact angle (θ_a) and hysteresis are evaluated. Fig 3.19 shows that adhesion decreases linearly with cellulosic ratio (R^2 =0.54). This relationship is not expected. It is also contrary to what was observed previously on untreated WPCs for which increasing cellulosic content corresponded to increasing peel load. Interestingly the relationship becomes stronger when the plasma treated WPC data is excluded from the series (insert). While unexpected, one may reckon that the treatments applied in this work are all derived from practices of neat plastics. As a result, one may expect that if efficient on the plastic fraction of the WPC, these treatments may increase the adhesion of WPCs all the more when there is a larger plastic concentration on the surface. In this perspective, it is no longer surprising that with increasing plastic content (or decreasing OH/CH ratio); the surface treatments become more effective resulting in higher peel load.

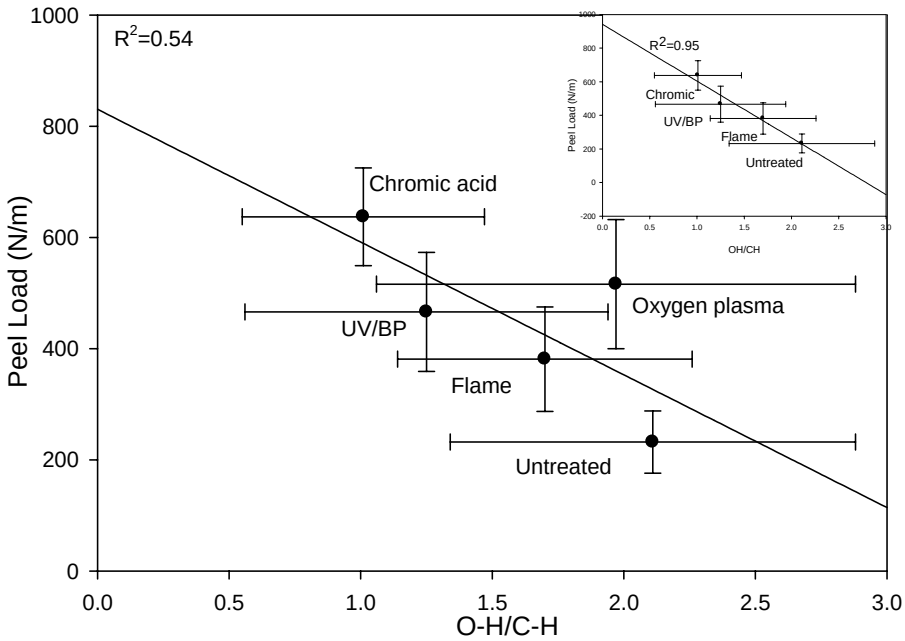

Figure 3.19: Relationship between peel load (N/m) and surface O-H/C-H for untreated and treated surface of WPCs (R^2=0.54). Inset: Relationship between peel load and surface OH/CH for the chromic treated, UV/BP treated, flame treated and untreated WPCs (R^2=0.95)

Figure 3.20 shows the plot between the peel load and surface oxidation (OC/CH). There is no clear trend between peel load and oxidation ratio, albeit when the plasma treated WPC is excluded from the series, a strong negative linear relationship is found. This suggests that the low oxidation ratios are strongly correlated to high peel strength. Again this trend is unexpected. This observation may be an artifact of co-linearity between the surface chemistry and other properties such as contact angle or surface roughness.

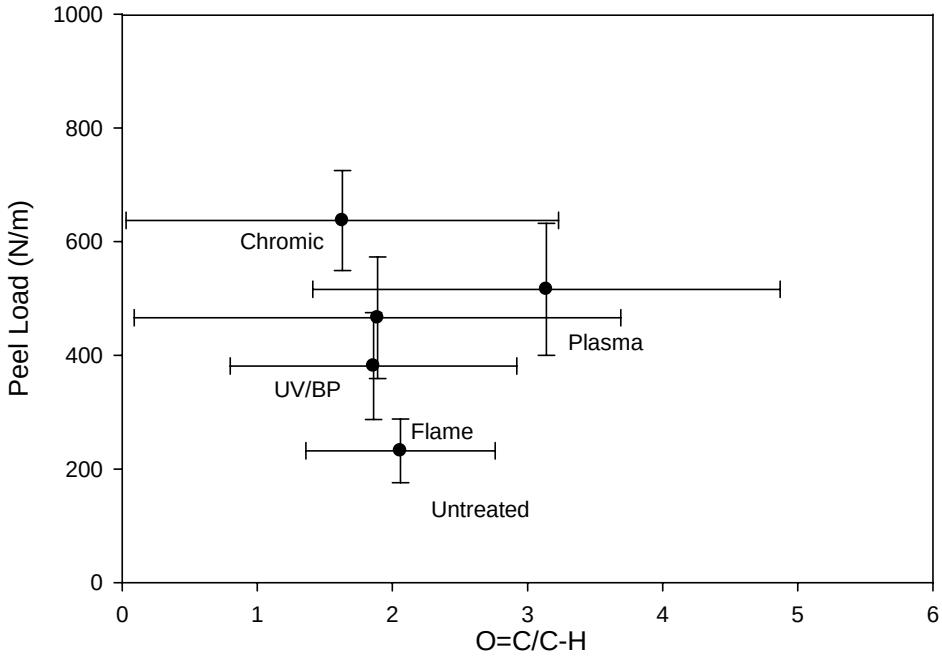

Figure 3.20: Plot between the peel load (N/m) and the surface O=C/C-H for the untreated and treated WPCs.

Figure 3.21 shows the plot between the peel load and θ_a. There is no particular trend. Thus, as observed in a previous study (Gupta and Laborie 2006) thermodynamic measurement of wettability is not a factor defining the practical work of adhesion. Additionally, it was previously found that the contact angle hysteresis correlates (R^2= 0.9) strongly with the peel load for the untreated WPC formulations (Gupta and Laborie 2006). A linear increasing relationship had been found observed. In the case of treated WPCs, a general trend of increasing peel load (Fig 3.22) is observed with the increasing hysteresis again.

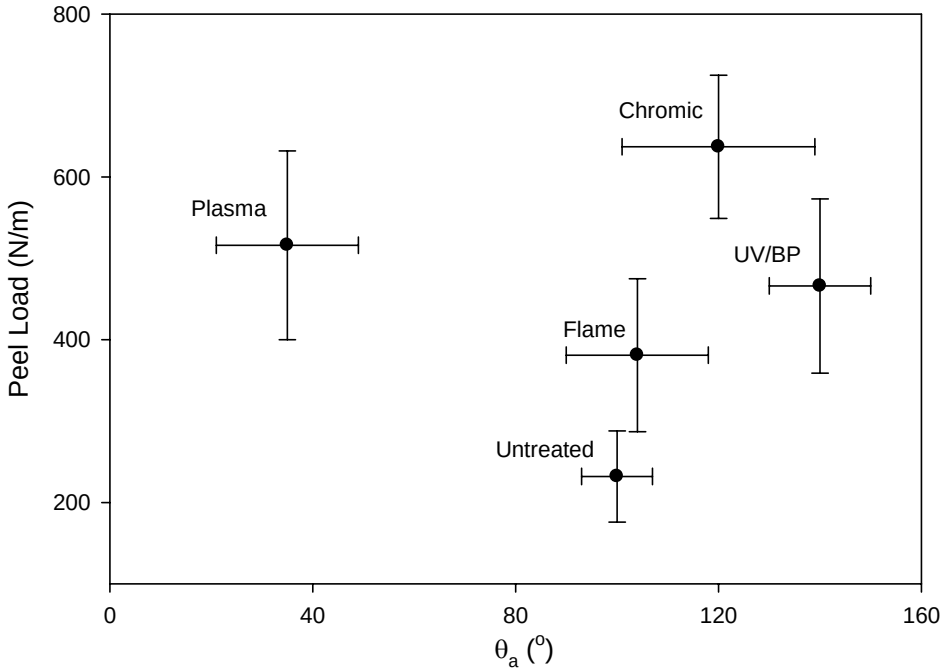

Figure 3.21: Plot between the peel load (N/m) and θ_a (^{o}) for the untreated and treated WPCs

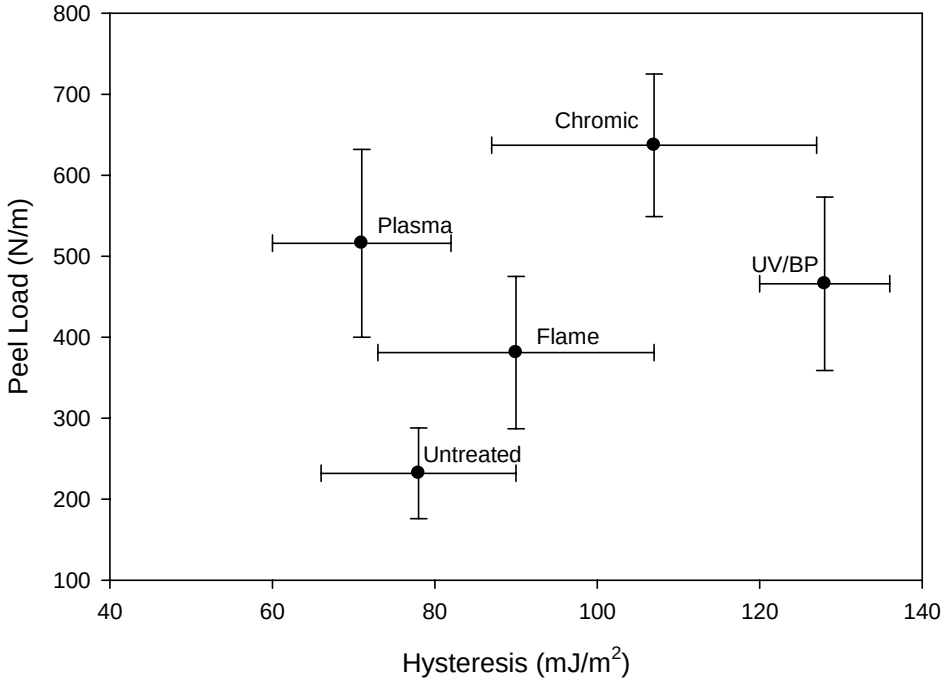

Figure 3.22: Plot between the peel load (N/m) and the wetting hysteresis (mJ/m^2) for the untreated and treated WPCs

Altogether, hysteresis and surface roughness play a certain role in developing adhesion mechanisms between the acrylate coating and WPCs. The apparent inverse relationship between cellulosic ratio (OH/CH) and peel load likely arises from the fact that the surface treatments evaluated are developed for neat plastics and therefore are most efficient with the high surface plastic content, that is, the treatment efficiency is higher for the low cellulosic content. As previously hypothesized, increased adhesion with increased hysteresis suggest greater surface roughness and therefore greater interfacial area. Mechanical interlocking and energy dissipation mechanisms have also been proposed to explain the higher adhesion observed on neat polyolefins that have high surface roughness (Kinloch 2001). The adhesion of plasma treated WPC may also involve another mechanism, that is surface oxidation and therefore secondary and or primary interactions with the coating.

3.5 Conclusion

Eight formulations of WPCs were pretreated with the chromic acid, oxygen plasma, flame, and UV/Benzophenone (BP) treatments. The surface chemistries of the treated WPCs were quantified by the ATR-FTIR spectra and the wettability was measured by the dynamic contact angle analysis. The acrylate primer adhesion strength to WPCs was measured by 180° peel test. The treatment conditions had significant effect on the surface chemistry, wettability and peel load of WPCs. The flame, UV/BP and chromic treatment increased the plastic content on the WPC surface. Moreover, the surface treatments enhanced the primer adhesion strength to WPCs by 1.5-2.5 times as

compared to the untreated conditions (232 ± 56 N/m). Chromic acid treatment had superior effect on WPCs in terms of primer adhesion strength (637 ± 88 N/m). The studies revealed that the increases in surface roughness during the chromic acid etching have favored an increase in energy dissipation process to enhance the practical work of adhesion. Oxygen plasma treated WPCs showed maximum surface polarity, low contact angle and consequently a high primer adhesion strength (516 ± 116 N/m). UV/BP treated WPCs indicated chemical modification and a moderate primer adhesion strength (466 ± 107 N/m). Flame treated WPCs exhibited morphological modification and slightly higher primer adhesion strength (381 ± 94 N/m) than the untreated conditions. In general, all the pretreatment methods increased the primer adhesion to WPCs. Additionally, it was observed that the surface plastic content had higher effect while the wood cellulose content had little effect in defining the primer adhesion to the treated WPCs. Additionally, except for the flame treated WPCs the peel load for the treated formulations of WPCs was satisfactory as compared to the peel load for the wood at 524 N/m as was observed in the earlier study. Overall, the surface roughness and surface oxidation were the two principal parameters for predicting the primer adhesion to WPCs.

Acknowledgements:

Katie Miyashi, Matt Chastagner, Jen-ho Chang, Patrick D. Pedrow, Charles Knaack, Mark Fuller, Isabela Reiniati

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CHAPTER FOUR

INFLUENCE OF SKIN-CORE MORPHOLOGY ON PAINT ADHESION TO WOOD PLASTIC COMPOSITES (WPCS)

4.1 Abstract:

Wood plastic composites (WPCs) are gradually getting importance in exterior and interior applications. However, manufacturing defects leading to the skin-core morphology is a challenge in coating of WPCs. Several studies have been performed on the paint adhesion to the truly extruded 'skin' surface and the bulk 'core' material. Yet thorough studies on the chemical and morphological aspects of the core and bulk of WPCs are lacking. Consequently, this study reports the elemental and morphological composition of the bulk and core material of WPCs and their effect on the paint adhesion. The X-ray photoelectron spectroscopic (XPS) study revealed high polymer and lubricant content in extruded surface while the bulk material has high wood content. Moreover, crystallinity measurement by the X-ray diffraction (XRD) study revealed higher polymer crystallinity in the bulk material compared to the extruded surface. Additionally, the acrylate primer adhesion to the sanded surface (212 $\pm$ 11 N/m) is similar to the bulk material (219 $\pm$ 22 N/m). However, the extruded surfaces have low primer adhesion (135 $\pm$ 24 N/m) due to the presence of lubricants and absence of wood.

4.2 Introduction:

WPCs are generally manufactured by the extrusion processing, injection molding or compression molding. Previous studies (Barbosa and Kenny 2000, Stark et al 2004) have reported skin-core morphology for the injection-molded and extrusion processed short glass fiber reinforced composites. Barbosa and Kenny (2000) reported that fiber orientation increases from the center to the skin for the extrusion processed composites. Additionally, the researchers found higher fiber protrusion from the surface with the decreasing shear rate during extrusion. Moreover, they observed increasing surface roughness with increasing fiber content due to the increasing fiber protrusion from the surface. Similarly, Clemons et al (1999) reported layered structure for cellulose fiber reinforced injection molded composites. The researchers observed parallel orientation of the fibers at the surface and perpendicular orientation at the core. Moreover, Lo et al (1999) reported the presence of lubricant layer at the extrudate surface causing reduction in viscosity and adhesive failure for the Dynamar-polyethylene blend. Dorris and Gray (1978[a, b]) and Li and Reeve (2004) performed X-ray photoelectron spectroscopic (XPS) study on wood and reported patches of lignin on the wood. Schultz (2001) reported heterogeneous nucleation for the polymer-matrix composites at the fiber-matrix interface. Additionally, Kazayawoko et al (1999) performed XPS study on the bonding aspects of maleated anhydride (MAPP) with the wood fiber and found little contribution of the anhydrides to the total carbonyl content. Similarly, Stark and Matuana (2004) performed XPS study on the 50% WPC composites and found increase in oxygen content on the extruded WPCs after weathering. In another study Stark et al (2004) performed Fourier

transform spectroscopic (FTIR) analysis for the extruded and sanded WPC surface. The researchers reported higher wood content on the sanded surface as compared to the extruded surface. On the other hand, Gardner et al (2005) reported greater epoxy adhesion to the sanded WPCs as compared to the extruded surface.

The studies suggest that there is an effect of fiber content on the extruded skin layer and core material of composites. However, no work has been conducted, till date, to chemically differentiate and correlate the paint adhesion to the extruded and bulk surface of WPCs. The surface analyses and treatments conducted in the previous chapters were truly performed on the WPC specimens taken from the bulk of an extruded lumber. Bulk material was deemed more appropriate for a fundamental understanding of WPC surface behavior and response to surface activation treatments because bulk specimens are likely more homogeneous and their properties not so dependent on the processing. However the bulk and the extruded surface of WPCs may be different.

It is, therefore, not clear whether the findings of the previous chapters could be applied directly to the WPC extruded surface. In addition, before application of an adhesive or a coating, a surface is generally refreshed by simply sanding and or planing the surface. Of course, sanding the surface of a WPC prior to coating application could be very easily implemented on an online extrusion line. As a result, one can also wonder whether a sanded surface resembles the bulk surface such that the findings of the previous chapters could be utilized to coat freshly sanded WPC surfaces.

Thus, the present study aims to compare the surface chemistry, morphology and adhesion of an acrylate primer to the WPCs specimens taken from (a) the bulk of a component and (b) extruded surface of the component. In addition, the study aims to compare the adhesion strength of an acrylate coating applied on the extruded, bulk, and sanded WPC surfaces.

4.3 Experimental:

Materials: The raw materials for WPCs were wood flour, thermoplastic polyolefins, maleic anhydride grafted polypropylene (MAPP), talc and lubricant. The 60 mesh Pine (*Pinus spp*) wood-flour was obtained from the American Wood Fibers. The high density polyethylene (HDPE, LB0100, melt index 0.40 g/10min, density 0.95 g/ml) and MAPP (950P, density 0.93g/ml, free maleic anhydride content <0.9%) were obtained from the Innovene Inc., Equistar Chemicals and Honeywell respectively. The ester-stearate lubricant (OP100) and talc (Nicron 403) were obtained from the Honeywell and Luzenac America Inc respectively. A water based white acrylic primer (Raykote 2000, sp. gravity 10.57 and coating VOC 132.67) was used as supplied by Drew Paints, Inc for testing the paint adhesion to WPCs. The dried wood flour, polymer, talc, lubricant and coupling agent (when used) were dry blended prior to the extrusion and fed into the extruder.

Extrusion processing: Pine wood flour (59 wt %), HDPE (33.8 wt %), MAPP (2.3 wt %), talc (4 wt%) and lubricant (1 wt%) were dry blended and extruded by a twin screw extruder. Extrusion was performed on a 35 mm intermeshing twin screw extruder

(Cincinnati Milacron) operating at a 5-8 rpm screw speed and 500-800psi (3.45 – 5.52 MPa) melt pressure. The barrel temperature and die temperature for the HDPE formulations were 163°C and 171°C respectively. Similarly the barrel temperature and die temperature for the PP formulations were 185-193°C and 185°C respectively. A rectangular die (38mm x 10mm) set up was used to extrude the WPC components. The extruded components were conditioned in a water bath and stored in a dry shade before converting into small specimens.

Specimen preparation: Small sections (36x10x10mm^3) were sliced from the extruded WPC components perpendicular to the flow direction to yield rectangular pieces. Specimens for spectroscopic characterization were prepared by slicing the rectangular pieces parallel to the extruded surface with a microtome (5x5mm^2). Thus thin (<1mm) flat specimens were made to represent the extruded 'skin' layer and the 'core' bulk material. The thin pieces were placed in clean glass vials for the spectroscopic analysis. The second batches of specimens were prepared for the adhesion test. In this case 3 surface preparations were considered. The extruded surface and the bulk surface were considered as before. Again the bulk surface was generated by microtoming the sample surface. In addition, the extruded surface was lightly sanded to evaluate whether sanded surface had the characteristics similar to the bulk. For the adhesion test, 36x10x10mm^3 rectangular pieces were surface coated with the acrylic primer. The specimens prepared were washed with acetone (Baker analyzed, A.C.S. reagent) to remove the dust and surface contaminants, then dried (~40°C for 1hr) and conditioned in desiccators with

drierite (overnight) for next day testing and analysis. The surface, sanded surface and bulk material of WPCs was coated with a white acrylate primer.

XPS: X-ray photoelectron spectra (Axis 165, Kratos Analytical, AlKα source, Pass energy 40eV, 90° electron take off angle, Vision 1 software) were recorded for the extruded surface and the bulk surface of WPCs. The sensitivity factors used (O1s=0.734 and C1s=0.318) were empirically derived by the software. The survey spectra consisted 1s electrons from carbon (C1s) and 1s electrons from the oxygen (O1s). High resolution spectra (Gaussian fit) were performed at 278-292eV range to evaluate the C1s peaks. Similarly, high resolution spectra (Gaussian fit) were performed at 525-540eV to evaluate the O1s peaks. O/C was measured by normalizing the O1s peak area with the C1s peak area.

XRD: X-ray diffractrometric study of WPCs was performed to determine the crystallinity of HDPE at the surface and the bulk (Kristalloflex Diffractometer, D 500, Siemens Daco MP) using Cu-Kα radiation and scanning from 5.0 to 25.0 of 2θ with a step size of 0.01. Previous study reveals that wood shows three α-cellulosic peaks at (a) $2\theta \sim 15^0$ for (101) reflection, (b) $2\theta \sim 16^0$ for $(10\bar{1})$ reflection and (c) $2\theta \sim 22^0$ for (002) reflections in accordance with the previous research by Zhang and Kamdem (2000). The neat orthorhombic-HDPE (Li et al 2003) have two peaks at (d) $2\theta \sim 22^0$ for (110) reflection and (e) $2\theta \sim 24^0$ for (200) reflections in agreement with the research by Murthy et al (2000). However, WPCs shows distinct peaks only at - (a) $2\theta \sim 9^0$ for Talc (Obata et al) and (b) $2\theta \sim 22^0$ for wood and HDPE and $2\theta \sim 22^0$ for HDPE. Consequently, relative crystallinity

was measured by calculating the peak areas at $2\theta \sim 10^0$, 22^0 and 24^0. 3 replicates were chosen for each substrate.

$$Crystallinity(\%) = \alpha_i = (\frac{A_i}{(A_{10} + A_{22} + A_{24})}) * 100$$

Adhesion test: An acrylate primer was applied (0.28-0.41 mm) onto the 8 WPCs formulations, Maple wood and neat PP and HDPE with the help of a wire wound draw down bar (#32, Diversified Enterprises) to test the adhesion strength by the peel test. Wet film thickness was measured by a thickness gauge (S. G. Pinney & Ass. Inc.). A substrate-coating-cloth assembly was prepared following the procedures of ASTM D 6083. A strip of cheese cloth was adhered to the uncured coated surface of WPCs. Consequently, the assembly was cured at room temperature (~23°C) for 1 hr and a second layer of primer was applied and cured for 48 hrs. Before peeling, the free end of the cloth was wrapped with a mask tape (3M 250, flat stock paper backing, rubber adhesive, adhesion to steel 89N/100mm width) to prevent elongation of the cotton cloth. 180° peel test was performed with an Instron tensile grip (model 4426) at a crosshead speed of 2.0 cm/min (Ranby 1995). Peel load (N) was reported against 10^3mm specimen width.

4.4 Results and Discussion:

Figure 4.1 shows the XPS low resolution spectra of WPCs. Table 4.1 shows the elemental composition. It is apparent that the carbon (82.17-84.07%) and oxygen (11.95-14.47%) are the major chemical components of the WPCs. These values are in the same range as those measured by Stark and Matuana (2004). Traces of magnesium and silicon in the extruded and bulk surface likely stem from the talc present in the extrusion formulation. Overall, the elemental composition shows higher carbon concentration (84.07%) and lower oxygen concentration (11.95%) in the extruded surface as compared to the bulk material. This suggests that the extruded surface is richer in polyolefin than the bulk surface. Conversely, this suggests higher wood concentration in the bulk of the WPC compared to the extruded surface.

To further understand the chemical differences between the extruded and bulk WPC surfaces, high resolution XPS that focuses on the carbon and then on the oxygen region is evaluated. Figures 4.2-4.3 shows the XPS high resolution spectra for O1s and C1s peaks for WPCs.

Table 4.1: Elemental composition (atomic conc %) of the extruded surface and the bulk material of WPCs

Element	*Extruded Surface ('skin')*	*Bulk ('core')*	*HDPE* [a]	*50% WPC* [a]	*Pine*
C	84.07	81.83	82.96	82.59	74.05 [b], 74.7 [c], 76.27 [d]
O	11.95	14.43	13.28	14.12	25.95 [b], 25.2 [c], 23.73 [d]
Si	1.86	0.67	1.78	1.64	--

[a]Stark and Matuana (2004)
[b]Nzokou and Kamdem (2005)
[c]Kazayawoko et al (1999)
[d]Yuan et al (2004)

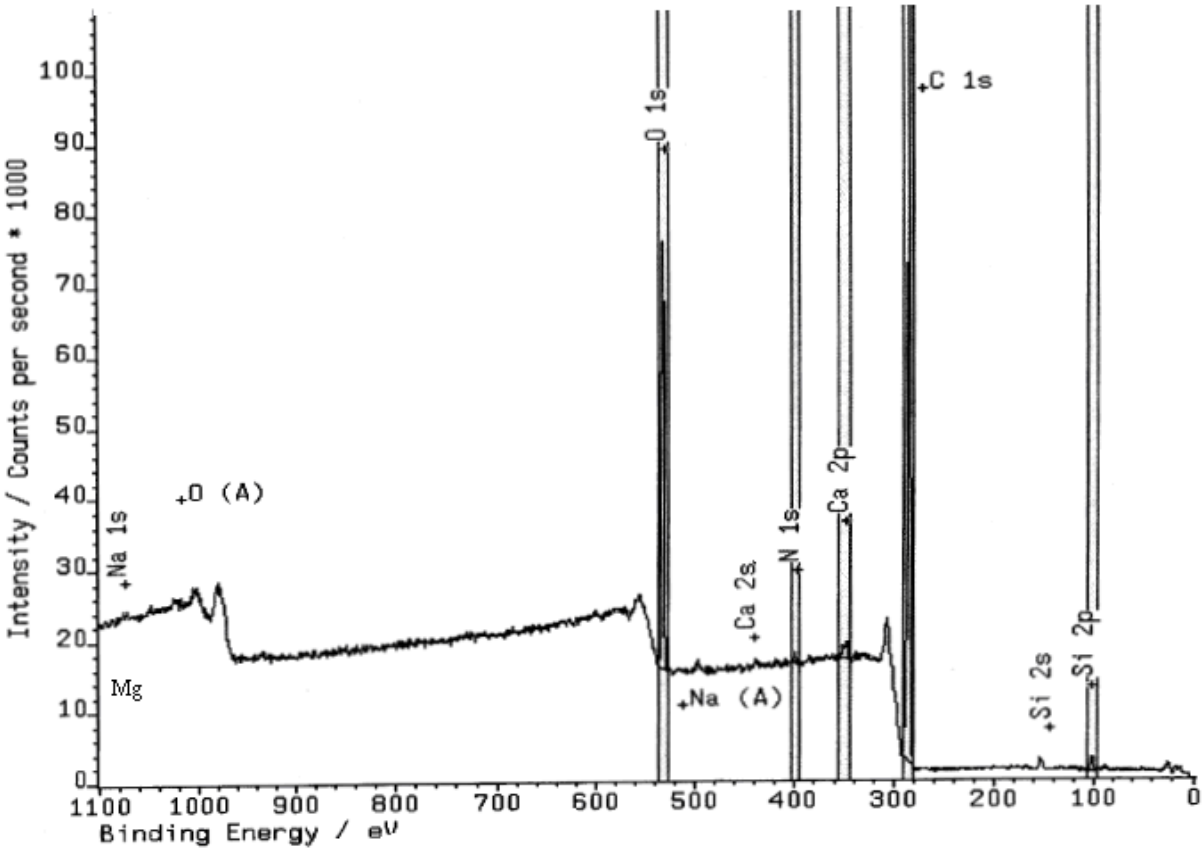

Figure 4.1: XPS low resolution survey spectra for WPCs

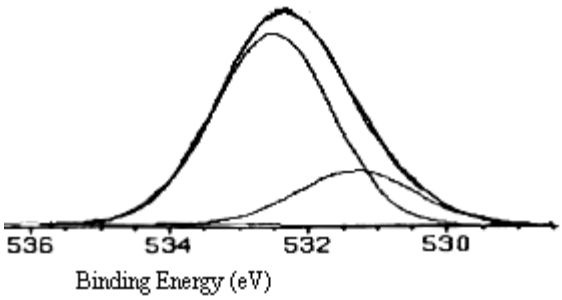

Figure 4.2: XPS high resolution O1s spectra for WPCs

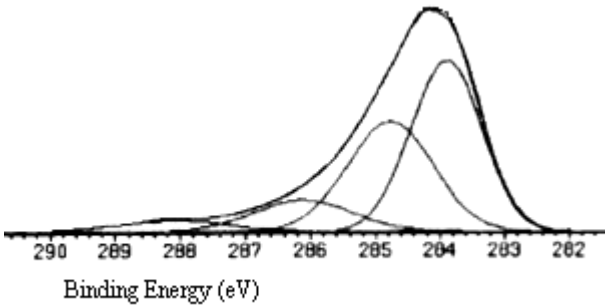

Figure 4.3: XPS high resolution C1s spectra for WPCs

C1s Peaks: Wood shows carbon spectra due to the presence of carbons (74.05-76.27%) in extractives, lignin and cellulose (Dorris and Gray 1978[b], Kazayawoko et al 1999, Yuan et al 2004, Nzokou and Kamdem 2005). Dorris and Gray (1978 [a]) reported four different types of carbon atoms in wood (Table 4.2). C1 denotes a carbon atom bonded only to a carbon or a hydrogen atom (C-H/C-C), C2 denotes a carbon atom singly bonded to a oxygen atom (C-O) other than a carbonyl atom, C3 denotes a carbon atom single bonded to two oxygen atoms or to a single carbonyl atom (O-C-O/C=O) and C4 denotes a carbon atom single bonded to a oxygen atom and to a carbonyl oxygen atom (O-C=O).

Table 4.2: Result of C1s and O1s high resolution spectral fitting for the extruded surface and bulk surface of WPCs (Atomic conc. %)

	Extruded Surface	Bulk Surface	HDPE[a]	50% WPC[a]	Pine
Carbon group					
C1 (C-H/C-C)	83.69	80.60	78.01	69.54	69.9[b], 62.85[c]
C2 (C-O)	5.68	14.86	14.74	19.9	19.6[b], 23.72[c]
C3 (O-C-O/C=O)	4.97	3.29	4.63	6.34	5.3[b], 6.14[c]
C4 (O-C=O)	5.66	1.25	2.62	4.22	5.2[b], 7.29[c]
Oxygen group					
O1 (O-C=O)	54.79	22.31	--	--	18.94[c]
O2 (C-O)	45.21	77.69	--	--	81.06[c]
O/C	0.14	0.18	--	0.16	0.31[d], 0.34[b], 0.35[c]

[a]Stark and Matuana (2004)
[b]Kazayawoko et al (1999)
[c]Nzokou and Kamdem (2005)
[d]Yuan et al (2004)

As expected, C1 (C-H/C-C) is the major carbon component in WPCs. It is higher in the extruded surface compared to the bulk. The higher percentage of C1 in extruded surface may be interpreted as a result of greater concentration of polyolefin and lubricants at the extruded surface compared to the bulk. Conversely, there is a low concentration of C2, in the extruded surface as compared to the bulk. The bulk material has very high concentration of C2 (C-O) which is quite similar to the reported value of C2 on Pine (19.6-23.7). This may be interpreted as a result of greater concentration of wood cellulose and lignin in the bulk of WPCs.

Overall, the carbon spectra reveals high amount of polymer on the extruded 'skin' layer and high amount of oxygenous material on the bulk 'core' material.

O1s Peaks: The deconvolution of the O1s spectrum originating from the wood gives two oxygen peaks. The O1 is assigned to an oxygen atom linked to a carbon atom by a

double bond (O-C=O) while the O2 is assigned to an oxygen atom linked to a carbon atom by a single bond (C-O) (Nzokou and Kamdem 2005). Table 4.2 shows that out of the total 100% oxygen atom available in the extruded surface, 54.8% of oxygen atom are in O1 form while 45.2 % are in O2 form. This is quite reasonable with the findings of C4 (5.7%) and C2 (5.7%). Moreover, O-C=O bond is absent in cellulose. Thus, the O1 fraction of the oxygen may be assigned to the polyester (lubricant) fraction in the extrusion formulation and to a small amount to the wood lignin and extractives. Furthermore Table 4.2 shows that out of the total 100% oxygen atom available in the bulk surface, 22.3% of oxygen atoms are in O1 form while 77.7 % of oxygen atoms are in the O2 form. This is quite reasonable with the findings of the C4 (1.3%) and C2 (14.9%) amount. Moreover, this result shows 3.5 times of C-O bond compared to the O-C=O bonds. This suggests that the presence of the polyester lubricant at bulk is not significant. Importantly, this result is in good agreement with the previous findings on Pine wood showing 18.9% of O1 against 81.1% of O2 (Nzokou and Kamdem 2005) which leads to the assumption that the bulk material contains wood within the probe depth of XPS.

O/C ratio: The XPS result shows an O/C ratio of 0.14 for the extruded surface and 0.18 for the bulk material (Table 4.2). The O/C ratio of the bulk material of WPCs is higher than that of the extruded surface of WPCs. This further confirms higher amount of woody material in the bulk compared to the extruded surface.

Overall, the XPS study of the extruded surface and the bulk surface reveals that the extruded surface is rich in polymer while the bulk is comparatively high in wood content. In addition, additives and lubricants in particular concentrate at the surface of the extruded WPC compared to the bulk.

Crystallinity: The results are summarized in Table 4.3 and Figure 4.4. α_{10} represents the relative crystalline amount for the talc; α_{22} represents the relative crystalline amount for the combination of cellulose and HDPE, while α_{24} represents the relative crystallinity for HDPE. Neat HDPE shows a crystallinity of 78.2 $\pm$ 0.6 % at $2\theta \sim 22^0$ and 21.8 $\pm$ 0.6 at $2\theta \sim 24^0$. However, the percentage crystallinity of HDPE is much less in WPCs as compared to the neat HDPE. This may have resulted because of the presence of wood fiber which physically hinders the growth of HDPE spherulites. Additionally, WPC bulk shows greater concentration of crystalline talc in the bulk as compared to surface. This is consistent with the XPS study showing higher polymer content on the extruded surface and consequently smaller concentration of other WPC components including talc at the extruded 'skin' layer as compared to the bulk surface. Moreover, WPC bulk has a little higher crystallinity than the surface. This may have occurred either due to less nucleation at the surface or due to supercooling occurred during chilling of the molten WPC blend. Moreover, the presence of wood component in the bulk may have acted as nucleation site for the HDPE leading to heterogeneous nucleation and transcrystalline morphology.

Table 4.3: The surface and the bulk crystallinity and peel adhesion to HDPE and WPCs

	Crystallinity (%)			*Peel Load (N/m)*
	$\alpha_{10\ talc}$	α_{22}	α_{24}	
HDPE	0.0	78.2 ± 0.6	21.8 ± 0.6	48 ± 1
Extruded WPC Surface	10.0 ± 0.9	75.6 ± 1.6	14.4 ± 1.8	135 ± 24
Bulk WPC	11.6 ± 3.2	72.5 ± 3.0	15.9 ± 1.0	219 ± 22
Sanded WPC surface	--	--	--	212 ± 11

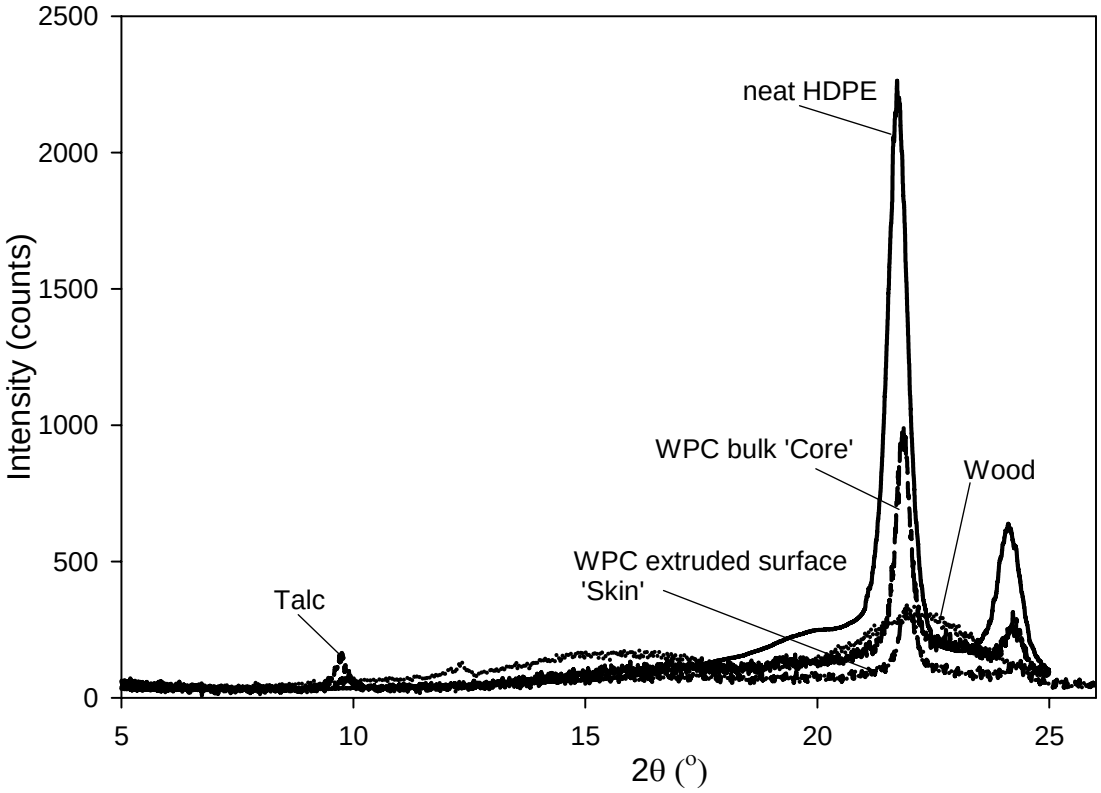

Figure 4.4: XRD traces of neat HDPE, wood, extruded surface and bulk material of WPCs

Adhesion Test: The results for primer adhesion to the neat HDPE, extruded surface of WPCs, sanded surface of WPCs and bulk surface of WPCs are summarized in Table 4.3.

The peel adhesion strength for the acrylate primer to the sanded surface (212 $\pm$ 11 N/m) and the bulk (219 $\pm$ 22 N/m) are higher than the peel adhesion to the extruded surface (135 $\pm$ 24 N/m). The low primer adhesion to the extruded surface is consistent to the XPS study showing absence of polarity (C=O/O-C-O) and high polymer content at the extruded surface. Moreover, the results suggest that the lightly sanded surface have primer adhesion similar to the bulk surface of WPCs (219 $\pm$ 22 N/m). This is consistent with the fact that sanding removes the weak boundary layer (WBL) from the extruded WPCs thereby exposing fresh surface for bonding with the acrylate. More importantly this suggests that it is possible to remove the extruded polymer rich surface by light sanding to obtain better paint adhesion. In addition, the results suggest that the bulk material of WPCs (219 $\pm$ 22 N/m) has higher paint adhesion as compared to the extruded surface.

This is consistent to the XPS study showing higher amount of oxygen and O/C ratio in the bulk as compared to the surface. Thus polar interaction, hydrogen bonding and adsorption of the acrylates on the WPCs may be the reasons to improve the adhesion strength. However, this is inconsistent with the XRD result showing little higher crystallinity of HDPE in the bulk as compared to the surface. Higher crystallinity indicates less availability of the substrate polymer chain to interact with the applied primer. However, this may be interpreted by the fact that the WPC extrusion formulation contains only 34% of polymer against 59% of wood. Thus, the role of the polymer in dictating the adhesive interaction is not important in this case. Overall, the surface polarity is the dominant factor in determining the primer adhesion to WPCs.

4.5 Conclusion

The chemistry and morphology of the extruded 'skin' surface and bulk material was performed by the XPS and XRD. The acrylate primer adhesion to the extruded and bulk material of WPCs was measured by 180° peel test. The elemental study by the XPS revealed higher amount of polymer at the extruded 'skin' surface as compared to the bulk 'core' material. Additionally, the extruded surface showed the presence of lubricant which was absent in the bulk. Contrarily the bulk material showed higher amount of oxygen component due to the presence of wood. In addition, the XRD study revealed higher crystallinity of the HDPE in neat HDPE as compared to the crystallinity in WPCs. Moreover, higher amount of crystalline talc was observed in the bulk as compared to the extruded surface. Furthermore, the primer adhesion to the sanded surface (212 ± 11 N/m) was similar to the bulk surface (219 ± 22 N/m). However, the primer adhesion to the sanded surface was greater than the primer adhesion to the extruded surface (135 ± 24 N/m). Thus, the lack of polarity and presence of lubricants in the extruded surface are the possible reasons for the low paint adhesion to the extruded 'skin' layer as compared to the sanded and bulk surface. Additionally, this study suggests that good bonding of paints to WPCs can be achieved by a light surfacing of the extruded composites.

Acknowledgements:

Louis Scudiero, Charles Knaack

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RECOMMENDATIONS

The specific objective of this work was to propose a plausible technology for good paint adhesion to WPCs. The results showed that the primer adhesion to WPCs increases with increasing wood content on the surface. On the other hand, the presence of maleated anhydride (MAPP) as a coupling agent lowered the primer adhesion to WPCs. Besides, the hardwood maple (*Acer spp*) formulations demonstrated greater primer adhesion as compared to the softwood pine (*Pine spp*) formulations. However, the primer adhesion to WPCs was intermediate to that of wood and polyolefins. Polyolefins have inactive surface which leads to low primer-substrate interaction. Therefore, in industrial sector, various types of pretreatment techniques are employed to improve substrate-coating adhesion and prevent easy fall off of coatings from the plastic surface. Consequently, four common plastic surface treatment methods, namely- (i) oxygen plasma, (ii) flame, (iii) ultraviolet (UV) and (iv) chromic acid etching- were employed to verify the effect on primer adhesion to WPCs. Out of the four treatments employed, the flame, UV and plasma treatments were dry processes while the chromic acid treatment was a wet process. Additionally, it was observed that the thermodynamic parameter of wetting and surface polarity had little effect on the practical work of adhesion defined by the peel load. Surface roughness had a major role in defining the primer adhesion. Consequently, a study with sanding/ surface refreshing was performed to study the effect of sanding on the primer adhesion to WPCs. Sanding improved the primer adhesion to WPCs in a considerable way; however, the sanded-pretreated surface imparted much higher primer adhesion compared to the simply sanded surface.

Performance wise - chromic, oxygen plasma and UV treatment created a surface which offered paint adhesion to WPCs similar to that of wood. In fact, the chromic and oxygen plasma treatment methods were found to be superior to the other treatment techniques. The oxygen plasma treatment is the high priced technique compared to the other treatment methods. On the other hand, for the chromic acid treatment, the after-treatment chromic residue is a source of environmental hazard and would require purification / re-processing of the waste to comply with the environmental need. This would add cost to the original treatment set-up.

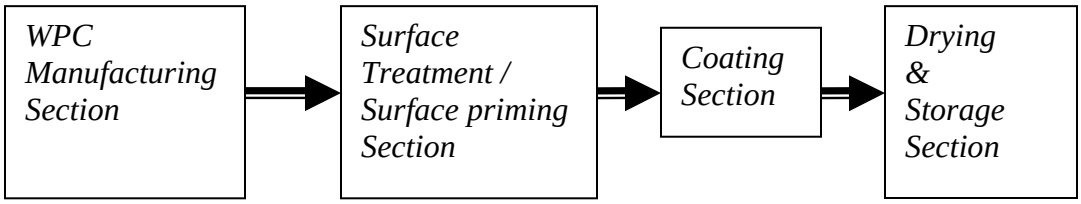

Figure 5.1: Flow chart for the proposed line-up for WPC surface coating

APPENDIX-A

ATR-Spectral analysis

The previous study on the measurement of surface oxidation (OC/OH) was performed by normalizing the area at 1840-1530cm^{-1} , representing the C=O groups, against the area at 1530-1410cm^{-1} representing the C-H bending and scissoring motion. However, the C-H band at 1530-1410cm^{-1} simultaneously represents the polyolefin and wood components. Hence, in order to evaluate the sole effect on plastic components, the wood spectra were subtracted from the WPC spectra. Consequently, the band representing the O=C at 1840-1530cm^{-1} was normalized against the band of C-H stretch at 3010-2700 cm^{-1}. The band at 3010-2700 cm^{-1} purely represents the plastic component and consequently would serve as a good reference region.

$$OC/CH = \frac{A_{1840-1530}}{A_{3010-2700}}$$

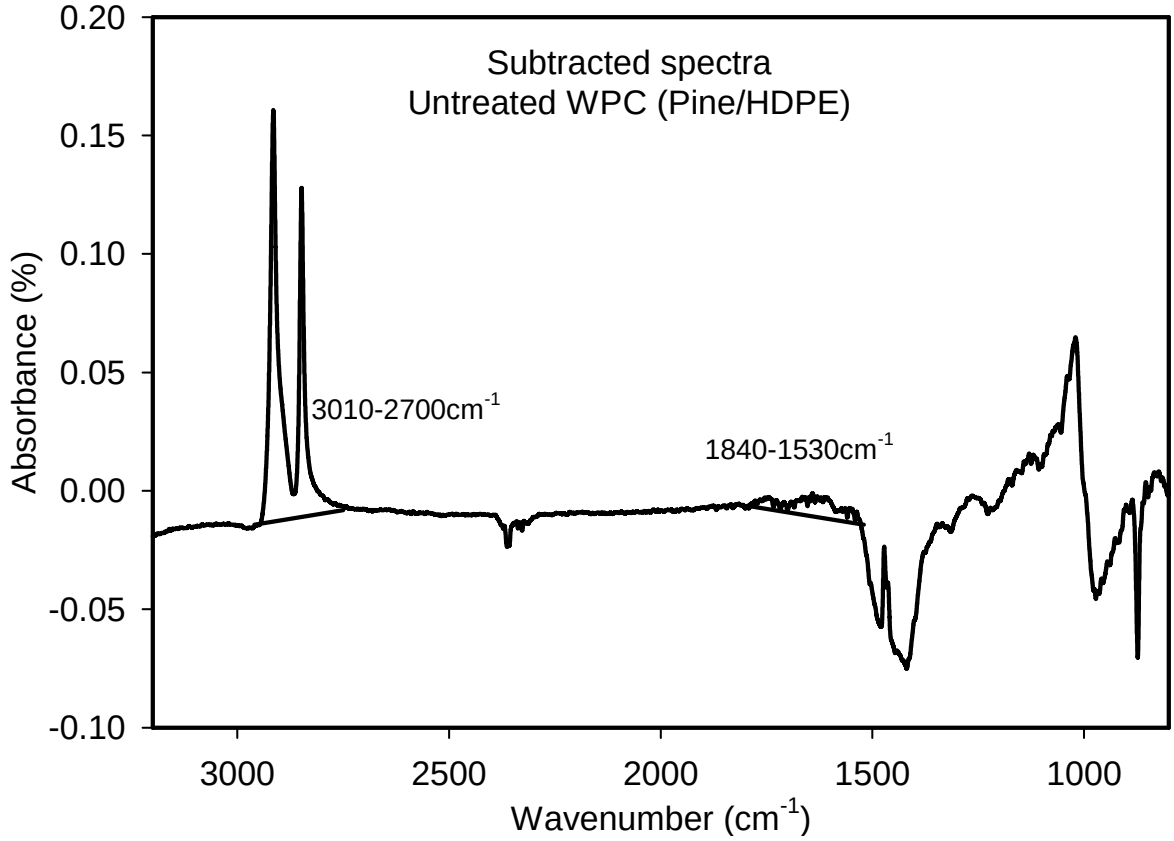

Figure A1: Subtraction ATR-FTIR spectra of Pine/HDPE

Table A1: Effect of various treatments on OC/CH of WPCs

Treatment	O=C/C-H
Untreated	1.58 ± 1.45 (A)
Flame	1.38 ± 1.06 (A)
Chromic	0.6 ± 0.6 (B)
UV/BP	1.89 ± 1.08 (A)
O_2 Plasma	1.17 ± 1.08(A)
P value	0.0256

Discussion:

The effect of different treatment conditions on OC/CH of WPCs are summarized in the Table A1. It is clear that there is a significant effect (p=0.0256) of treatment conditions on the measured OC/CH ratio. Specifically the chromic acid (0.6 ± 0.6) treated WPCs have low OC/CH as compared to the untreated (1.58 ± 1.45), flame treated (1.38 ± 1.06), plasma treated (1.17 ± 1.08) and UV/BP treated WPCs (1.89 ± 1.08). It appears that the there is a significant decrease in OC/CH for chromic acid treated WPCs. Figure A2 represents the original spectra for all the treated conditions. It is evident that except for the plasma treated WPCs; all other treatment conditions have high C-H peak intensity suggesting greater surface concentration of plastics. Consequently, any subtraction of wood spectra from the treated spectra may result to the removal of the oxidation stretch of plastics itself. Thus the results from Table A1 may not represent the actual oxidation of the treated surfaces.

Additionally, Figure A.3 represents that there is no specific trend between the peel load plot and the OC/CH suggesting that the OC/OH may not be a true representation of the adhesion property of the composite surface. Other factors like increasing surface

roughness and removal of weak boundary layer (WBL) may be acting dominantly over the surface OC/CH.

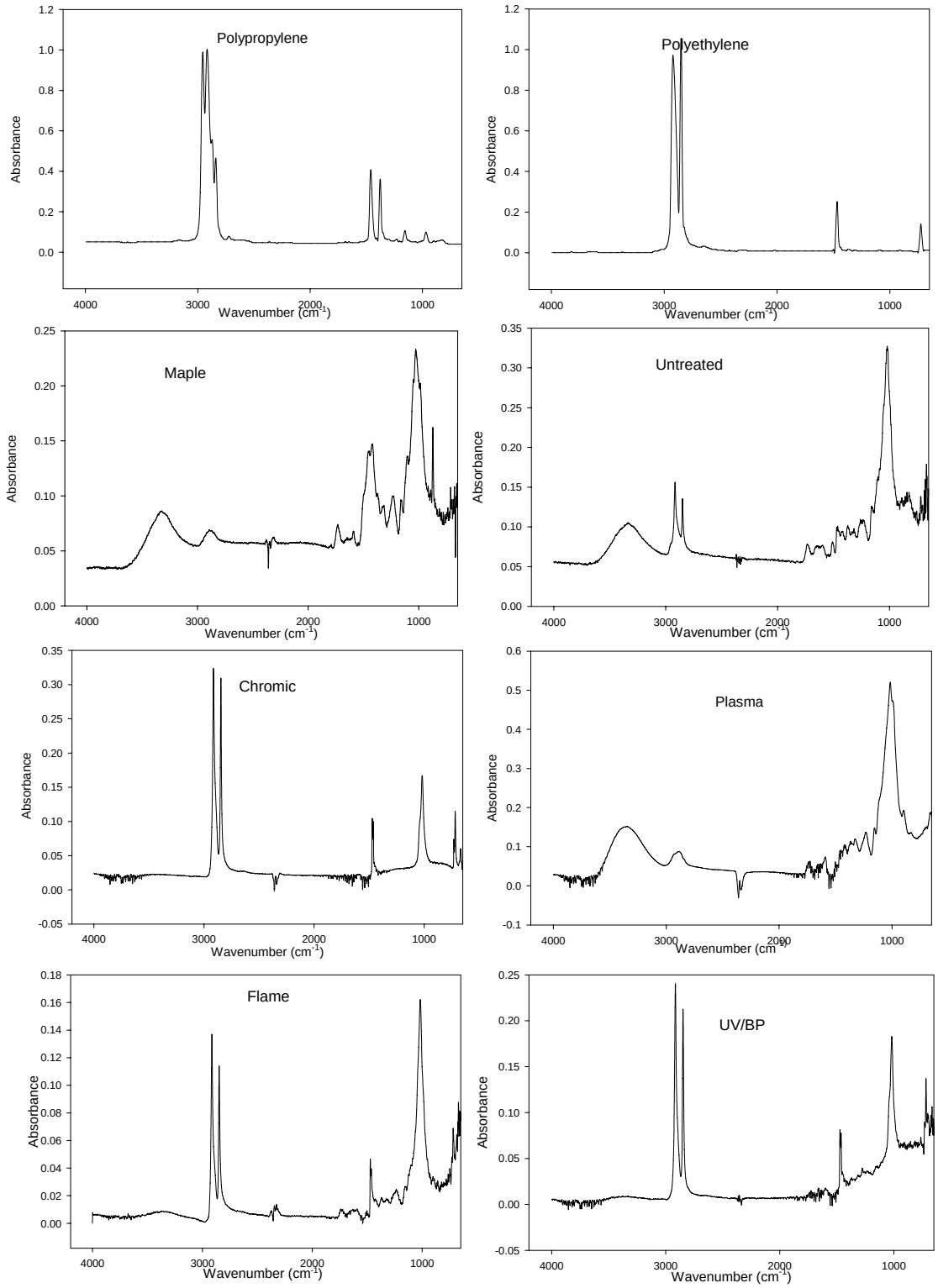

Figure A2: ATR-FTIR spectra of wood, PE, neat WPC and treated WPCs

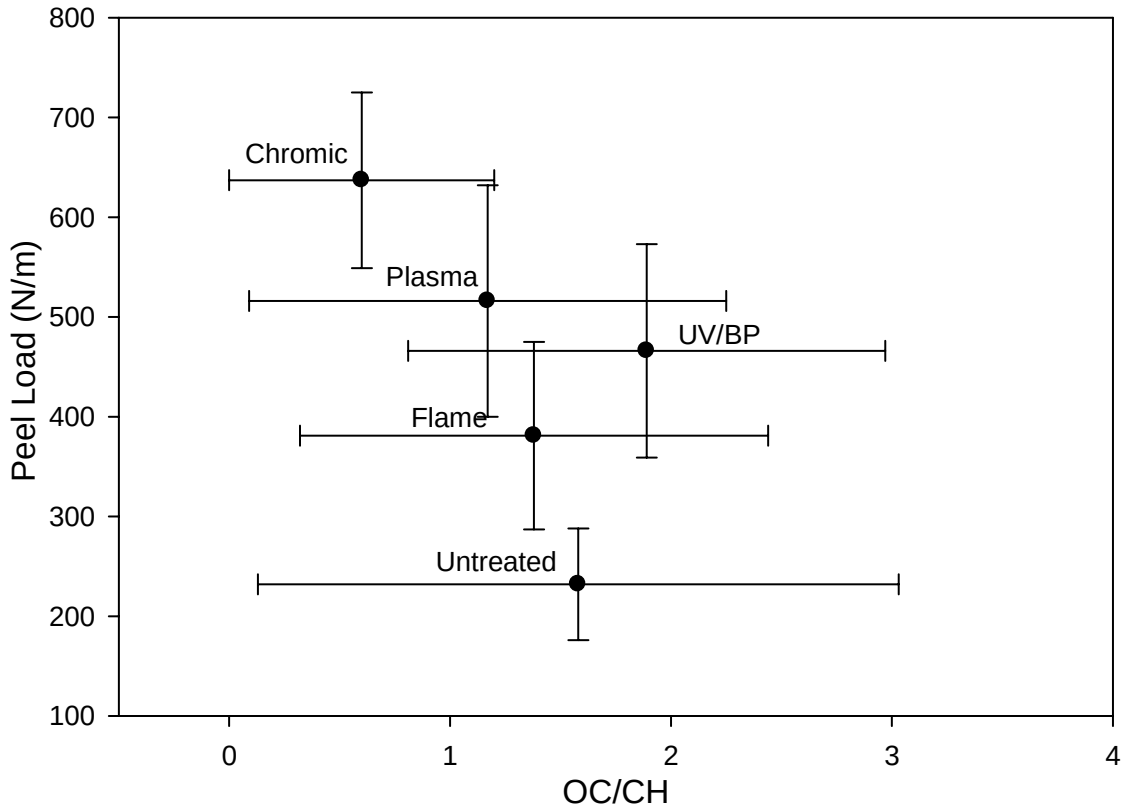

Figure A3: Plot showing the relationship between peel load (N/m) and OC/CH