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Effects of Chemical and Mechanical Weathering Processes on the Degradation of Plastic Debris on Marine Beaches

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Graduate Program in Geology

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

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EFFECTS OF CHEMICAL AND MECHANICAL WEATHERING PROCESSES ON
THE DEGRADATION OF PLASTIC DEBRIS ON MARINE BEACHES

(Spine title: Chemical and Mechanical Weathering of Plastic Beach Debris)

(Thesis Format: Monograph)

By

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Graduate Program in Geology

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

The School of Graduate and Postdoctoral Studies
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London, Ontario, Canada

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THE UNIVERSITY OF WESTERN ONTARIO
School of Graduate and Postdoctoral Studies

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Effects of chemical and mechanical weathering processes on the degradation of plastic debris on marine beaches.

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ABSTRACT

Plastics are an integral part of everyday life, and the use of plastic products for consumer goods, food packaging, recreational and commercial fishing and medical and sanitary applications continues to increase. The durability, low cost, light weight and hydrophobic nature of plastic make it a desirable material for numerous applications; however, these same characteristics make plastic debris in natural environments a pervasive problem. Increases in plastic use and low economic incentive for recovery, result in accumulation of debris in marine environments. Degradation of plastics through chemical weathering occurs in the open ocean or along shorelines where polymers are exposed to seawater and UV radiation. Plastic particles were both experimentally degraded, and sampled from beaches on the island of Kauai, Hawaii, U.S.A. and in and near Gros Morne National Park, Newfoundland, Canada. Daily accumulation rates of 484 pieces per day were recorded in Kauai and approximately 6000 plastic particles were collected over a 10 day period. Relationships between composition, surface textures and level of oxidation were studied using FTIR (Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscopy). Surface textural analysis showed evidence of cracks, fractures, flakes, grooves, pits, adhering particles and vermiculate textures. Increased surface oxidation of different polymer types was determined by measuring increased IR absorbance in the 1710 cm^{-1} wavenumber region of the IR spectra. Results obtained from both analytical techniques indicate a strong relationship between chemical and mechanical degradation of plastics, suggesting that plastics degrade most efficiently on beaches compared with other natural environments. Vermiculate textures were only

present on polyethylene particles sampled from Kauai indicating that biological activity, water salinity or temperature may play key roles in the degradation of plastics in subtropical climates. Analysis of debris collected from Kauaiian beaches indicates that small particles and pellets comprise the largest portion of plastics which is in contrast to Newfoundland beaches which have more intact and nearly intact debris relative to the overall plastic load. Size distribution of plastic debris closely mimicked natural sedimentary grain size distribution in natural environments suggesting that plastics may become a significant component of the sedimentary deposit record.

Keywords: Plastic marine debris, Polyethylene, Polypropylene, SEM, FTIR, Kauai, Hawaii, Gros Morne National Park, Newfoundland, UV radiation

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CHAPTER 1

INTRODUCTION

1.1 Overview of Plastics Production and Pollution

A great variety of polymer types have been developed since creation of the first synthetic polymer known as Bakelite in 1907. During the past 60 years, increased applications for plastic have resulted in an exponential increase in its use (Laist 1987; Thompson et al. 2009). Plastic has become the primary choice of manufacturers for packaging of food, chemicals, cosmetics, pharmaceuticals and many other consumer products due to the low cost of production and physical properties of plastic, including its lightweight nature, durability, strength and resistance to water (Laist 1987; Pruter 1987; Andrady and Neal 2009). There was a 25-fold increase in global plastics production between 1960 and 2000, and as of 2008 there were 65,000 plastic processing facilities in China and India, which indicates that the demand for plastic resins continues to grow rapidly (Moore 2008). However, due to little economic incentive or limited options for re-use, less than 5% of material is recovered (Moore 2008).

Plastic now accounts for 10% of all waste generated, with global use exceeding 260 million tonnes per annum (Barnes et al. 2009; Thompson et al. 2009). In the United States, 50% of waste plastic is sent to municipal waste facilities, 5% is recycled, and approximately 20% is re-used in some form as durable goods. The remaining 25% (12.5

million tonnes) unaccounted for is a possible source for the increased amount of plastic debris entering the natural environment (Moore 2008). Sampling conducted by The Algalita Marine Research Foundation (AMRF) at one locality near the Los Angeles and San Gabriel Rivers in California, recorded 60 tonnes (representing 2.3 billion pieces) of plastic debris >1mm in size travelling towards the ocean over a 3 day period (Moore et al. 2005). Moore (2008) found a UNEP (2001) report grossly underestimated the amount of plastic debris entering the environment at 8 million pieces per day. AMRF data suggest that this accounts for only 1% of all plastic pieces travelling out to sea in a single day in the Los Angeles area.

Traditionally, marine debris researchers have classified debris sources into two categories, 1) land-based or 2) ocean/waterway based, depending on where debris enters the water system. Up to 80% of the world's marine pollution is derived from land-based sources (Derraik 2002). These sources generally include metropolitan and urban areas, which typically produce plastic debris in the form of packaging materials as well as plastic bottles, containers and food wrappers (Derraik 2002; Gregory and Andrade 2003). Inappropriately or illegally dumped garbage, littering, open dumpsters, fishermen, beachgoers, landfills and processing facilities are considered some of the largest contributors to the accumulation of marine debris (Sheavly and Register 2007). Some waste reaches appropriate facilities, but with approximately half of the world's population living within 80km of the ocean, significant amounts of lightweight plastic garbage often blow or run off into the sea (Moore 2008). There are many dynamic linkages between litter sources and sinks (Figure 1.1). Offshore there is an increase in

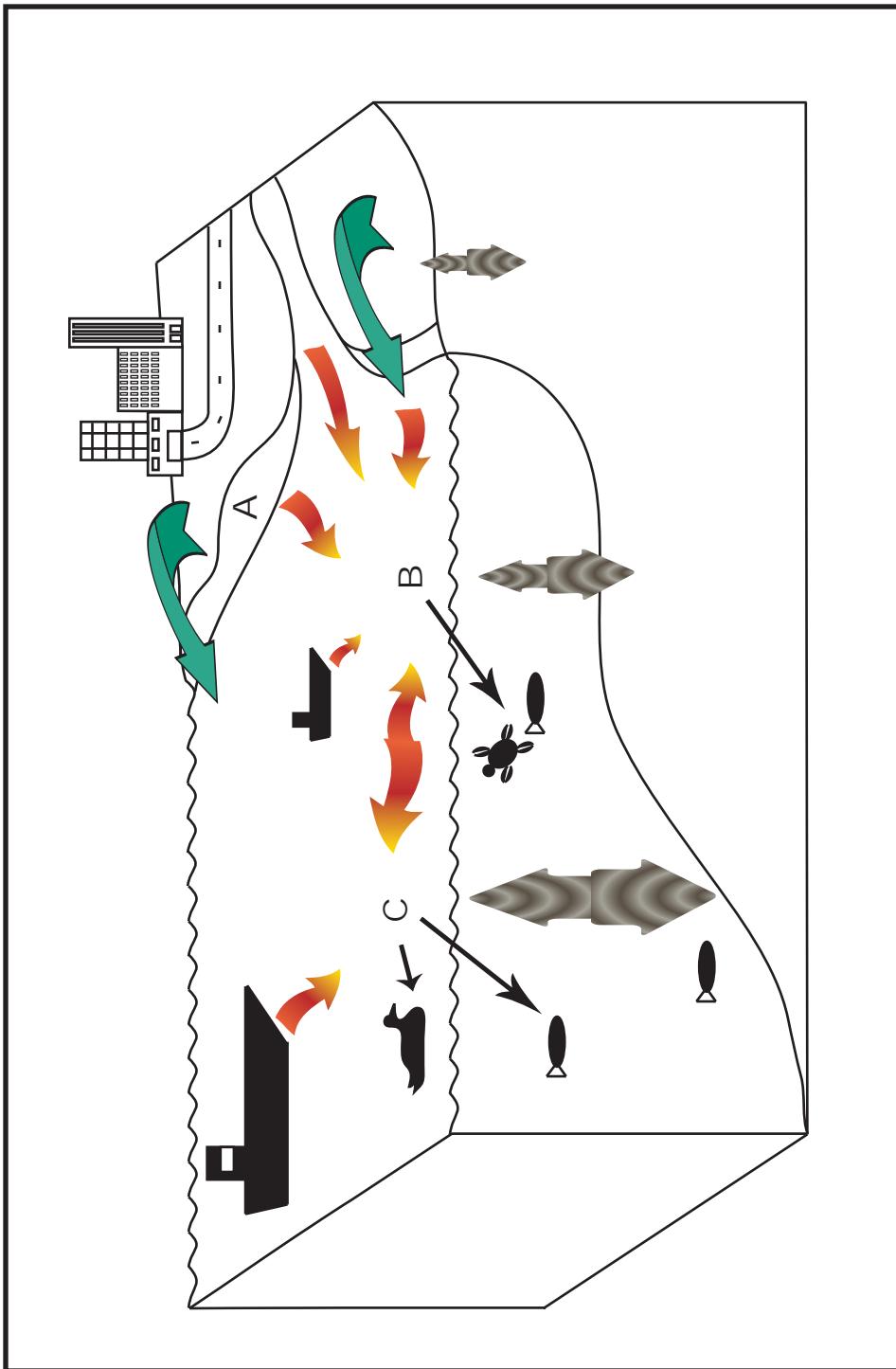


Figure 1.1 Schematic diagram indicating the pathways and modes of movement for plastic in the marine environment. A) coastal waters and sediments, B) beaches, C) open ocean. Green arrows indicate wind-blown debris, grey arrows display vertical movement through the water column including sea floor deposition and burial, black arrows point to ingestion and entanglement by marine organisms, and red arrows indicate water borne debris (modified from Ryan et al. 2009).

ship-based litter, however, the total litter load decreases with the exception of aggregation in mid-ocean gyres (Ryan et al. 2009; Pichel et al. 2007). Litter discarded on streets, roads, parking lots and beaches reaches the ocean by wind or through municipal drainage systems such as storm water drainage and sewage outlets. However, the majority of ocean plastic debris originating inland is carried through natural watercourses such as streams and rivers and inevitably becomes deposited on shorelines or in the open ocean (Pruter 1987; Williams and Simmons 1997).

Ocean and waterway-based sources can include commercial fishing vessels, cruise ships, recreational boats, and military, merchant and research vessels, as well as offshore petroleum platforms and the vessels that supply them (Derraik 2002; Lee et al. 2006; Sheavly and Register 2007). Significant amounts of debris enter the water from commercial and recreational fishermen who dump ship-generated garbage overboard or neglect to retrieve fishing gear such as nets, ropes, buoys or trawl floats (Sheavly and Register 2007).

1.2 Detrimental Effects of Plastic Marine Debris

Plastic debris that has entered the marine system has the potential to travel great distances and as a consequence has become one of the most common and persistent pollutants in ocean waters and on beaches throughout the world. Marine debris is composed of 60-80% plastic, and as much as 90-95% in some locations (Derraik 2002; Moore 2008). During the last four decades, plastic debris has been recorded in habitats from the poles to the equator (Thompson et al. 2004). Plastics are unique when compared to other marine litter in that they become the most prominent debris type with distance from the source. Denser materials such as glass and metal do not transport as easily as plastics, and less dense materials such as paper deteriorate much more quickly in the natural environment (Ryan et al. 2009).

Ocean and wind currents transport plastic debris great distances, which results in large quantities of plastic particles floating throughout the oceans (Derraik 2002; Moore 2008). Plastic debris characterizes coastal waters, the open ocean and sediments, but inevitably large quantities will be deposited on beaches (USEPA 1992; Derraik 2002). Islands are considered sinks for ocean-borne plastic debris and often accumulate substantial amounts of plastic fragments and pre-production pellets on their beaches (Moore 2008). McDermid and McMullen (2004) sampled 9 Hawaiian beaches and collected 19,100 pieces of plastic debris between 1 and 15 mm in size, of which 2100 pieces were pellets. Moore (2008) collected 2500 plastic particles >1mm on the surface of one square foot of beach sand on Kamilo Beach, Hawaii; 20% of the particles

collected were pellets. No plastic production facilities are located in the state of Hawaii, and therefore the abundance of pellets provides evidence that plastic pollution has far-reaching implications (McDermid and McMullen 2004; Moore 2008).

The greatest concentration of plastic processors in the United States is in California, and a study of Orange County beaches conducted by Moore et al. (2001) found beach debris to be comprised of 98% pellets with an estimated count of over 105 million particles sampled. These findings substantiate a common theory among researchers that the west coast of North America is the primary source for plastic marine debris in the North Pacific Ocean.

Distribution of plastics in the marine environment poses a serious threat to many organisms such as fish, birds, and turtles (Whiting 1998; Gregory and Andrade 2003; McDermid and McMullen 2004; Sheavly and Register 2007). Entanglement and ingestion are primary concerns as they are most commonly seen in mainstream media and affect a large number of marine biota. Additional concerns include drift plastic as a possible transport method for invasive species, ingestion and transport of persistent organic pollutants (POPs) and the accumulation of plastic debris on the sea floor (Derraik 2002; Gregory and Andrade 2003; Moore 2008).

1.3 Aim of the Study

The benefits of plastic and the exponential increase in its use indicate that polymers will continue to be important for the foreseeable future. An unfortunate circumstance of this trend is that a large quantity of plastic debris will enter Earth's ecosystems. The overall aim of this study is to determine which polymer types are most conducive to chemical and mechanical degradation in natural beach environments. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to examine samples of polyethylene and polypropylene, which are the most prevalent polymer types found in the natural environment. Surface textures, polymer composition and level of surface oxidation were examined in order to determine the effects of weathering on the breakdown of plastics. Particles were degraded experimentally, and samples were collected from subtropical beaches on Kauai, Hawaii, U.S.A. and temperate beaches in and near Gros Morne National Park, Newfoundland, Canada. These sampling areas were chosen because large quantities of plastic debris accumulate on their beaches, and it is anticipated that variations between tropical and temperate climates will produce differences in chemical and mechanical weathering textures. Compared with Newfoundland plastics, Kauaiian samples are expected to have higher levels of oxidation and well defined surface textures associated with increased water, air and beach sand temperatures. In addition, plastic samples deposited on Hawaiian beaches are believed to primarily originate from distant sources (Moore 2008), which would suggest a longer exposure time to chemical and mechanical degradation processes while at sea. The temperate climate of Newfoundland is expected to result in

lower levels of chemical weathering of plastic debris. The secondary objectives of the research are to determine, 1) the major types of plastic debris, 2) distribution and depositional patterns of plastic debris on beaches, and 3) an example of a daily accumulation rate.

1.4 Significance

This research is the first to provide valuable insight into the chemical and mechanical degradation properties of the most commonly used polymer types. Improved understanding of the fate of plastic debris in natural beach environments may lead to a shift away from use of polymer types with longer sediment residence times. In addition, our research will contribute to the literature database concerning the abundance and distribution of plastic fragments in the environment. Finally, very few publications deal with the behaviour of plastics as part of the sedimentary pile. The present study considers plastic particles as sediment grains, rather than fragments of exotic materials.

1.5 Relationship to published work

Part of this thesis has been published in and submitted to two peer reviewed journals, presented at four conferences, and displayed at the Gros Morne National Park visitor information centre:

- 1) Cooper, D.A., and Corcoran, P.L. 2009. The Beaches of Kauai: A Plastic Paradise. 6th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2009 (Oral presentation).
- 2) Cooper, D.A., and Corcoran, P.L. 2010. Effects of Chemical and Mechanical Processes on the Degradation of Plastic Beach Debris. 7th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2010 (Oral presentation).
- 3) Cooper, D.A., and Corcoran, P.L. 2010. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. Marine Pollution Bulletin, 60: 650-654.
- 4) Cooper, D.A., and Corcoran, P.L. 2010. Effects of chemical and mechanical weathering processes on the degradation of plastic beach debris. Bridging Science with Communities SETAC North America 31st Annual Meeting, Abstract Volume MP068, Portland, Oregon, November 2010: 9 (Poster Session).
- 5) Cooper, D.A., and Corcoran, P.L. 2011. Plastic Marine Debris: A New Type of Beach Sediment. 8th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2011 (Oral presentation).

- 6) Cooper, D.A., and Corcoran, P.L. 2011. Plastic beach debris on North America's Atlantic coast: A New Type of Sediment? Water, Air and Soil Pollution (Submitted). Manuscript number WATE7618.
- 7) Cooper, D.A., and Corcoran, P.L. (2011) Distribution, deposition, and degradation of Plastic Beach Debris in and near Gros Morne National Park, Newfoundland, Canada. Gros Morne National Park Visitor Information Centre park pollution awareness campaign (Poster).

Most of the text in this thesis has been modified from the journal articles, but some passages are included verbatim. Certain figures and photos have already been published, but the figure contents and descriptions have been slightly modified for the thesis. Fieldwork, sampling, and research for Cooper and Corcoran (2010) and Cooper and Corcoran (submitted), in addition to the actual writing, were conducted by the first author. The second author, P. Corcoran, edited the manuscripts, contributed to research and was responsible for funding of the project.

CHAPTER 2

THREATS OF PLASTIC POLLUTION

2.1 Entanglement

Wildlife living near, in or on the water is at particular risk to entanglement, as nets, ropes, fishing lines and other debris pose a serious threat. When seabirds, seals, dolphins, turtles or other marine animals become entangled, they face the risk of drowning or strangulation (Laist 1987; Derraik 2002; Sheavly and Register 2007). Entanglement can also affect an animal's mobility, which reduces the ability to eat, migrate, or escape possible predator species (Gregory and Andrade 2003). Death due to failed predator avoidance, skin lesions and ulcerating wounds, and debilitation due to interruption of feeding activities are all biologically harmful effects of entanglement (Gregory and Andrade 2003).

Younger, inexperienced, or curious animals such as seals are often attracted to floating debris and will roll and play in it (Mattlin and Cawthorn 1986). As they approach the plastic debris, seal pups will often poke their heads through loops and holes. The lie of their hair allows the plastic to easily slip onto their necks, but at the same time prevents the plastic loops from slipping off (Mattlin and Cawthorn 1986). As the seal pup grows, the plastic strapping becomes increasingly tighter, eventually severing the seal's arteries or strangling it. Due to its physical properties, the resilient nature of the plastic

ring allows for this type of scenario to repeat itself once the animal dies and decomposes (Mattlin and Cawthorn 1986).

Derelict or abandoned fishing gear may be deadly to marine species for years after being lost. The process known as *ghost fishing* results when discarded or abandoned fishing nets continue to catch and kill marine animals (Laist 1987; Moore 2008). It is estimated that 10% of all static fishing gear is lost, which results in a 10% loss of the target fish population (FAO 1991). Lost or discarded nets are, at least in part, linked to the decrease in population of marine animals such as the northern sea lion, Hawaiian monk seal, and northern fur seal (Derraik 2002). Mattlin and Cawthorn (1986) found the population of fur seals in the Bering Sea, west of Alaska, that were entangled in plastic bands rose from 0 to 38% in just 4 years (1969-1973). As of 1976, the population was declining at a rate of 4-6% per annum. Lost or abandoned nets have the ability to continually kill large quantities of small fish but have also been identified on the mouths and tails of much larger animals such as whales when they surface during feeding (Laist 1987; Weiskopf 1988; Moore 2008). However, ghost net fishing not only affects surface and shallow waters. Trawl gear during the past 20 years has been deployed across sea floor surfaces at depths between 500 and 2000m. This netting has the potential to cause severe damage to deep water coral reefs, and with little to no ultraviolet radiation may continue to ghost fish indefinitely (Watling and Norse 1998). A terrestrial analogy for the potential effects of the disturbance to seabed environments would be that of forest clear cutting (Watling and Norse 1998).

2.2 Ingestion

Few plastic objects are intended to resemble natural food to marine organisms with the possible exception of fishing lures. However, with the variations in colour, size and shape, plastic fragments can mimic the appearance of naturally occurring food to many marine animals (Carpenter et al. 1972; Moser and Lee 1992; Shaw and Day 1994; Eriksson and Burton 2003). Plastic pellets resemble fish eggs whereas plastic bags submersed in the ocean may look like jellyfish to a feeding turtle (Gregory 2009). Research conducted by Moser and Lee (1992) found that seabirds often mistake certain plastic shapes and colours as potential prey species. Marine animals mistaking plastic fragments for food swallow the items, which then become lodged in their throats or digestive tracts (Azzarello and Van Vleet 1987). Debris that remains in the stomach may give a false sense of satiation resulting in starvation (Derraik 2002; Gregory and Andrady 2003; Sheavly and Register 2007; Gregory 2009). Ingested plastic particles in seabirds reduce meal size by limiting the ability of the stomach to store food; the result is a limited ability to lay down fat deposits which ultimately reduces fitness (Ryan 1988). Other physiological effects of plastic ingestion in sea birds include blockage of gastric enzyme secretion, lowered steroid hormone levels, delayed ovulation, and reproductive failure (Azzarello and Van Vleet 1987). Small fish that ingest plastic fragments can also experience internal injury or possibly death due to blockages of the intestinal tract (Carpenter et al. 1972; Ryan 1988; Azzarello and Van Vleet 1987; Zitko and Hanlon 1991).

Ingestion of marine plastic debris affects at least 267 species worldwide including sea turtles, seabirds and marine mammal species (Laist 1997). Literature focusing on the effects of plastic ingestion on marine species is abundant and the issues researched are on a global scale (Gregory 2009). Moser and Lee (1992) sampled over 1000 birds off the coast of North Carolina, U.S.A. and found plastic particles in the guts of 55% of species sampled. Plastic spherules were found in 8 of 14 fish species examined off the coast of New England, U.S.A. with some species representing as much as 33% of the contaminated individuals (Carpenter et al. 1972). Baird and Hooker (2000) documented at least 26 species of crustaceans known to ingest plastic particles and there is evidence that the survival of sea turtles is being hindered by plastic debris (Duguy et al. 1998). Turtles often mistake polyethylene bags submerged in ocean currents as prey (Mattlin and Cawthorn 1986; Bugoni et al. 2001), with young sea turtles being most susceptible (Carr 1987). Balazs (1985) reported 79 cases in which various types of plastic debris were found in the guts of turtles. A more specific case by O'Hara et al. (1988) found one turtle in coastal waters off New York that had ingested 540m of fishing line. Kenyon and Kridler (1969) examined 100 albatross carcasses collected from the beaches and reefs of Hawaii. Ninety-one birds contained non-food items, 30% of which was plastic debris. Albatross rarely ingest food or other items from the shore, therefore it was concluded that ingestion of plastic debris by albatross occurred at sea and was passed by parents to their young with regurgitated food (Kenyon and Kridler 1969). Despite the abundance of published reports, the actual number of animals affected by plastic debris may be underestimated, as many are likely eaten by predator species or simply go undiscovered in the open ocean (Wolf 1987).

2.3 Invasive Species, Ecotoxicology and Seabed Debris

2.3.1 Invasive Species

The presence of industrial pellets on beaches free from the influence of petrochemical facilities and pellet processing plants is an indication of long-range marine transport (Costa et al. 2010). Like all natural or artificial floating debris, plastic can provide a mechanism for encrusting and fouling organisms to disperse over great distances (Winston et al. 1997). Logs, pumice and other flotsam have traversed the open ocean for millennia (Gregory 2009), and the introduction of hard plastic debris to the marine ecosystem may provide an appealing and alternative substrate for some opportunistic colonizers (Gregory and Andrade 2003; Gregory 2009). It is estimated that if biotic mixing occurs, global marine species diversity may decrease by up to 58% (McKinney 1998). Barnes (2002) estimates the propagation of fauna in the sea has doubled in the tropics, and more than tripled at high latitudes ($>50^\circ$), due to the input of anthropogenic debris. The hard surfaces of plastics provide an ideal substrate for opportunistic colonizers. Pelagic plastics are most commonly colonized by bivalve molluscs, however, other encrusting organisms include bacteria, diatoms, algae and barnacles (Carpenter et al. 1972; Derraik 2002; Gregrory and Andrade 2003; Gregory 2009, Widmer and Hennemann 2009). Plastic substrates may also contain multispecies habitats composed of organisms that would normally inhabit different ecological niches (Winston et al. 1997). Drifting plastic debris may also increase the range of certain marine organisms or possibly introduce species to new environments which they had

previously not inhabited (Winston 1982). Sensitive or at-risk littoral, intertidal and shoreline ecosystems could be negatively affected by the arrival of unwanted and aggressive alien species with potentially damaging environmental consequences (Winston et al. 1997; Gregory 1991, 1999, 2009). The absence of biological organisms on plastic debris may be an indication that the particles were not present in the marine environment long enough for fouling to occur. Instead, these items probably have a more local, land-based origin (beachgoers, storm-water drainage), than more heavily encrusted debris (Widmer and Hennemann 2009).

2.3.2 Ecotoxicology

Several studies have reported the presence of polychlorinated biphenyls (PCBs) in plastic samples collected from the northwestern Atlantic and South Pacific Oceans (Carpenter and Smith 1972; Carpenter et al. 1972; Gregory 1978). PCBs used as plasticizing additives during the manufacturing process were considered to be the source, although adsorption and concentration from ambient seawater was also suggested (Carpenter and Smith 1972; Gregory 1978). Over the last decade, adsorption has been experimentally confirmed and research indicates that plastic pellets may be both a source and transport medium for toxic chemicals in the marine environment (Mato et al. 2001; Rios et al. 2007). Ingestion of plastic fragments by seabirds and fish may be the source of bioaccumulation of heavy metals, PCBs, dichlorodiphenyltrichloroethane (DDT), and other toxins (Ryan 1988). Absorption and transfer of these chemicals by filter feeding

organisms and invertebrates may lead to reproductive disorders, disease, altered hormone levels, or death at higher trophic levels (Ryan 1988; Ryan et al. 1988; Gregory 1996; Lee et al. 2001).

2.3.3 Seabed Debris

Human factors, geomorphology and hydrodynamics all influence the geographical distribution of plastic debris (Barnes et al. 2009). Abundance and distribution is evident when assessing plastic debris found at the surface in the open ocean and on beach strandlines. However, extensive research into the effects of plastic debris on the seabed has been restricted to continental shelves, as access to the seabed has been limited by sampling challenges and high costs (Barnes et al. 2009). Therefore, the effects of materials resistant to gas and water exchange partially covering the seabed have not been fully investigated (Moore 2008). It is widely accepted, however, that the sea floor is considered the largest sink for marine debris (e.g. Williams et al. 1993; Goldberg 1997).

Rapid and heavy fouling by bacteria, algae, animals and accumulated sediment can weigh down floating plastic causing debris to sink to the seabed. There may be periodic episodes in which grazing organisms ‘clean’ fouled surfaces, thus resulting in alternating resurfacing and submergence episodes until permanent seabed settlement occurs (Ye and Andrade 1991). Plastics comprise the largest portion of debris found on the sea floor in the same way it dominates floating litter and beach debris (Ryan et al.

2009). Assessments of plastic on the sea floor have shown that greater than 50% of debris is comprised of plastics (Barnes et al. 2009). Similar to stranded debris, sea floor plastic debris accumulation is dependant on local sources, topography and location (Galgani et al. 2000; Moore and Allen 2000; Barnes et al. 2009). However, patterns in deposition in shallow subtidal areas can be significantly different than that of the adjacent strandlines (Barnes et al. 2009). For example, Oigman-Pszczol and Creed (2007) found the nearshore Brazilian seabed contained a much greater proportion of debris relative to the shore.

The overall effects of plastic debris on the ocean floor are still unclear. Notwithstanding, Goldberg (1997) suggested that anoxia and hypoxia induced by inhibition of gas exchange between pore and sea water may be a result of the blanket effect caused by large deposits of plastic debris on the seabed. Furthermore, pelagic plastic weighed down by sediment may accumulate on the seabed leading to a creation of artificial hardgrounds (e.g. Harms 1990). Polymers in the marine environment degrade through photo- and thermal- oxidation when exposed to heat, UV radiation and mechanical abrasion (e.g. Gregory and Andrade 2003; Shah et al. 2008; Sing and Sharma 2008; Corcoran et al. 2009; Cooper and Corcoran 2010). Such properties are significantly decreased or non-existent in the deep ocean, and therefore, plastic debris in these environments may persist much longer than the estimated hundreds to thousands of years on the ocean surface or on land (Andrade 2000; Barnes et al. 2009).

CHAPTER 3

COMPOSITION AND DEGRADATION OF POLYMERS

3.1 Polymer Composition

Polyethylene (PE) and Polypropylene (PP), expressed as C_nH_{2n} , have a wide range of applications and thus have become the two most prominently used polymer types (Arutchelvi et al. 2008). PE is a linear molecule produced in a variety of densities ranging from 0.91 to 0.97 g/cm³. Density differences among PE are dependant on where branching on the carbon backbone occurs. Low density PE has low packing of the polymer chains due the randomness of the branching, whereas high density PE has minimal branching and is thus more linear, which leads to a higher packing density (Figure 3.1) (Arutchelvi et al. 2008). Polypropylene is derived from the monomer, propylene, which is obtained as a petrochemical byproduct and was first synthesized by Ziegler and Natta in 1956. The various orientation of methyl groups in PP results in three possible geometrical orientations, isotactic, syndiotactic and atactic (Figure 3.2) (Rabek 1996; Arutchelvi et al. 2008). Isotactic structures have all methyl groups (CH_3-) on one side of the carbon chain, whereas methyl groups on syndiotactic structures alternate from one side of the carbon chain to the other. Methyl groups on atactic structures occur in a random order on either side of the carbon chain (Arutchelvi et al. 2008). Most commercial PP produced has an isotactic configuration due to the physical properties associated with its regular structure. The highly crystalline nature of isotactic PP provides

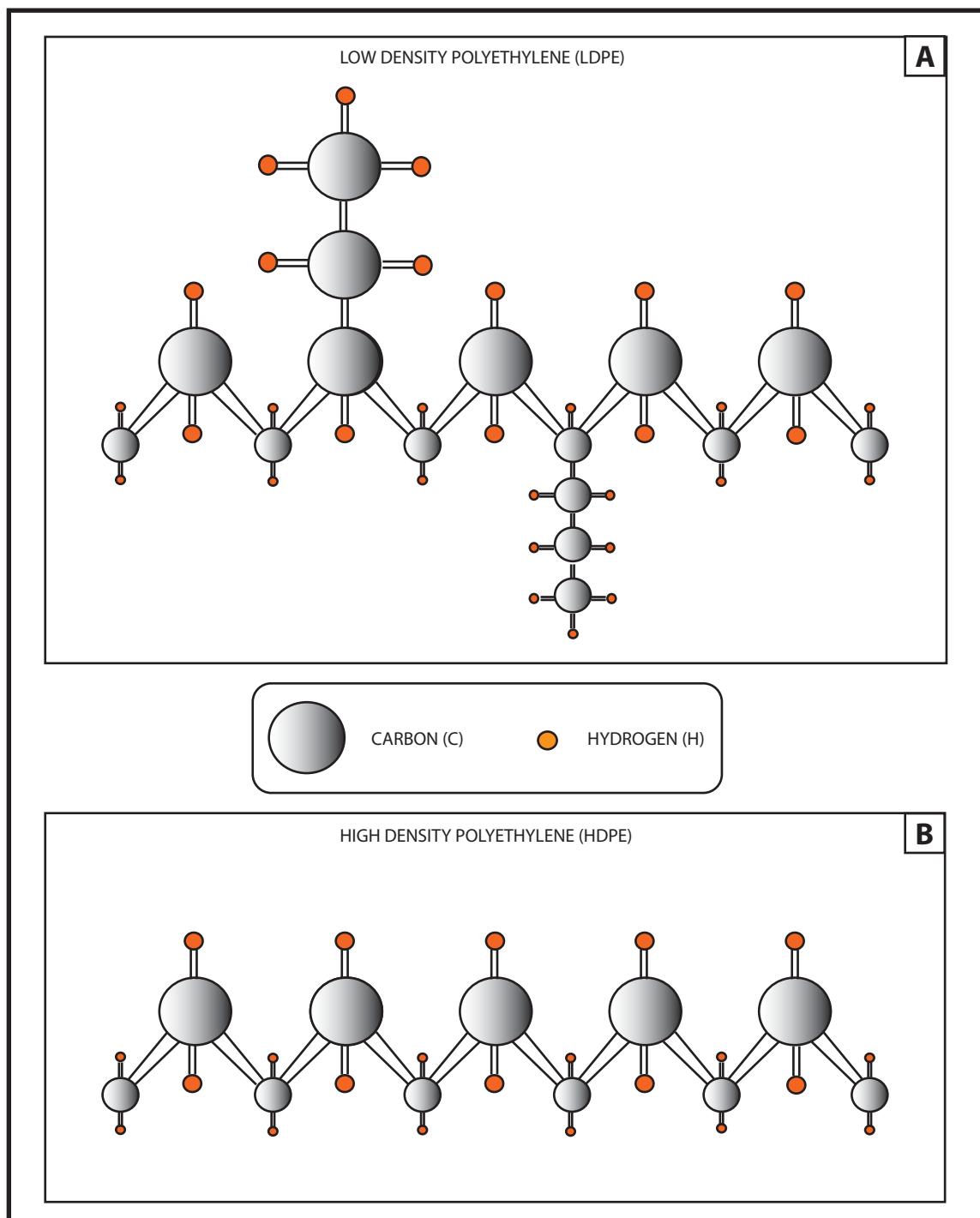


Figure 3.1 Schematic diagram showing stereochemistry differences of, A- low density polyethylene (LDPE) and B- high density polyethylene (HDPE). The more linear alignment of carbon atoms in HDPE allows for a higher packing density.

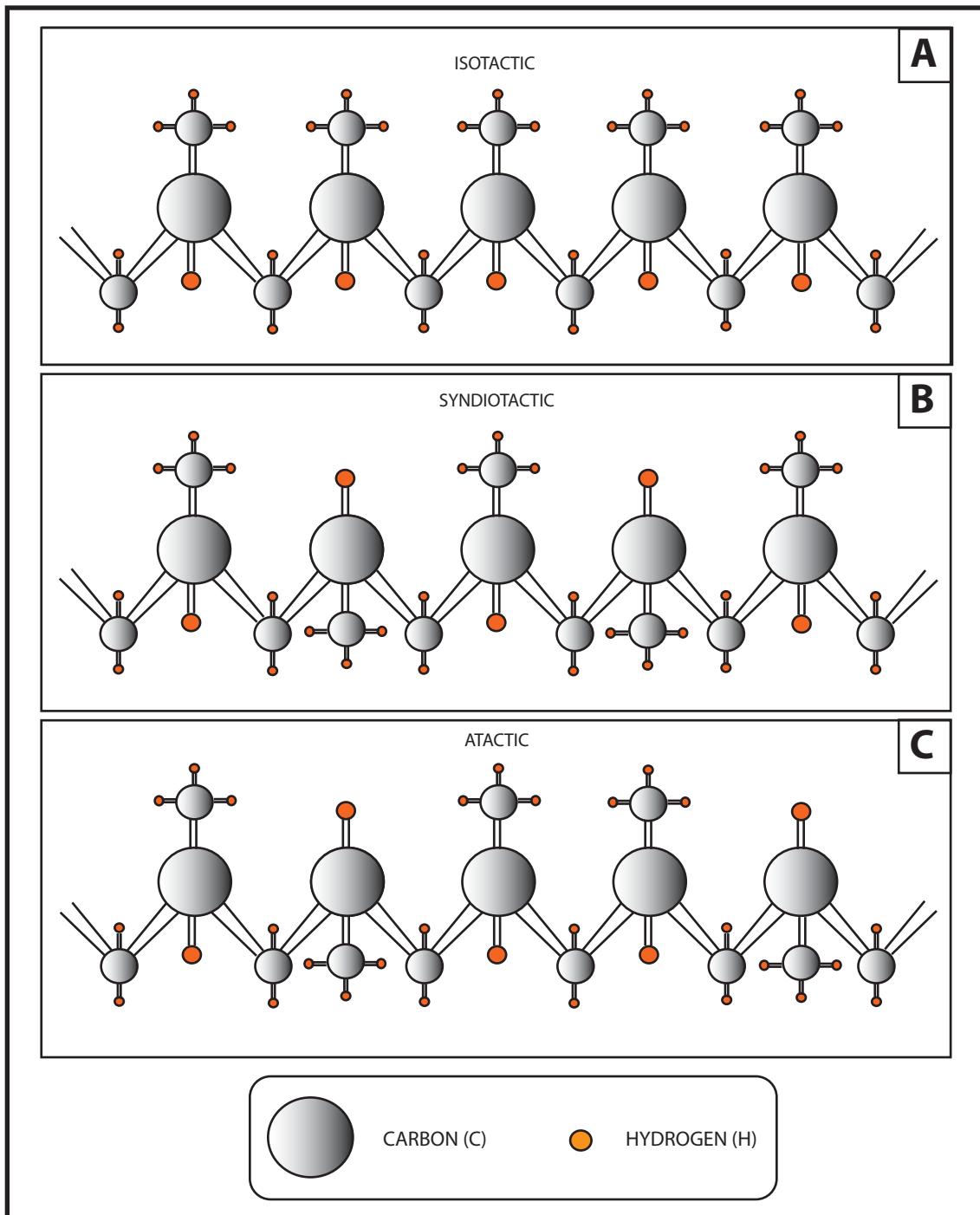


Figure 3.2 Schematic diagram showing the stereochemistry of polypropylene. The location of methyl groups relative to the carbon backbone result in three possible geometrical orientations A- isotactic, B- syndiotactic, and C- atactic.

the polymer with stiffness, hardness and tensile strength. PP, which is chemically resistant, moisture resistant, and has a melting point of 208°C, is stable to heat and light (Nishimoto and Kagiya 1992).

The composition of polymers is determined by utilizing FTIR. Spectra from polyethylene blanks display characteristic peaks around 2916, 2849, 1471, and 718 cm^{-1} wavenumber regions (Figure 3.3A). Polypropylene blanks produce five distinct peaks at wavenumbers 2952, 2919, 2870, 2839 and 1652 cm^{-1} as well as numerous peaks in the lower wavenumbers between 631 and 1458 cm^{-1} on the IR spectra (Figure 3.3B).

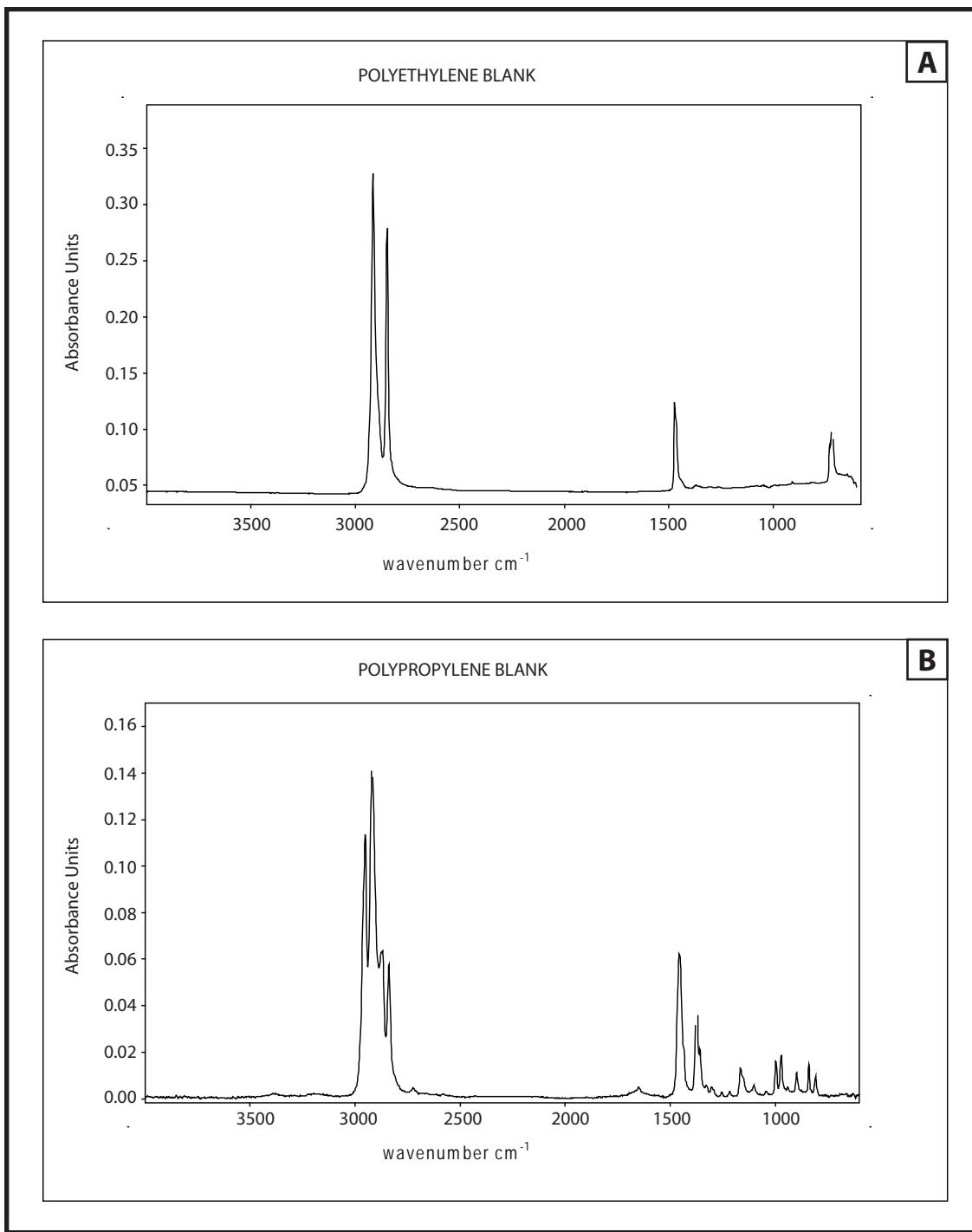


Figure 3.3 Fourier Transform Infrared Spectroscopy (FTIR) spectra indicating characteristic absorption peaks of pure untreated A- polyethylene and, B- polypropylene.

3.2 Polymer Degradation

Polymer degradation can be categorized as any physical or chemical changes resulting from environmental factors, including light, heat, moisture, chemical conditions and biological activity. This includes processes which induce changes to polymer functionality or deterioration through chemical, biological or physical reactions resulting in bond scission and chemical transformations (Shah et al. 2008). An effective way of distinguishing between the various modes of polymer degradation is to subdivide them by modes of initiation (Hamid et al. 1992). The degradation processes that polymers are subjected to in everyday life include:

1. Thermal/thermo-oxidative: Refers to the exposure of the polymer to elevated temperatures and the influence of heat, either during processing or use. Chemical changes are initiated without the involvement of other compounds. Thermo-oxidative degradation differs from thermal degradation in that random scission occurs in the polymer backbone rather than randomly and/or at the chain end.
2. Mechanical: Occurs due to the application of physical forces or when subjected to shear.
3. Ultrasonic: Polymer chains may vibrate and split when exposed to the application of sound at certain frequencies.

4. Hydrolytic: When moist or acidic conditions are present in the environment, chain scission may occur as a result of hydrolysis of the main chain. Hydrolysis occurs in polymers with functional groups that are sensitive to the effects of water.
5. Chemical: Refers to corrosive chemicals, gases or liquids. Ozone, atmospheric pollutants, and acids like nitric, sulfuric, and hydrochloric will attack and degrade most polymers through chain scission and oxidation.
6. Biological: Specific to only a few polymer types, this is a process where bacteria, fungi, yeasts, and enzymes degrade a polymer through an attack of certain functional groups such as some stabilizers and plasticizers.
7. Photooxidative/Radiation: The absorption of radiation by polymers, or their impurities, due to exposure to sunlight or high energy radiation. The highest energy UV waves of the solar spectrum can break the chemical bonds in polymers resulting in photodegradation (Allen and Edge 1992; Hamid et al. 1992; Kulshreshtha 1992; Pielichowski and Njuguna 2005).

Of the seven processes described above, the most important degradation routes with regards to plastic debris, and the most widely researched, are thermal/thermo-oxidative, biological, and photooxidative (Allen and Edge 1992; Shah et al. 2008; Singh and Sharma 2008). Each degradation route has specific requirements in order for degradation to occur and propagate (Table 3.1).

Table 3.1 Possible degradation routes of synthetic polymers (modified from Shah et al. 2008)

Requirements	Photo-degradation	Thermal/Thermo-oxidative Degradation	Biodegradation
Active Agent	UV-light/high energy radiation	Heat and/or Oxygen	Microbial Agents
Heat Requirement	None	Above ambient temperature	None
Degradation Rate	Slow initiation, fast propagation	Fast	Moderate

Thermal and photo-degradation are similar and are often classified as oxidative degradation with the main difference being the initial sequence of steps leading to auto-oxidation cycle (heat/UV radiation) (Singh and Sharma 2008). Biological degradation is the process by which living organisms break down organic structures (Shah et al. 2008).

Rates of degradation of polymers at sea are much slower than those on land. The reduction of degradation processes occurring at sea may be attributed to the following:

1. Reduced heat build-up: A significant amount of UV radiation impinging on the plastic is absorbed as heat. The plastic may maintain a temperature as much as 30° C higher than that of the surrounding air depending on the nature of the plastic, velocity of air around the plastic and the temperature difference between the plastic and its surroundings. However, at sea, bulk temperature increases do not occur, which significantly slows rates of degradation.
2. Fouling of samples in sea water: Plastics floating at sea undergo significant fouling, which results in coverage of the material by a biofilm. The biofilm shields the plastic from exposure to sunlight and yields a slower rate of degradation relative to particles on land. In addition, the nonuniformity of surface fouling may lead to uneven degradation (Rabek 1996; Gregory and Andrade 2003).

3.3 Chemical Degradation

Chemical degradation of polymers is a process that affects the performance of all plastic materials used in our daily lives and is a field which has been widely researched (Kulshreshtha, 1992). Changes that occur in polymers during degradation are manifested differently depending on which degradation processes are involved. Chemical degradation results in changes to the chemical structure of the polymer including bond scissions and the formation of functional groups (Allen and Edge 1992; Singh and Sharma 2008). The most relevant chemical degradation processes to plastic beach debris are thermal and photooxidative degradation. Biological degradation is another important degradation process for plastics and is closely tied to thermal and photo degradative processes, therefore these processes are described in more detail below.

3.3.1 Thermal Degradation

Thermal degradation of polymers refers to chemical changes affecting polymers exposed to elevated temperatures without the simultaneous involvement of any other compound (Pielichowski and Njuguna 2005). All polymers can be degraded chemically by heat; however polyolefins such as PE and PP are known to be sensitive to thermal oxidation because the high temperatures used during manufacturing generate impurities in the material (Kulshreshtha 1992; Singh and Sharma 2008). The two different mechanisms of polymer degradation are depolymerisation and statistical fragmentation of

chains. When heated to the extent of bond rupture, polymers will follow three major pathways: side-group elimination, random scission and depolymerisation. Polyolefins such as PE and PP do not depolymerise (Kulshreshtha 1992; Pielichowski and Njuguna 2005) and therefore only random scission and side group elimination will be discussed further.

1. Random Scission: Results from the formation of free radicals at some point along the backbone of the polymer. This produces small repeating series of oligomers of differing chain length (by number of carbons). When free radicals form along PE, chain scission occurs, resulting in fragmentation which produces a molecule with one unsaturated end and the other with a terminal free radical. Polymers such as PE do not depolymerise, therefore thermal stress generally results in fragments, which break into smaller fragments.
2. Side Group Elimination: Generally this takes place in a two stage process. The first step involves stripping or elimination of side groups attached to the backbone of the polymer, which leaves an unsaturated chain. An unstable polyene macromolecule is formed which undergoes further reactions such as scission into smaller fragments. PE and PP do not produce any quantitative amount of monomers during thermal degradation (Kulshreshtha 1992, Pielichowski and Njuguna 2005, Singh and Sharma 2008).

3.3.2 Photo-oxidative Degradation

Photo-oxidative degradation is the process by which the molecular weight of polymers is reduced resulting in degradation and embrittlement through exposure to sunlight in the presence of air (Kulshreshtha 1992; Singh and Sharma 2008). This is considered one of the most important sources of damage exerted on polymers at ambient conditions (Gijsman et al. 1999; Singh and Sharma 2008). There are two mechanisms for which UV radiation can be absorbed 1) through impurity chromophores and 2) through direct absorption by units or groups which form part of the chemical constitution of the polymer. Polymers of the first type include polyolefins such as PE and PP (Allen and Edge 1992). Most synthetic polymers are susceptible to photo-oxidative degradation, and occurs where chromophores, which absorb wavelengths of the solar spectrum on Earth (>290nm), are present in the polymer (Gijsman et al. 1999). Chromophores such as peroxide, hydro peroxide, and carbonyl groups, catalyst residues and polynuclear aromatic impurities are byproducts of the commercial production of polymers which are required to control the polymerization reaction processes (Kulshreshtha 1992; Gijsman et al. 1999). Absorption of radiation results from the presence of chromophores which are of two different types, 1) Type A: Internal or end-chain chromophores which are a result of the polymerization process, and/or the products of thermal and/or photo-oxidation, and 2) Type B: Chromophores which form part of the molecular structure of the polymer (Figure 3.4) (Allen and Edge 1992; Rabek 1996). When absorbed, UV radiation in the 290-400 nm range has sufficient energy to cleave most chemical bonds resulting in degradation of the polymer (Gijsman et al. 1999; Kulshreshtha 1992).

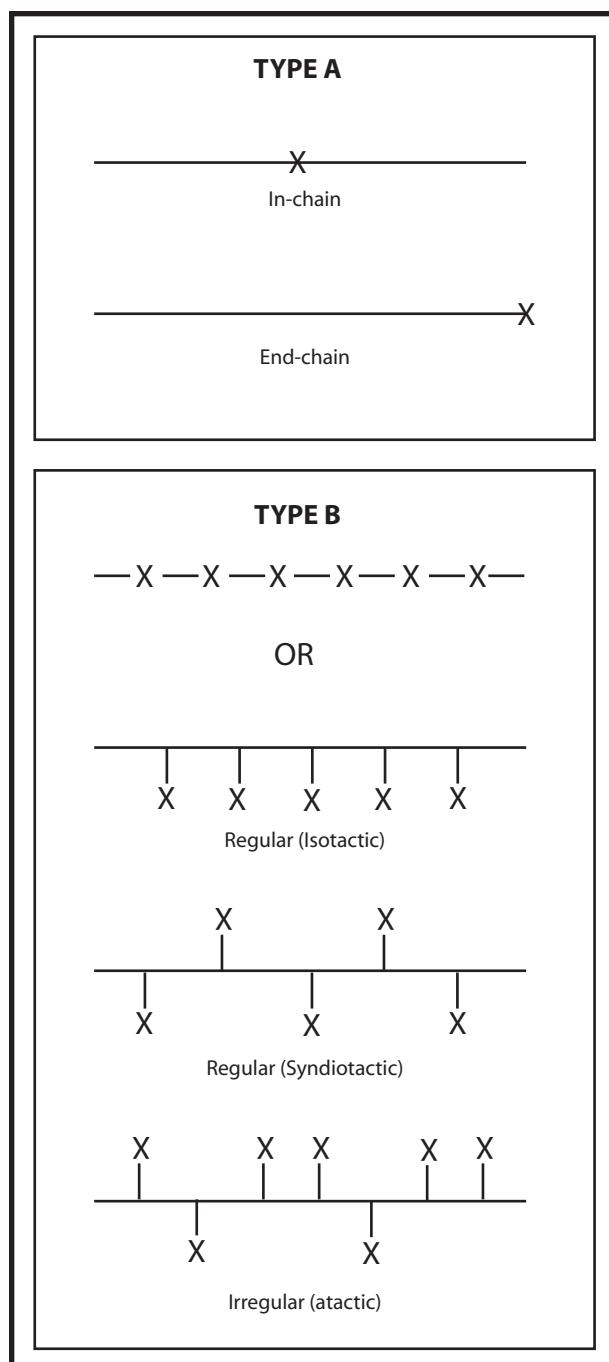


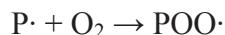
Figure 3.4 Schematic diagram depicting the possible orientations of chromophores. Type A- internal or end-chain, Type B-forming part of the molecular structure in various orientations. (modified from Allen and Edge 1992).

Changes in physical and optical properties of plastics are a result of photodegradation and lead to colour changes (fading, yellowing), loss of mechanical properties, embrittlement and changes in molecular weight (Kulshreshtha 1992; Singh and Sharma 2008). PE and PP are considered homochain polymers in that they only contain C-C and C-H bonds. Carbonyl and hydro peroxide groups are the most important species in the photooxidation of these polymers (Allen and Edge 1992).

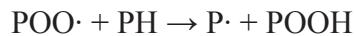
- Carbonyl groups: Carbonyl chromophores are considered to play a more important role in the photooxidation of PE than PP and the opposite is true of hydro peroxides. Two primary photochemical reactions occur when carbonyl groups are present on the molecular backbone of the polymer as ketones. They include Norrish type I, in which excited triplet states may cleave the polymer's molecular backbone and form radical pairs, and Norrish Type II, in which pairs of saturated and unsaturated chain ends form by hydrogen transfer.
- Hydro peroxide groups: Considered to be the most important and most common impurity chromophore in polymers containing carbon, hydro peroxides are incorporated during polymerization and/or processing. These groups are the major photo initiators in PP because they can be quickly produced through an intramolecular hydrogen abstraction process (Allen and Edge 1992; Singh and Sharma 2008).

Photo-oxidative degradation of polymers occurs by free radical mechanisms and includes processes such as photo-oxidation, chain scission and crosslinking. Photo-oxidation is the result of a radical-based auto-oxidative process and includes four stages: initiation, chain propagation, chain branching and termination (Figure 3.5) (Rabek 1996; Gijsman et al. 1999; Pielichowski and Njuguna 2005; Azuma et al. 2009).

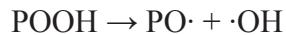
- Initiation: Results from the photo dissociation of chemical bonds in the main polymer chain through absorption of UV light.
- Propagation: All carbon backbone polymers have common propagating reactions, the key reaction is the formation of the polymer peroxy radicals ($\text{POO}\cdot$) by the reaction of polymer alkyl radicals ($\text{P}\cdot$) with oxygen.



The next propagation reaction step is the generation of a new polymer alkyl radical ($\text{P}\cdot$) and polymer hydro peroxide (POOH) through the extraction of a hydrogen atom by the polymer peroxy radical ($\text{POO}\cdot$), which occurs principally from the tertiary carbon atoms.



- Chain branching: Results in the formation of very reactive polymer oxy radicals. ($\text{PO}\cdot$) and hydroxyl radicals ($\text{HO}\cdot$).



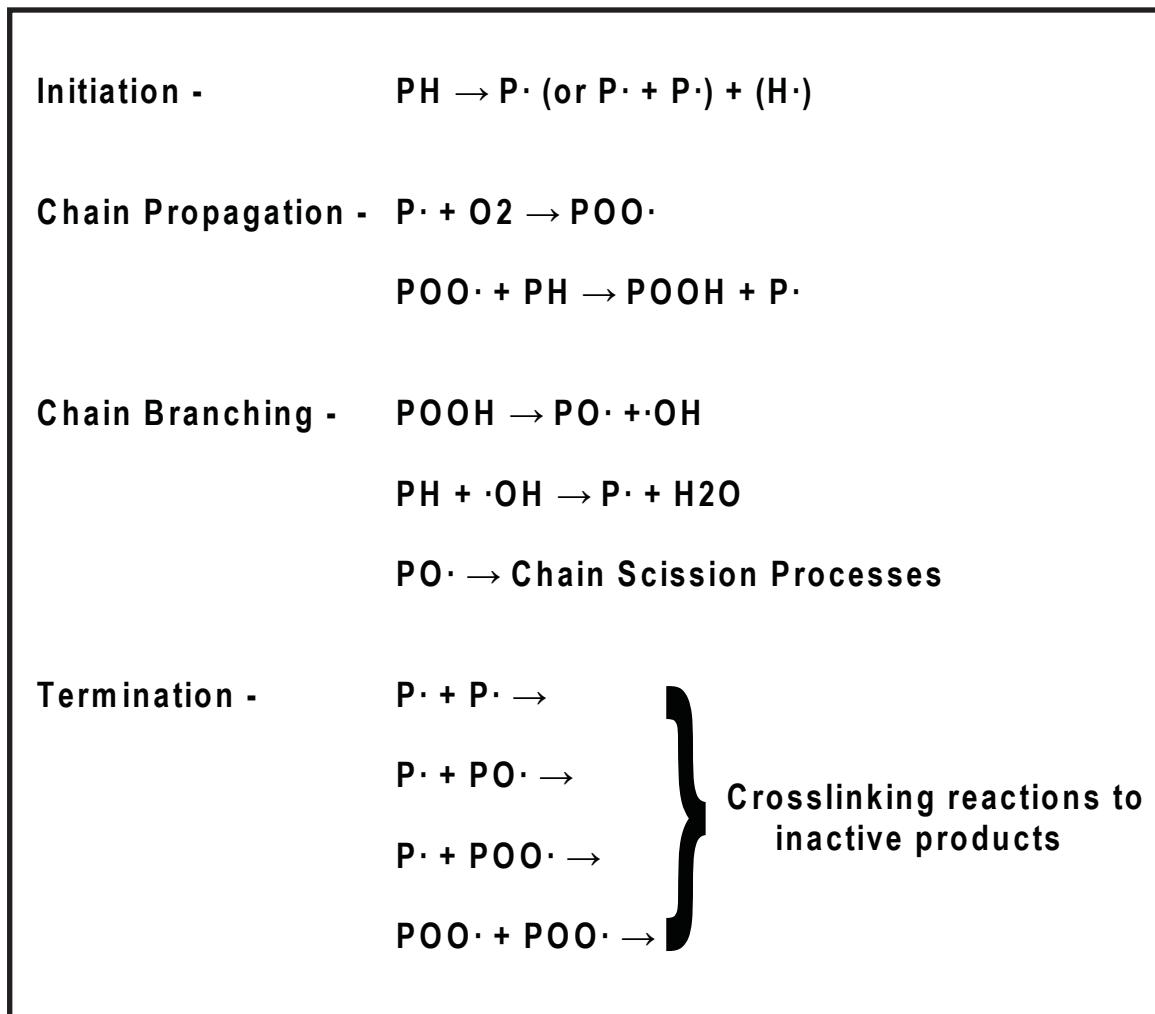
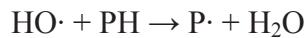
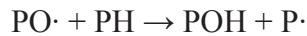
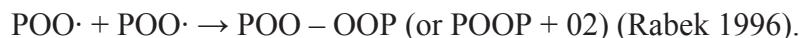
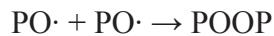
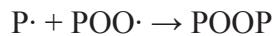
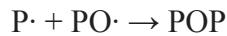
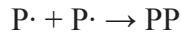


Figure 3.5 Stages of photo-oxidation processes including initiation, propagation, branching and termination.

A hydrogen atom is extracted from the same or nearby polymer (PH) molecule by polymer hydroxyl radicals ($\text{PO}\cdot$) and hydroxyl radicals ($\text{HO}\cdot$).



- Termination: Termination reactions of polymer radicals occur by bimolecular recombination. In the presence of high oxygen pressure (ambient conditions), the termination reaction occurs almost exclusively by reaction. Termination reactions occur naturally by combining free radicals or can be facilitated through the use of stabilizers. If polymer peroxy radicals are in neighbouring positions they can recombine to form stable molecules, other radicals may combine to produce a crosslinked, branched or disproportionate product resulting in a brittle polymer network.



Main chain scission involves the breaking of the C-C molecular backbone of the polymer and may occur from either primary photophysical processes (i.e. direct photo dissociation of a bond in the backbone) or as secondary processes (β -scission processes). The result is a decrease in the average molecular weight (Figure 3.6A). It is generally accepted that photodegradation of most polymers occurs through decomposition of alkoxy radicals (β -scission processes) (Rabek 1996). Crosslinking is the formation of new intramolecular bonds resulting in the binding of macromolecules (Figure 3.6B). Crosslinking is almost always accompanied by scission of the main chain (to some extent) during the photodegradation process (Rabek 1996).

3.3.2.1 Photodegradation of polymers under marine exposure conditions

If at sea long enough, all polymeric materials exposed to marine conditions will invariably undergo some degree of fouling. Microbial biofilms form rapidly on the polymer surface as a result of fouling, and over time the biofilm becomes opaque, limiting the amount of sunlight available to the plastic for photodegradation (Rabek 1996; Lobelle and Cunliffe 2011). Colonization of the plastic surface by macrofoulants such as bryozoans and barnacles is indicative of advanced stages of fouling (Figure 3.7). Plastics weighed down by macrofoulants, and the debris they entrap, may partially submerge the material over time resulting in a slower rate of photodegradation as the ultraviolet portion of sunlight is attenuated on passage through seawater (Rabek 1996). Most plastics are positively buoyant; however, the buoyancy of plastic debris can be controlled

significantly by biofouling which may cause debris to become heavier resulting in negative buoyancy (Lobelle and Cunliffe 2011). In addition, the biofilm may block damaging UV radiation and may reduce or prevent photodegradation from occurring (Figure 3.8).

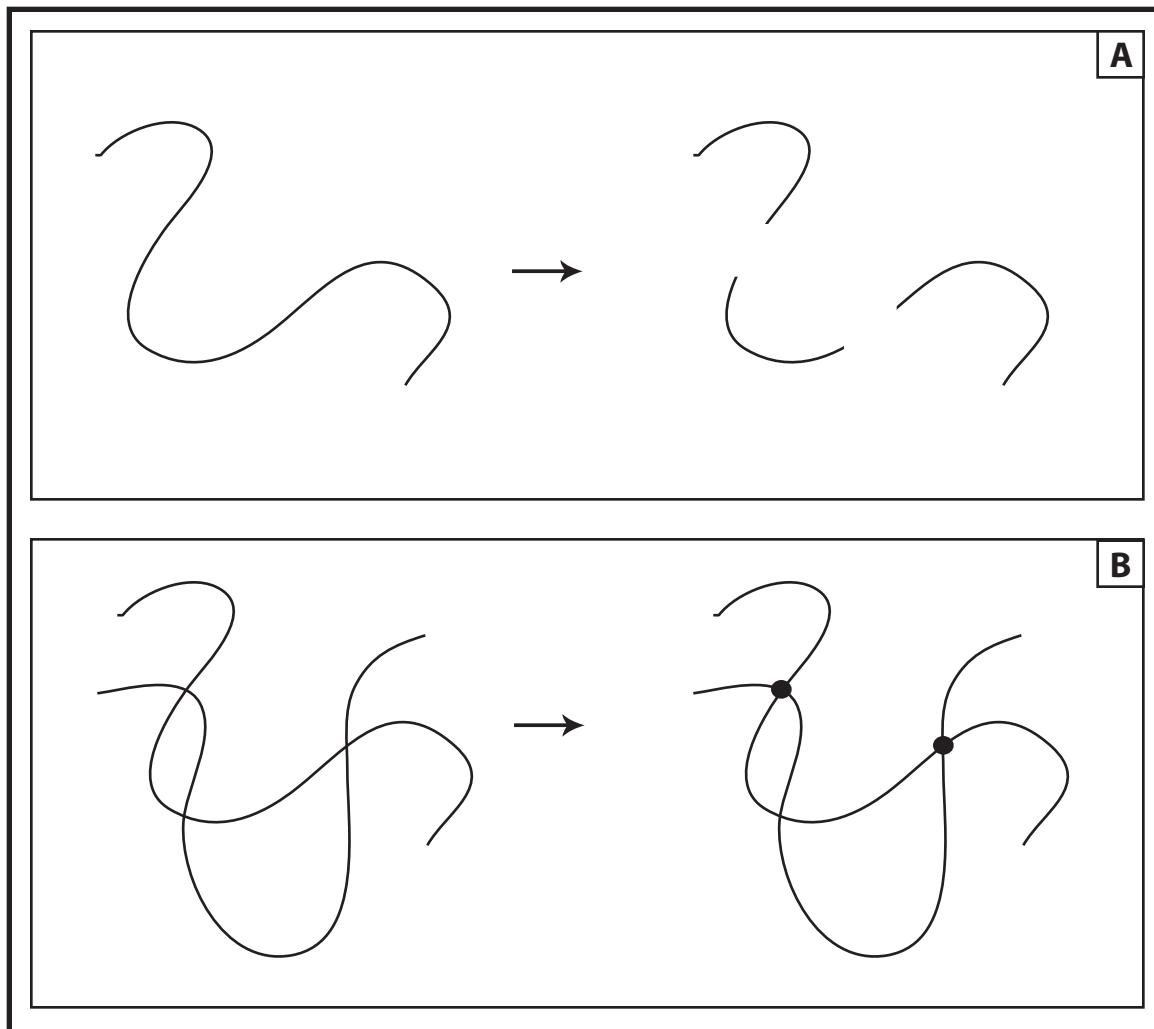


Figure 3.6 Schematic representation of, A- main chain scission in which the carbon backbone of the structure is broken, and B- crosslinking, which is the formation of new intramolecular bonds. These processes result in lower molecular weight and a brittle polymer network (modified from Rabek 1996).

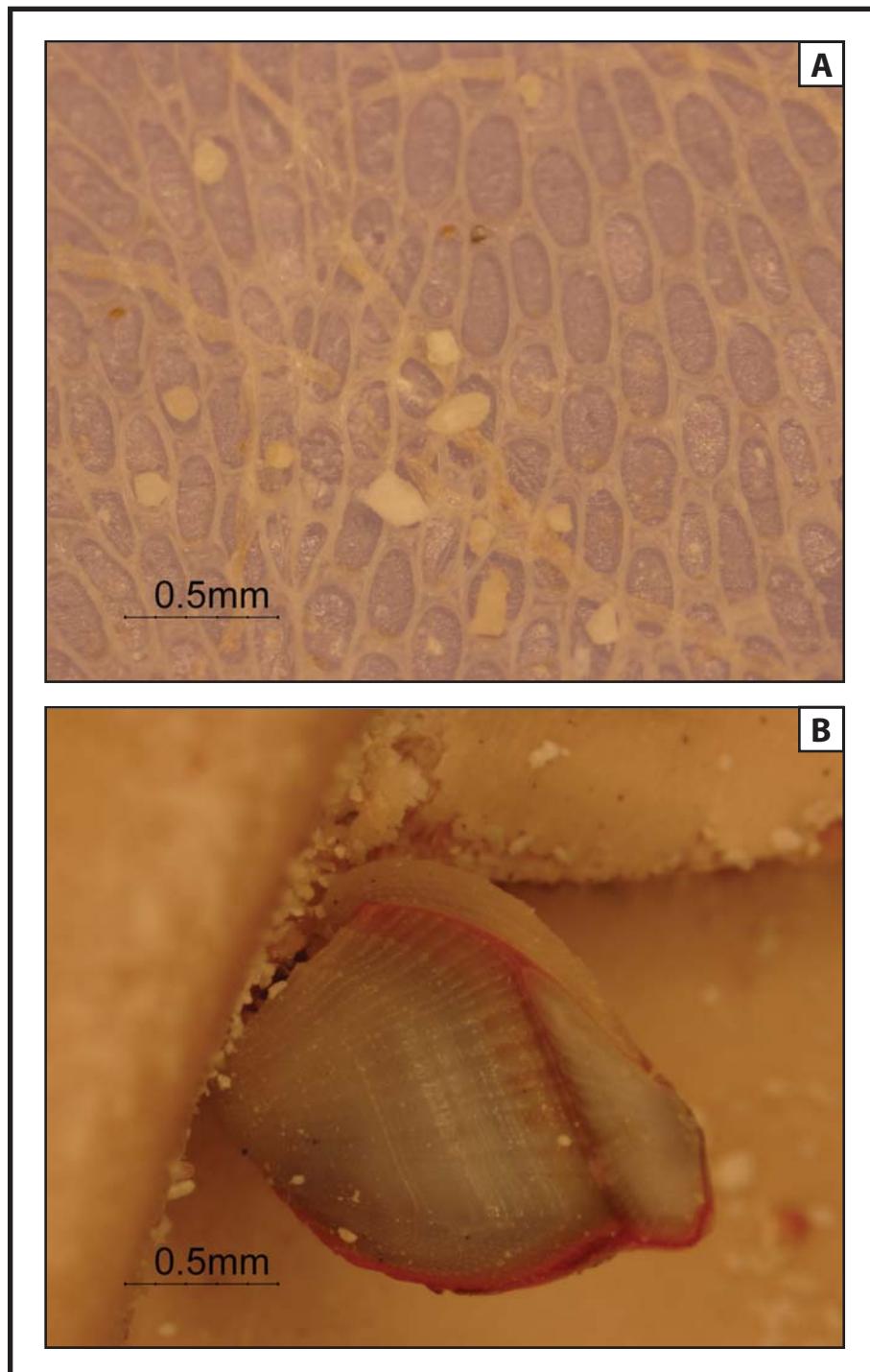


Figure 3.7 Digital photographs of A- bryozoan and, B- barnacle growth on plastic beach debris indicating advanced levels of biofouling.

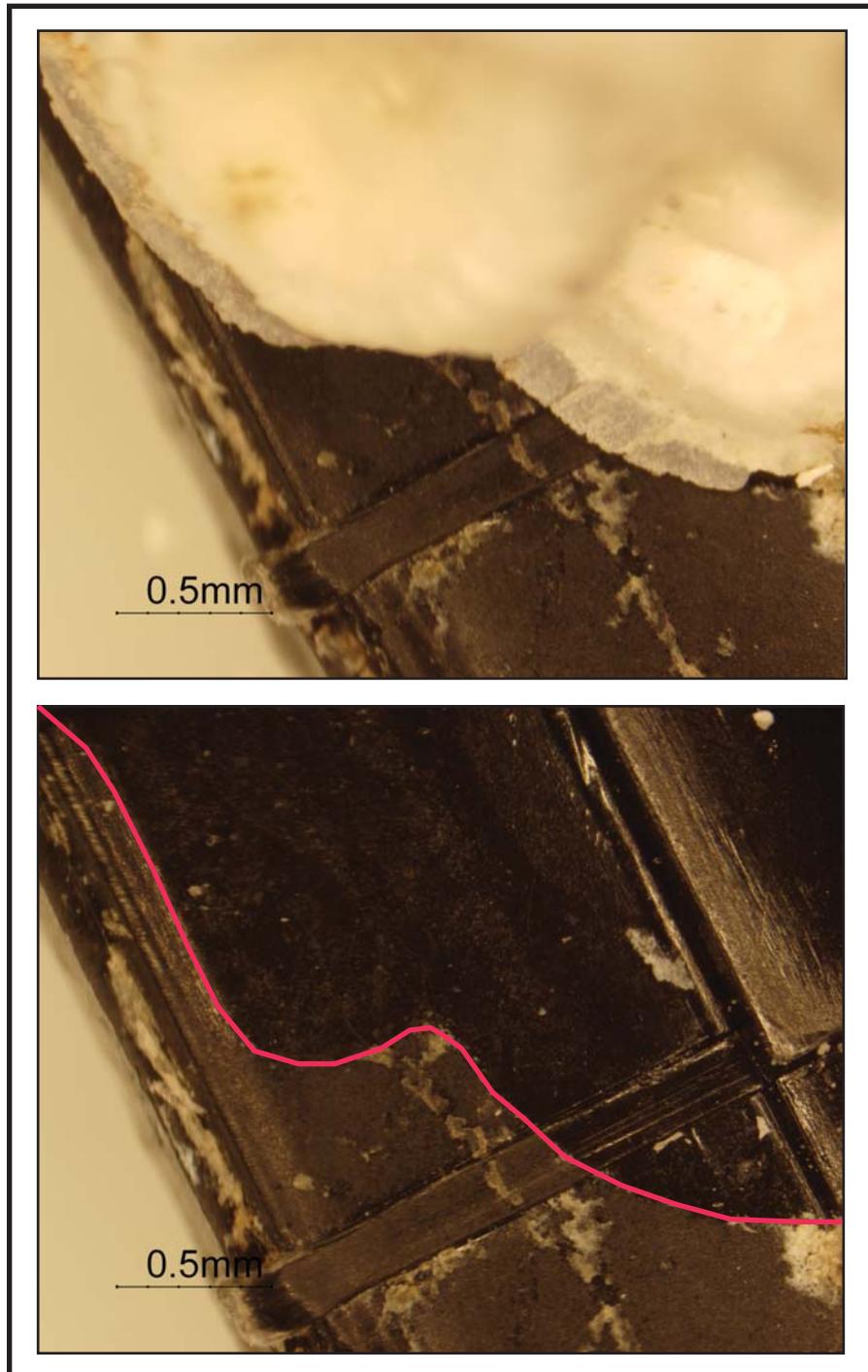


Figure 3.8 Digital photographs displaying how biofilms may protect polymers against the effects of UV radiation. Red line indicates the division between covered and exposed surfaces.

3.4 Biological Degradation

Biological degradation is the process by which organic substances such as bacteria, fungi, yeasts and their enzymes break down living organisms or use them as a food source (Allen and Edge 1992; Shah et al 2008). Polymers may be potential substrates for microorganisms; however factors including polymer characteristics and type of organism will govern the level of biodegradation. Polymer characteristics such as mobility, tacticity, crystallinity, molecular weight and types of functional groups all play important roles in the biodegradation of polymers. Other important factors are the addition of plasticizers and additives to the polymer (Shah et al. 2008). The biodegradation of polymers requires four steps:

1. Attachment of microorganisms to the polymer surface.
2. Use of the polymer as the carbon source resulting in growth of the microorganism.
3. Primary polymer degradation.
4. Ultimate degradation. (Arutchelvi et al. 2008).

Microorganisms can attach to polymers with a hydrophilic surface, however, PE and PP have only CH₂ groups on their main chains, therefore their surfaces are hydrophobic. Most commercial thermoplastics are immune to enzyme attack because the long carbon chain backbones of synthetic polyolefins make them non-susceptible to degradation by microorganisms (Allen and Edge 1992). However, a study conducted by

Yamada-Onodera et al. (2001) showed that polyolefins with low molecular weight could be utilized by microorganisms. Therefore it is possible for microbial degradation of these polymer types to occur when facilitated by physical and chemical degradation processes, which lead to the insertion of hydrophilic groups on the polymer surface (Arutchelvi et al. 2008; Shah et al. 2008). The biodegradability of polymers can be determined by several important physical and chemical characteristics:

1. Level of hydrophilicity as determined by availability of functional groups.
2. Polymer size, molecular weight and density.
3. Amount of amorphous and crystalline regions.
4. Structural complexity including linearity and amount of branching.
5. Presence of more easily broken bonds (e.g. ester or amide bonds).
6. Molecular composition.
7. Physical form of the polymer e.g. film, pellet, fragment, powder, fiber (Allen and Edge 1992).

If the hydrophilicity of the polymer changes, then microorganisms could attach to the polymer surface. Upon attaching to the surface, the organism may utilize the polymer as a carbon source. This results in a cleavage of the main chain which leads to the formation of low-molecular weight fragments. Polymers with high molecular weights such as PE and PP do not support the growth of fungi (Allen and Edge 1992). PE and PP are polyolefins prone to oxidation; however, these polymer types (particularly PP due to its substitution of a methyl group in the β position) are not susceptible to microbial attack

(Arutchelvi et al. 2008). The main reasons that synthetic polymers are not degraded through biological processes are:

1. The linear structure of the long carbon backbone chain provides high resistivity against hydrolysis.
2. The addition of antioxidants and stabilizers during the manufacturing process reduces or prevents atmospheric oxidation of the polymer.
3. High molecular weight.
4. High packing density (Arutchelvi et al. 2008).

The ultimate degradation of synthetic polymers through biological degradation may take several hundred years, as additives such as antioxidants and stabilizers may slow the degradation rate and/or be toxic to organisms (Arutchelvi et al. 2008).

3.5 Mechanical Degradation

Mechanical degradation processes acting on plastic debris may occur offshore, onshore or once the material is deposited on the beach. At sea, in areas where debris density is high and in areas of high vessel traffic, collisions may occur. In the littoral zone mechanical degradation features may be produced through the forces of wave action placed on plastic, which has been embrittled through chemical degradation. Following deposition on beaches, mechanical degradation occurs through interactions of the

polymer with natural beach sediment. The transfer of plastic debris across beach sediment, and/or the movement of sediment across stationary plastic particles occurs through both wind and wave action and results in mechanical degradation features on the polymer surface. Very little published information exists concerning mechanical degradation of plastics. This aspect of plastics breakdown should be investigated in future studies.

CHAPTER 4

REGIONAL SETTING AND METHODOLOGY

4.1 Regional Setting, Kauai, Hawaii, U.S.A.

4.1.1 Formation

The Hawaiian Islands are located within the North Pacific gyre, an area with an estimated three million tonnes of plastic debris (Moore et al. 2001), 96% of which is made up of small plastic fragments (Robards et al. 1997). The accumulation of plastic debris within the gyre results from the large-scale clockwise rotation of ocean currents and high atmospheric pressure (Moore et al. 2001; Moore 2008). The Coriolis effect combines with frictional surface currents caused by westerly winds on the north side of the gyre and easterly trade winds to the south to produce circulation around a centre of high pressure. The complex system of winds and currents results in an accumulation of water and debris in the centre of the gyre (Aguado and Burt 2004). The Hawaiian Islands work as a sink for ocean debris with large quantities being deposited from passing currents (Donohue et al. 2001).

The Hawaiian Archipelago stretches over 2500 km between 18° 54' to 28° 15' N latitude and 154° 40' to 178° 25' W longitude across the middle of the Pacific Ocean from Kilauea, an active volcano on the big island of Hawaii, northwestward to the atolls of

Midway and Kure (Donohue et al. 2001; Blay and Siemers 2004). The Pacific plate has migrated westward over the Hawaiian hotspot, a relatively stationary source of magma in the mantle, over the past ca. 40 My (Clague and Dalrymple 1988). Eight major islands including Hawaii, Kahoolawe, Maui, Lanai, Molokai, Oahu, Kauai, and Niihau (listed from youngest to oldest, Figure 4.1) have evolved through pre-shield, shield, post-shield, and rejuvenated stages (Clague 1987; Clague and Dalrymple 1987; Blay and Siemers 2004). There are 132 islands, reefs and shoals comprising the State of Hawaii, however, more than 97.5% of the state is submerged under the ocean surface (Blay and Siemers 2004). Kauai is one of the oldest and most northwestern islands of the principle Hawaiian Island chain (Clague and Dalrymple 1988; Reiners et al. 1999). Rejuvenated-stage volcanism ceased on the island by approximately 0.52 Ma (Clague and Dalrymple 1988).

Most beaches on Kauai have relatively consistent sediment size and type and are comprised of yellowish-orange calcareous sand, which is derived from the breakdown of skeletal remains of marine reef plants and animals. These beaches are composed primarily of coralline algae and carbonate skeletal material such as coral, foraminifera (shelled protozoans) and molluscs (snails and clams) (Blay and Siemers 2004). Beaches on the eastern side of the island are composed of 90.9% carbonates (Figure 4.2), which is due to the fringing platform reefs of Kauai that are composed mainly of coralline algae and are the main source of beach sediment. Abrasion along the nearshore fringing reef results in carbonate skeletal material being transported to the shoreline where it is further fragmented, rounded and polished (Blay and Siemers 2004).

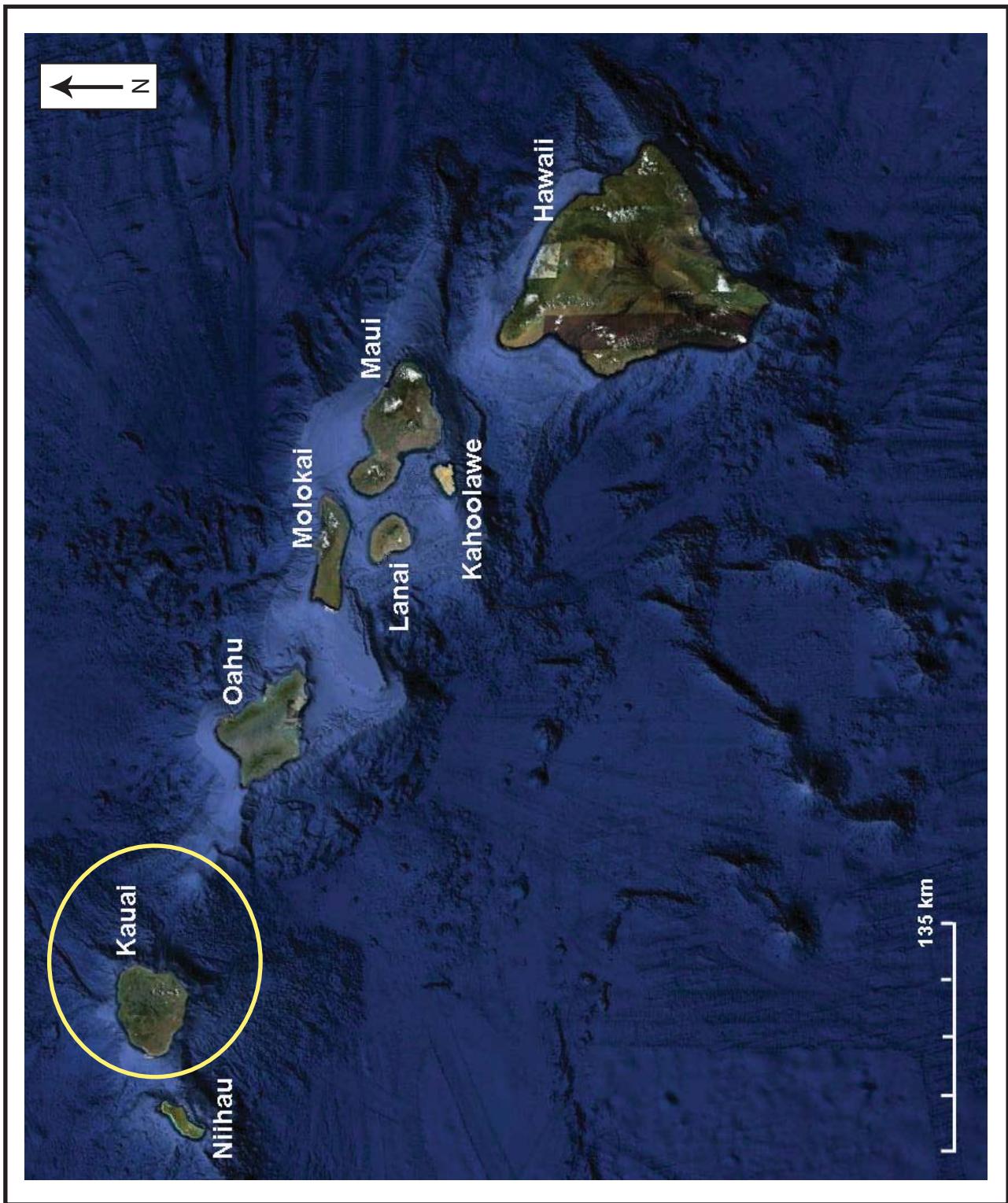


Figure 4.1 Satellite image (Google Earth) of the eight major Hawaiian Islands. Kauai (circled in yellow) is the northernmost, and second only to Niihau in age.

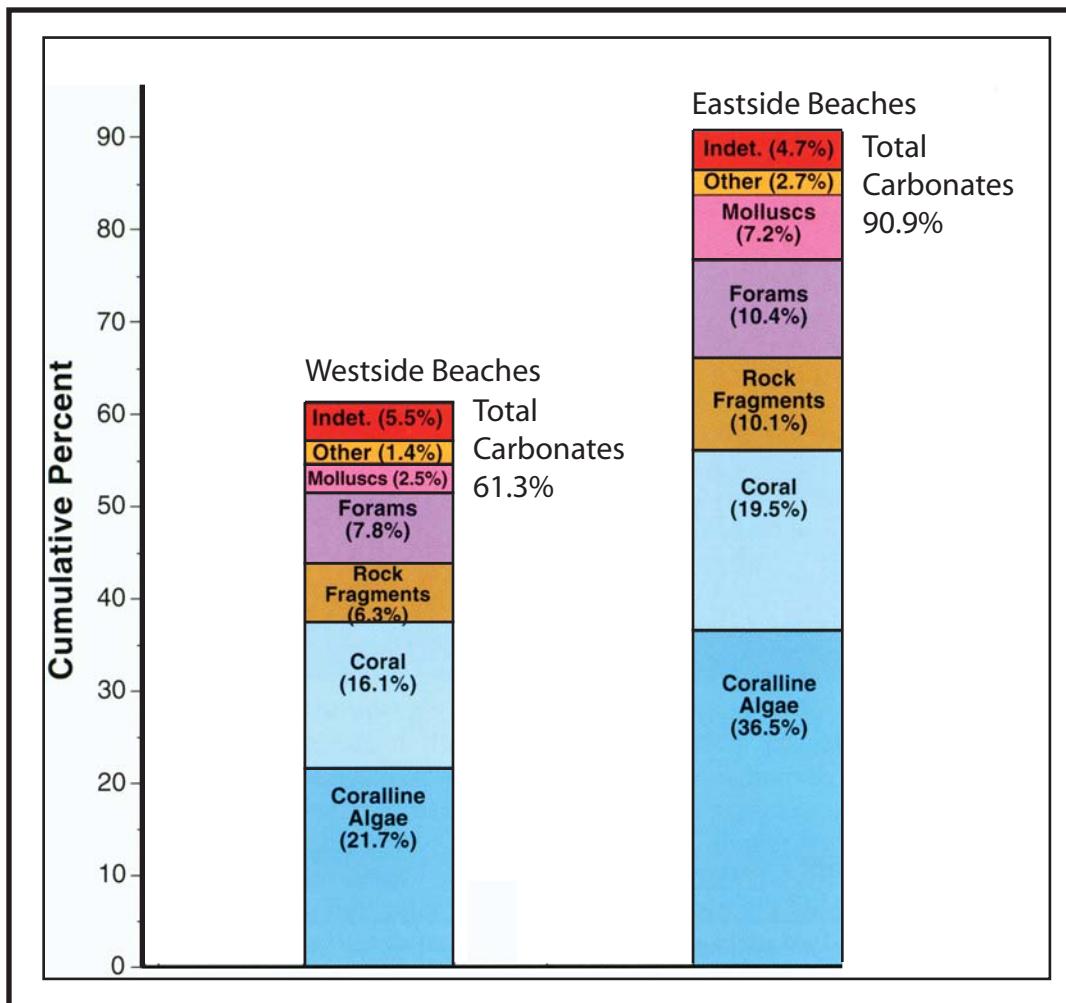


Figure 4.2 Compositional breakdown of Kauaiian beach sediment. Carbonate comprises the largest proportion of beach material on most beaches (modified from Blay and Siemers 2004).

4.1.2 Climate and Weather

Local atmospheric conditions are responsible for the weather that Kauai and the other Hawaiian Islands experience. Throughout most of the year, Hawaiian weather is controlled primarily by subtropical anticyclones which are the results of descending air from Hadley Cell global atmospheric circulation interacting with seasonally variable ocean surface temperatures. The North Pacific anticyclone, located northeast of the Hawaiian Islands, is the source of the trade winds that reach Hawaii (Aguado and Burt 2004; Blay and Siemers 2004). Seasonal movement of the North Pacific anticyclone results in changes in the Northeast Trade Winds. In summer, the anticyclone moves north and winds become stronger, more persistent and primarily travel in a westerly direction compared to during winter, when winds are weaker or absent and may originate from the east or the west (Figure 4.3) (Blay and Siemers 2004). Pacific Ocean storms move closer to the islands during the winter causing a slight disruption in trade winds and weather conditions (Schroeder 1993). Northeast Trade Winds control the island's local weather throughout most of the year and also produce short-period wind waves and long-period ocean swells that impinge on the eastern and northeastern coast lines (Figure 4.4) (Blay and Siemers 2004).

Daily air temperatures in Kauai average 27° C with little variation throughout the year. The longest days in Hawaii receive 13.5 hours of daylight and the shortest receive 11 hours. The relatively uniform day lengths result in small seasonal variations in solar radiation and temperature (NOAA 2011). Level ground in Hawaii receives 67% as much

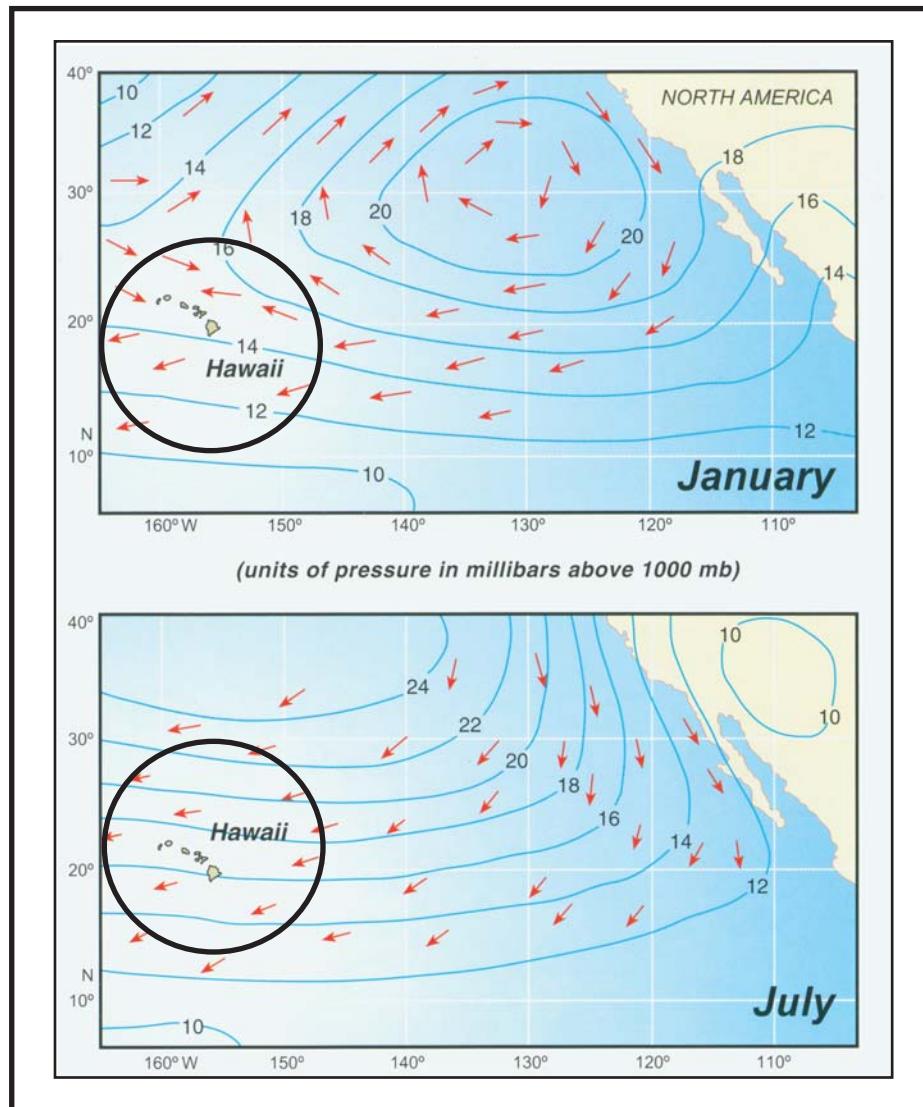


Figure 4.3 Seasonal wind pattern changes from summer to winter near Kauai. The direction of summer wind patterns are more consistent relative to winter winds (modified from Blay and Siemers 2004).

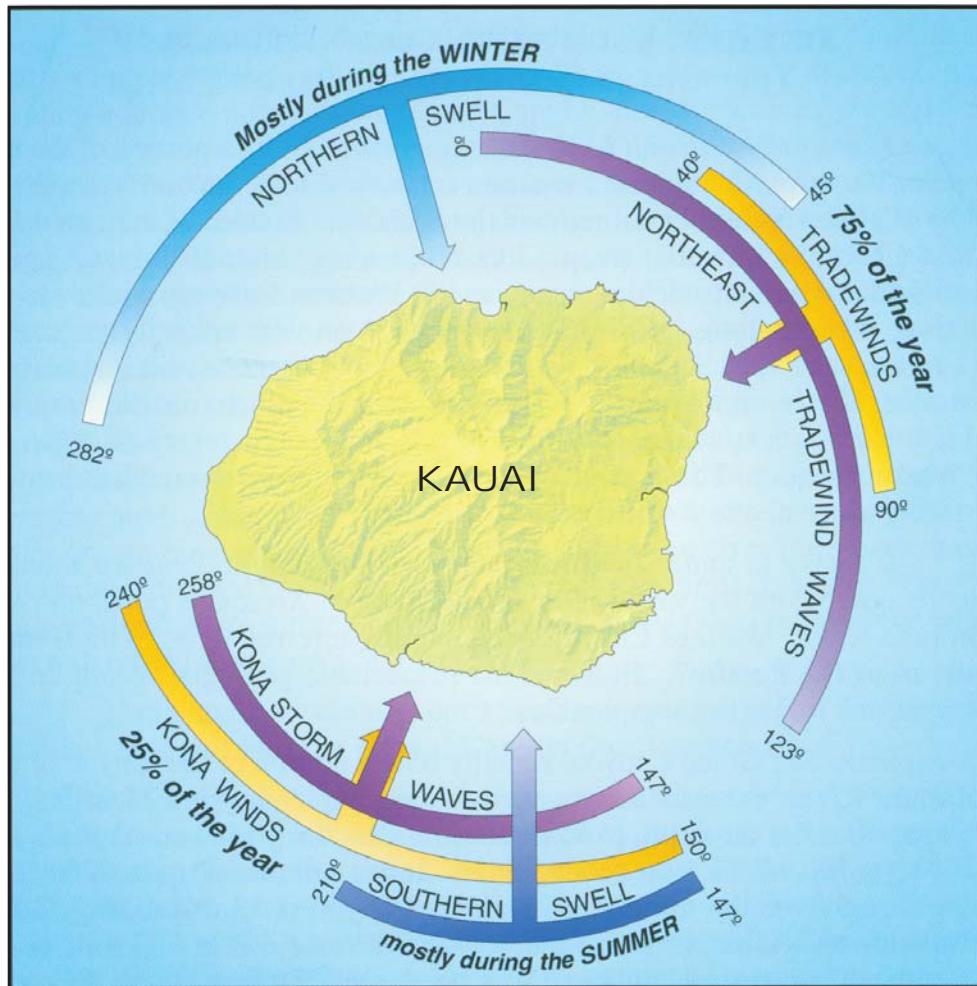


Figure 4.4 Image of wind patterns affecting the island of Kauai. During most of the year tradewinds blow in from the northeast (modified from Blay and Siemers 2004).

solar energy on a clear winter day as it does on a clear summer day, and therefore, temperature values between the warmest month (August) and the coolest month (February) differ by only 8° C (NOAA 2011; WRCC 2011).

The open ocean around the Hawaiian Islands averages 635 mm of rainfall per year, however, precipitation on any one of the major Hawaiian Islands averages 1905–2285 mm per year (Blay and Siemers 2004). Orographic lifting, in which warm, moist, trade-wind driven air is forced up the east/northeastern (windward) side of the island, results in a greatly diversified distribution of precipitation across the landscape. The combined effects of Kauai's topography and its position within the Northeast Trade Wind Belt results in record amounts of rainfall in the interior of the island (>10,000 mm annually), however, beaches on the leeward and windward sides of the island average just 500 mm and 1200 mm respectively, per year (Blay and Siemers 2004) (Figure 4.5).

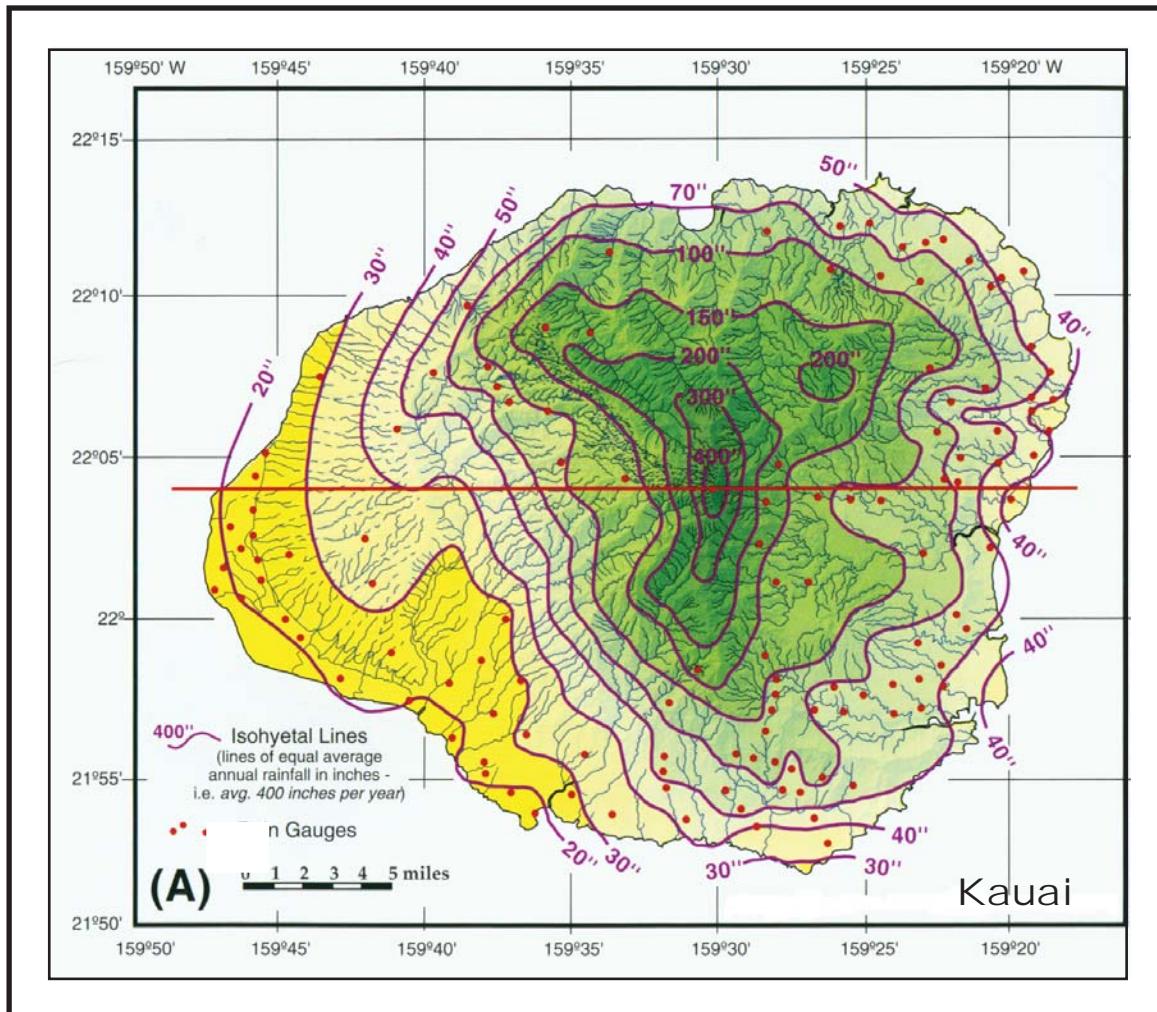


Figure 4.5 Annual rainfall amounts on the island of Kauai. Orographic lifting results in more rainfall on the eastern side of the island than the west. The centre of Kauai receives record amounts of rainfall each year (modified from Blay and Siemers 2004).

4.2 Regional Setting, Gros Morne National Park, Newfoundland, Canada

4.2.1 Formation

Gros Morne National Park is an 1805 km² protected area which represents two of Canada's natural regions, the Newfoundland Island Highlands and the St. Lawrence Lowlands (Figure 4.6). The park is a National Heritage Site as designated by the United Nations Education, Scientific and Cultural Organization (UNESCO) and is one of only nine world heritage sites within Canada that have received designation for their natural features (UNESCO 2011). Gros Morne National Park received its inception to the UNESCO list in 1987 due to its geological and glacial history as well as its dramatic scenery just 17 years after gaining national park status (Parks Canada 2011A).

Gros Morne National Park is considered to be one of the best illustrations of plate tectonics anywhere on Earth (UNESCO 2011). Several geological features are prominent throughout the park including the Long Range Mountains, which are the remains of a large mountain range formed through the collision of two plates approximately 1200 MYA. Later, the supercontinent began to separate and steep fractures were filled from below with molten rock, eventually cooling into the diabase dykes found in Western Brook Pond and Ten Mile Pond (Parks Canada 2011B). Bedrock records indicate that the formation and destruction of an ocean basin occurred between 700 and 470 Ma. As sands and silts eroded they were deposited in shallow water and formed what is now the top of Gros Morne Mountain (Brooks 1993). The current park geomorphology is a result of

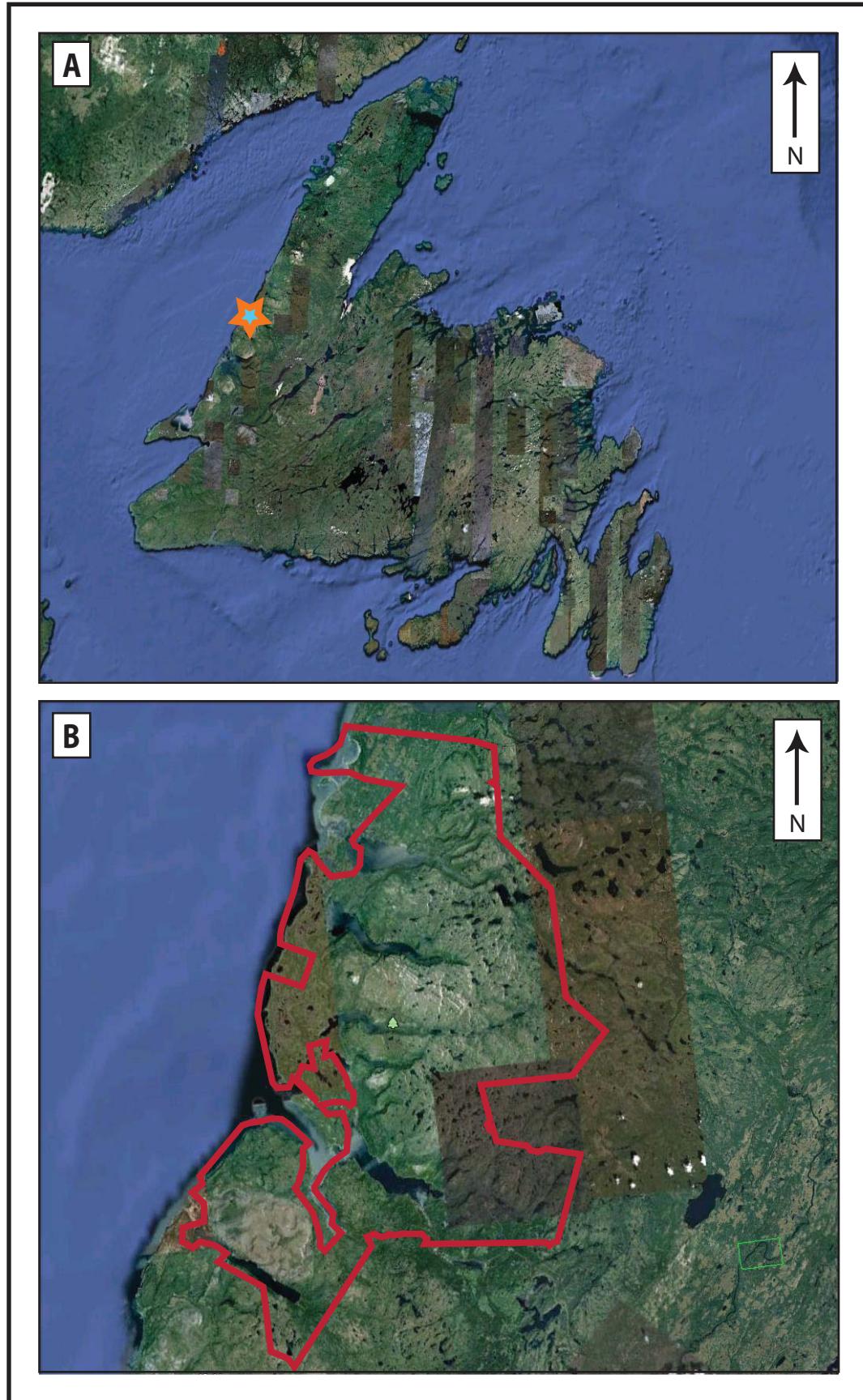


Figure 4.6 Satellite images (Google Earth) of the island of Newfoundland, and Gros Morne National Park. A- Orange star indicates the location of Gros Morne National Park. B- red line displays the boundary of the park.

repeated glaciations, deglaciations and sea level changes over the last 2 million years. These processes have combined to produce glacial valleys, sheer cliffs, waterfalls, lakes, fjords, coastal lowlands, and alpine plateaus (UNESCO; Brooks 1993). Beach sediment is primarily sourced from erosion of local rocks and the varied coastline and subsequent beach energies result in Gros Morne National Park beaches having a wide variety of sediment sizes (Figure 4.7).

4.2.2 Climate and Weather

Moderate seasonal temperature changes and moisture for abundant precipitation is provided to western Newfoundland by winds blowing inshore from the Gulf of St. Lawrence (Parks Canada 2011C). Using Rocky Harbour, which has a central location within Gros Morne, provides a representative example of weather conditions along the western shore of the park. June through September provides the warmest conditions with daytime temperatures averaging 13.3° C, and night time temperatures at least 5 degrees cooler. Higher elevations can be up to 10 degrees cooler, relative to the shoreline, when combined with wind chill. The prevailing winds are from the southwest and average 23-27 km/h throughout the year on the western shores (Figure 4.8) (Kahn and Iqbal, 2004). Winter temperatures average -6.4° C from December through March, but can be as low as -20° C at higher elevations (Parks Canada 2011C; Environment Canada 2011). Temperatures along the coast fluctuate approximately 20° C between summer and winter months, however extreme highs (30° C) and lows (-36° C) have been recorded

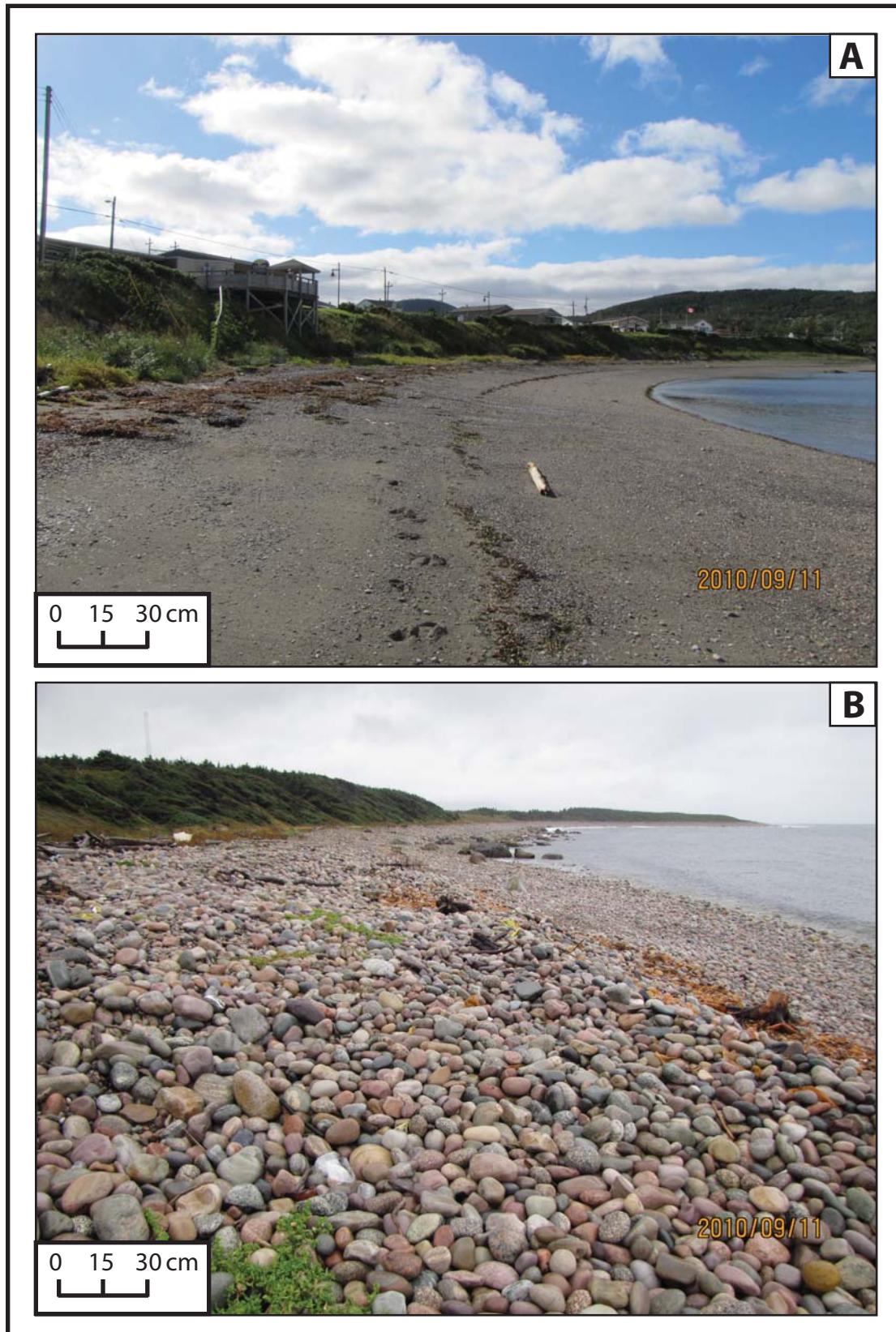


Figure 4.7 Photos illustrating the wide variety of sediment sizes characterizing Gros Morne National Park beaches. A- Rocky Harbour with fine sand and pebbles, and B- Green Point with cobbles and boulders.

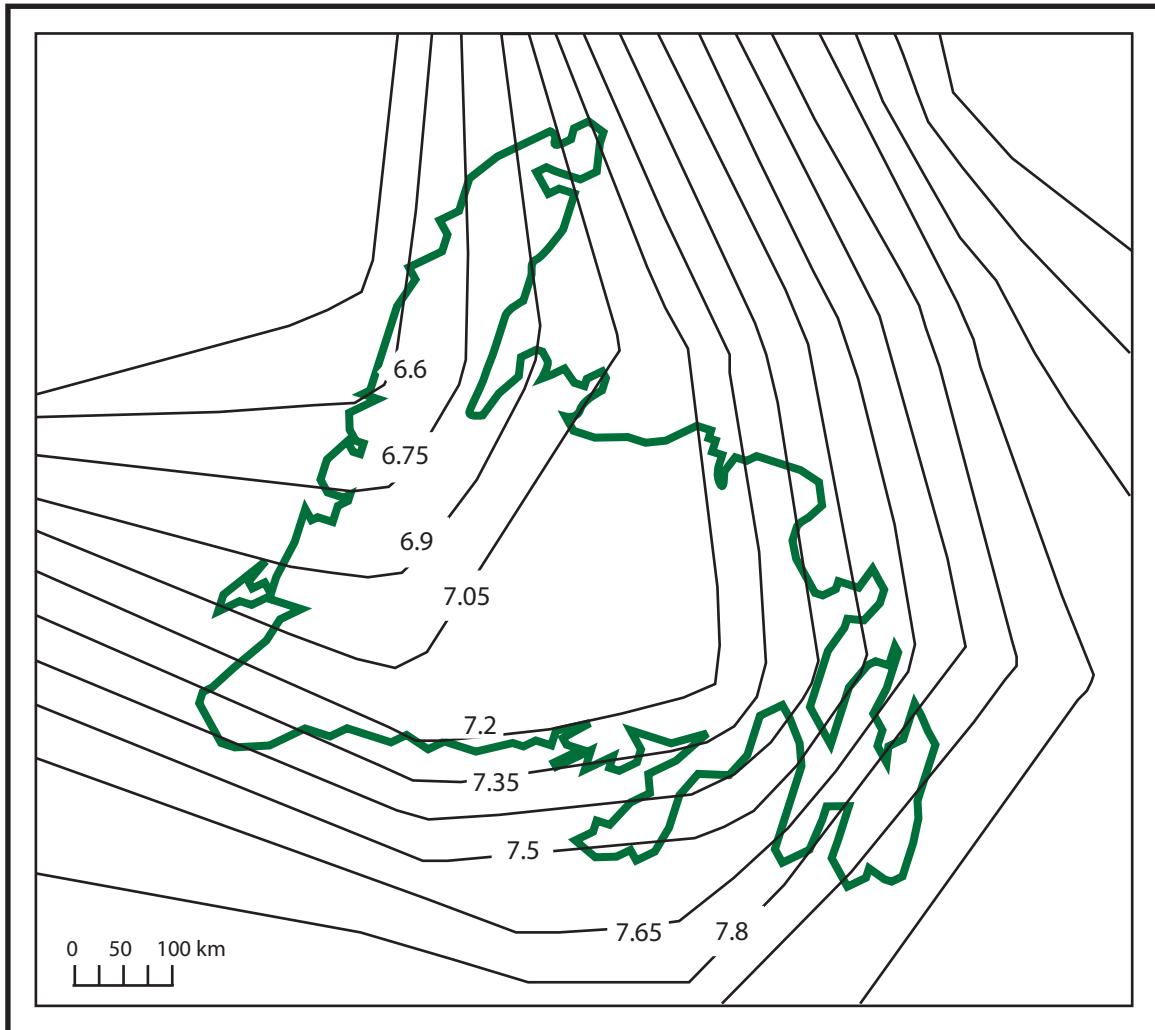


Figure 4.8 Wind map of Newfoundland (m/s) at surface level averaged over 55 years from 1948 to 2003 (modified from Khan and Iqbal 2004).

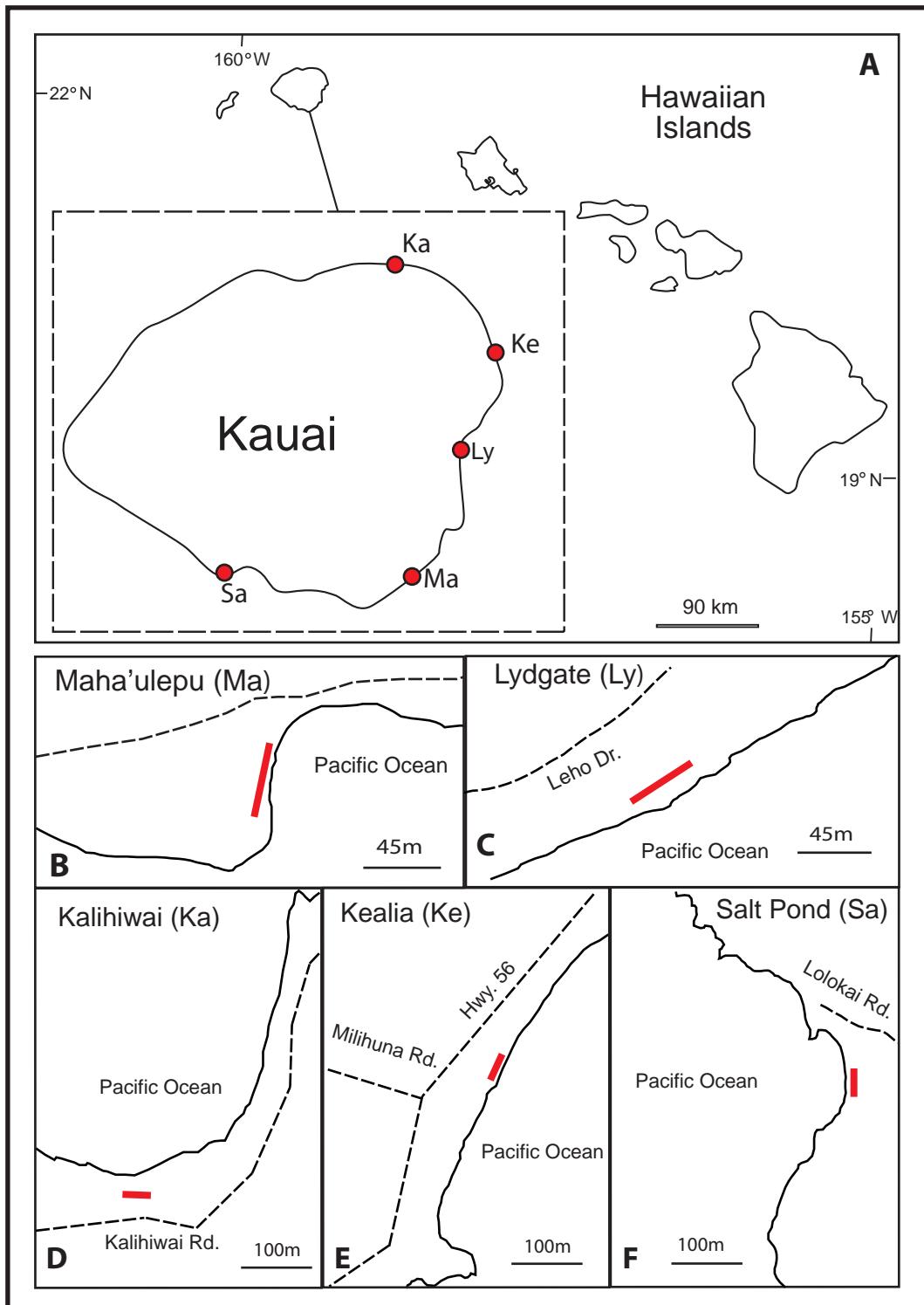


Figure 4.9 Sampling locations on the island of Kauai, Hawaii. Closed circles indicate beaches where plastic debris was visible to the naked eye. Solid lines represent the shoreline, dashed lines are roads, and thick red lines represent transect lines (modified from Cooper and Corcoran 2010).

each beach parallel to the shoreline. Plastic particles visible to the naked eye were collected from 50 cm-wide swaths at 10 m intervals stretching from the water to the vegetation lines. A stainless steel tablespoon was used to collect each plastic particle and <5 g of surrounding beach sediment. Caution was used in order to avoid scratching the surfaces of the plastic during sampling. Kalihiwai, Keaalia, Lydgate, Salt Pond and Maha'ulepu beaches were chosen as sampling sites to provide a proportional representation of plastic debris deposition on Kauai. Previous research by Corcoran et al. (2009) showed that of eighteen beaches sampled, only seven contained plastic debris visible to the naked eye, and all were located on the east coast of the island. Maha'ulepu beach accumulates large quantities of plastic debris and was chosen as the site to determine daily accumulation. Plastics were sampled from a 1 m x 5 m area at a depth of <3 cm daily for a period of eleven days from March 9-20, 2009 (Figure 4.10). On day 1 all plastic was cleared from the sampling site by sifting the top ~3 cm of sand through a hand held sifter with a 2 mm sized mesh opening. Each day at approximately 11:00 am the area was cleared of any plastic debris using the same procedure. Collected debris was placed in a one gallon pail with ocean water, and plastic was then separated from organic debris by type: pellet, small fragment (< 1cm²) and large fragment (>1cm²). The plastics were air dried and placed in sealed bags for transport back to the University of Western Ontario.

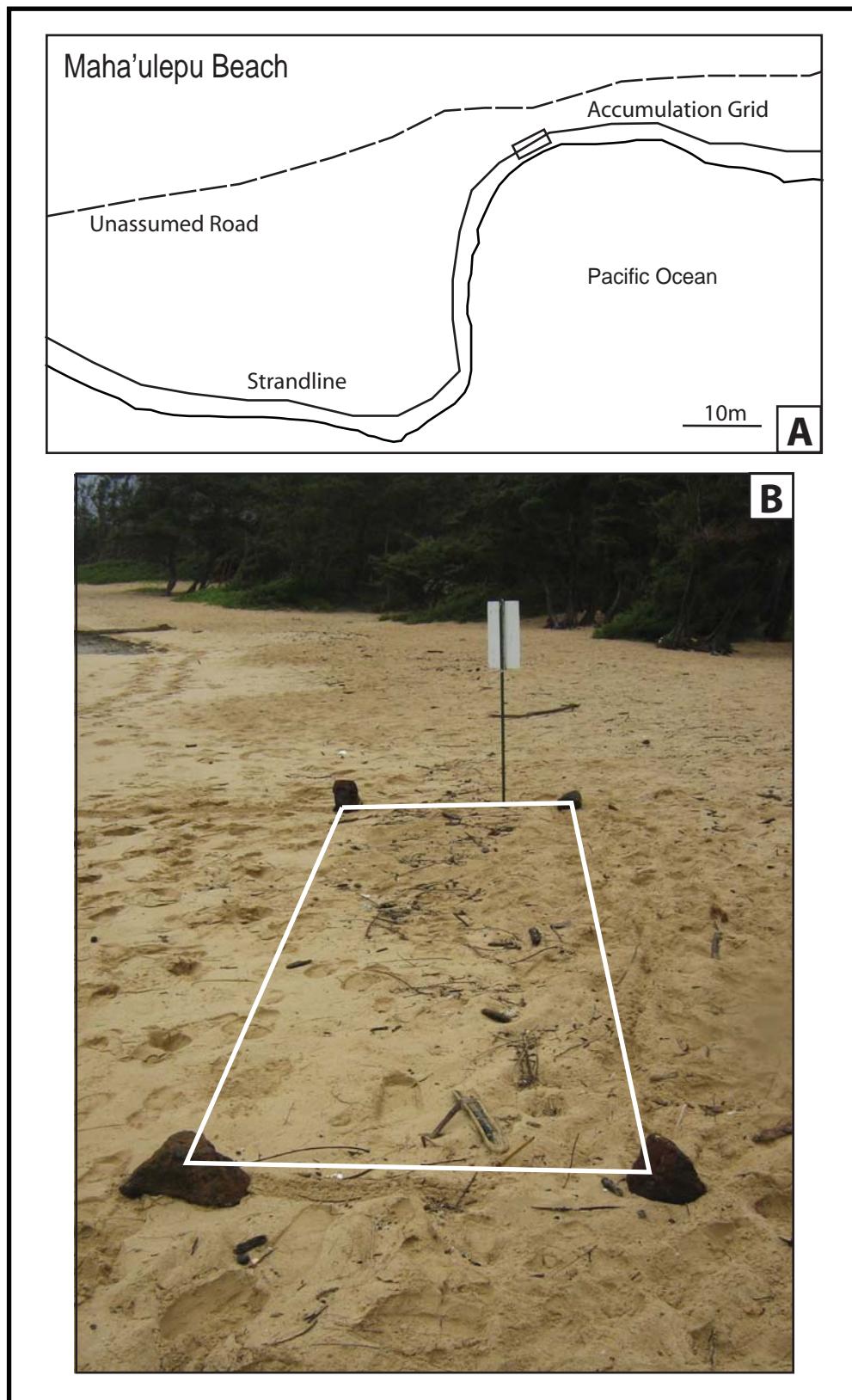


Figure 4.10 A- schematic diagram of sampling grid location on Maha'ulepu beach, and B- photograph of accumulation grid location on the beach. White box, and rocks at each corner define the perimeter of the grid at 1mx5m.

(Environment Canada 2011). ‘Total hours’ of bright sunshine, which is representative of the most intense sun during the day, averages 1307 hours/year. May through August receives the greatest amount of bright sunshine hours with an average of 179 hours/month. November through February receives considerably less, at an average of 36 hours/month (Environment Canada 2011).

Proximity to the Gulf of St. Lawrence provides the beaches of Gros Morne National Park with abundant precipitation throughout the year. Rainfall averages 898 mm/year and snow falls at an average of 418 mm/year for a total of 1316 mm/year of precipitation. June through September are the only months not to receive snowfall, but during these months an average of 107 mm/month of rain falls. The coldest months (December through March), receive an average of 33 mm/month of rain and 88 mm/month of snow (Environment Canada 2011). Gros Morne National Park receives typical maritime weather with a temperate climate and moderate temperature changes. This location was ideal for providing a variety of climatic conditions including significant changes in precipitation, sun, wind, and temperature.

4.3 Methodology, Kauai, Hawaii, U.S.A.

Plastics were sampled from Kauai over an eleven day period during the month of March, 2009. Plastic fragments were sampled from five beaches on the northeastern, eastern and southern shores of Kauai (Figure 4.9). One 40 m transect line was placed on

4.4 Methodology, Gros Morne National Park, Newfoundland, Canada

Two hundred seventy-one samples were collected over a four day period during the month of September, 2010. One 40 m transect line was placed on each beach parallel to the shoreline. Plastic debris visible to the naked eye was collected from 50 cm-wide swaths at 10 m intervals stretching from the water to the vegetation lines. Samples were collected using a stainless steel tablespoon with <5 g of surrounding sediment where possible. On beaches with coarse-grained sediment, >.5cm samples were collected by hand using vinyl gloves. Caution was used in order to avoid scratching plastic surfaces. All fragments were placed into sealed labeled containers.

Eight beaches were sampled along the western shore of the park with an aim to sample areas receiving debris from potentially different sources, including beaches conducive to public use as well as remote beaches with little direct human impact (Figure 4.11). In addition to usage, beaches with various sediment grades were selected to determine the effect of sediment size on the deposition, retention and degradation of plastic debris. Cow Head, St. Pauls, Broom Point, Sally's Cove, Green Point, Rocky Harbour, Woody Point and Trout River were chosen because these locations provided variations in use, wave energy, sediment type and size, and proximity to residential areas.

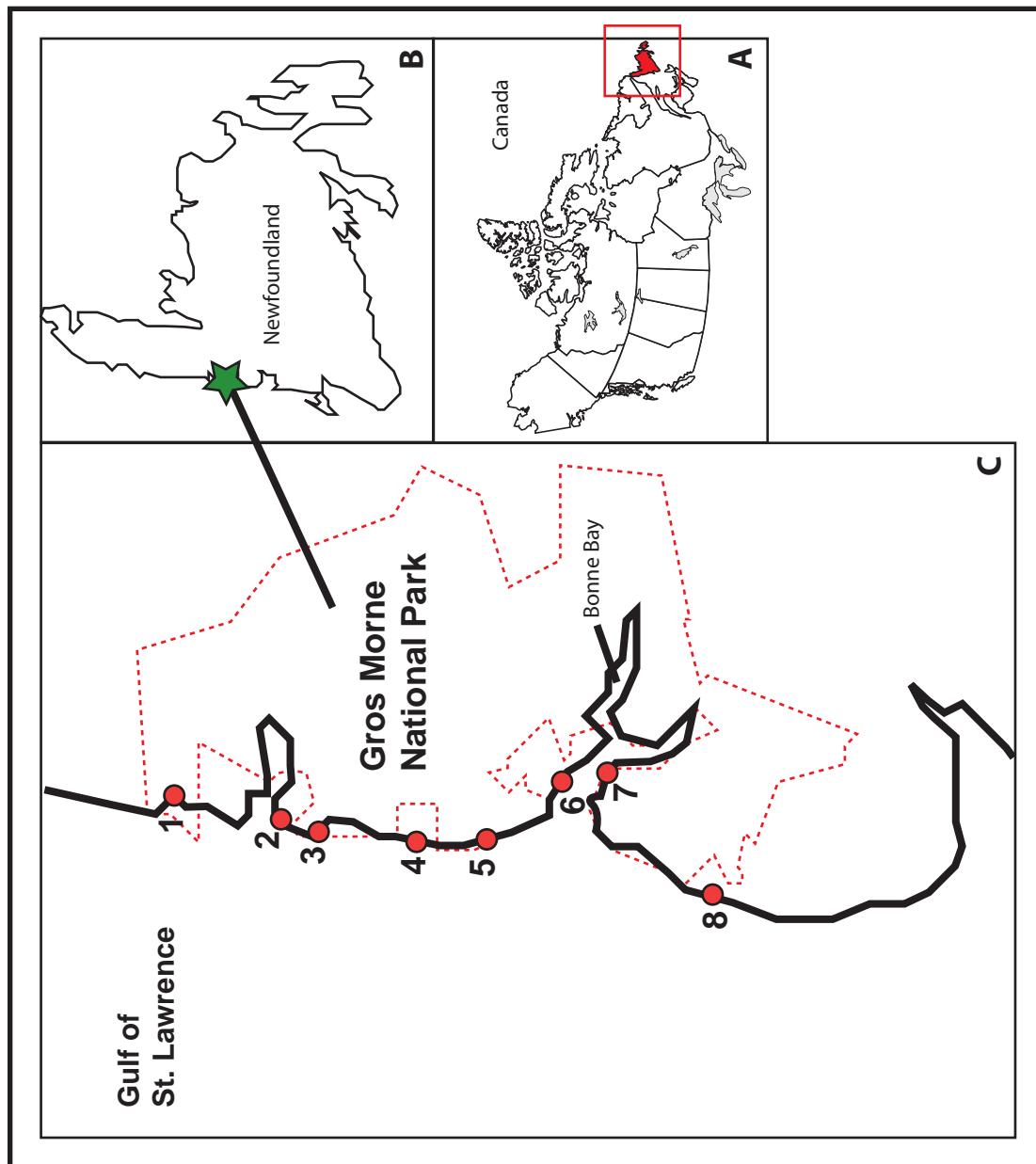


Figure 4.11 A) Location of Newfoundland within Canada, B) Location of Gros Morne National Park within the Province of Newfoundland, C) Red circles indicate sampling locations located in and near the park, red dashed line indicates the park boundary. 1- Shallow Bay, 2- St. Pauls, 3- Broom Point, 4- Sally's Cove, 5- Green Point, 6- Rocky Harbour, 7- Woody Point, 8- Trout River.

4.5 Analysis

In order to remove any loose debris, CaCO₃, NaCl or other residues, all samples were washed using de-ionized water for 4 minutes in a Branson ultrasonic cleaner, then dried in a Thelco precision laboratory oven at 35°C for 45 minutes. A Bruker IFS55 FTIR equipped with a microscopic stage attachment, located at Surface Science Western at the University of Western Ontario, was used to perform Fourier transform infrared spectroscopy (FTIR). A micro attenuated total reflection (micro-ATR) attachment was used to determine the composition of plastics and levels of surface oxidation. The ATR attachment allows for information to be collected from the surface of the sample, whereas Diffuse and Specular FTIR provide information from the bulk matrix and thin layers. Digital photographs of Kauaiian samples were taken at Surface Science Western using a Hitachi S-4500 field emission scanning electron microscope (FESEM) with a 10 kV electron accelerating voltage and a 30° sample tilt to analyze surface textures. All plastic samples were treated with a light coating of conductive gold prior to analysis to prevent sample charging. Gros Morne National Park samples were treated with a light coating of conductive carbon prior to analysis to prevent sample charging. Images were taken using a Hitachi SU6600 FEG-SEM field emission scanning electron microscope (FESEM) with a 3 kV electron accelerating voltage located in the Department of Earth Sciences at the University of Western Ontario.

4.5.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine levels of oxidation and polymer compositions. All molecules possess several energy levels which correspond to different vibrational states. The energy of radiation in the infrared region of the electromagnetic spectrum corresponds to the spacing between these levels. If radiation impinges on a molecule, it is absorbed and converted to molecular vibrational and rotational energy. Certain functional groups absorb energy at different frequencies specific to the vibrations of those functional groups. There are two main modes of vibration, 1) stretching vibrations which produce changes in bond lengths, and 2) bending vibrations which produce changes in bond angle (MacManus 1998). FTIR spectroscopy utilizes the absorption of radiation in the IR frequency range due to molecular vibrations of functional groups within the polymer chain. A plot is obtained of some function of radiation intensity against a level of frequency (Hamid et al. 1992). Molecular transitions between quantum states of different internal energies results in an infrared spectrum.

Figure 4.12 is a spectrum of untreated PP, which gives characteristic absorbance peaks due to C-H stretching and bending vibrations. The $4000\text{-}1300\text{ cm}^{-1}$ range is referred to as the functional group region; this region is useful for the determination of the presence or absence of functionality. The $1300\text{-}600\text{ cm}^{-1}$ range is the fingerprint region and is used for determining the composition of unknown samples by comparing spectra with known reference spectra (MacManus 1998). Molecular vibrations characteristic of chemical groups such as alkyl, hydroxyl or carbonyl are associated with

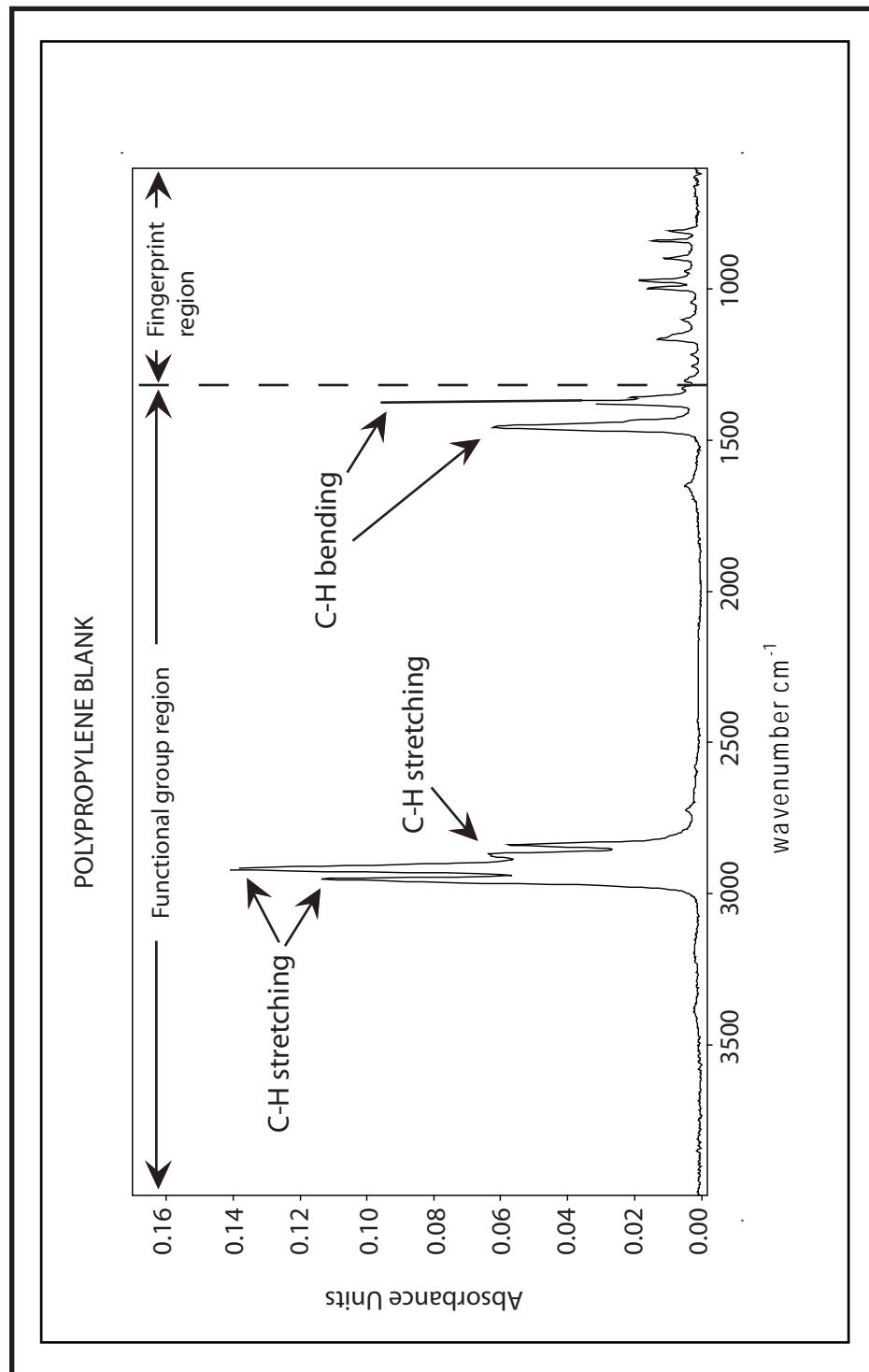


Figure 4.12 FTIR spectrum of untreated PP. C-H stretching and bending occur in specific ranges, which is useful for identifying the composition of unknown samples and determining functionality.

energy differences related to the frequency of emitted or absorbed radiation. Absorption bands between 1850 and 1700 cm⁻¹ indicate carbonyl groups such as carboxylic acids, aldehydes, esters and ketones and are associated with the products of degradation which relate directly to oxidation. FTIR has been widely used to examine the degradation of polymers, especially photooxidation, because weathering effects on polymers are concentrated in the surface layers (Hamid et al. 1992).

4.5.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is used to capture images of surface features and identify surface textures. SEM is performed on samples coated in some type of heavy metal. e.g. gold or carbon which prevents charging. Samples are placed in a chamber, above the chamber is a column containing electromagnetic lenses; a tungsten filament is the typical electron source at the top of the column (Mahaney 2002). The samples are then placed under high vacuum and bombarded with electrons from the heated tungsten filament. The electrons leave the filament and are accelerated by 1 to 40 kV, and then pass through magnetic lenses which reduce the size of the original beam from 0.002 inches to 100 Å (Krinsley and Doornkamp 1973; Mahaney 2002). A small aperture provides a large depth of field which is beneficial when examining rough surfaces. An electron field is scanned raster line by line across the sample by a deflection field, and when the secondary electrons are emitted from the surface they are picked up by a collector and form a signal. Secondary electrons are used to produce images of

surface topography in SEM because of their ability to image detailed surface structures (Mahaney 2002). A cathode ray tube is scanned at the same time as the electron beam so that each point on the cathode tube corresponds to spots on the item being scanned (Krinsley and Doornkamp 1973). The signal varies from point to point on the item surface as the number of electrons varies, which results in a variation of brightness or contrast on the face of the display tube. A three dimensional picture is obtained through the great depth of field, and high resolution is a result of the small probe size (Krinsley and Doornkamp 1973).

CHAPTER 5

DISTRIBUTION OF PLASTIC DEBRIS

5.1 Kauai, Hawaii, U.S.A.

Sampling results, supported by research conducted by Corcoran et al. (2009), confirm that plastic debris on Kauai is concentrated along the eastern shoreline of the island. Results from Corcoran et al. (2009) indicated that beaches on the west, north and south portions of the island contain no mm-size macro- or microscopic debris. Our findings are also consistent with McDermid and McMullen (2004) who collected small plastic debris from 9 beaches throughout the Hawaiian archipelago and identified 17,645 particles on Cargo Beach located on the north-east (windward) side of Midway Atoll and just 6 pieces on Nanakuli Beach Park located on the leeward coast of O'ahu.

Each sampling location on Kauai contained some measurable quantity of plastic debris, however, Kalihiwai, Lydgate and Maha'ulepu beaches all contained large quantities (>200 pieces/transect). In contrast, Kealia beach, located on the north shore, and Salt Pond beach, on the leeward side of the island, yielded a total of 70 and 2 pieces respectively (Figure 5.1). Plastic debris along transect lines at Kalihiwai, Kealia, Lydgate and Maha'ulepu beaches displayed similar patterns of distribution with fragments and pellets being concentrated along the high tide or storm lines (strandlines) (Figure 5.2). At each of these sampling sites, plastic debris was primarily interspersed with organic

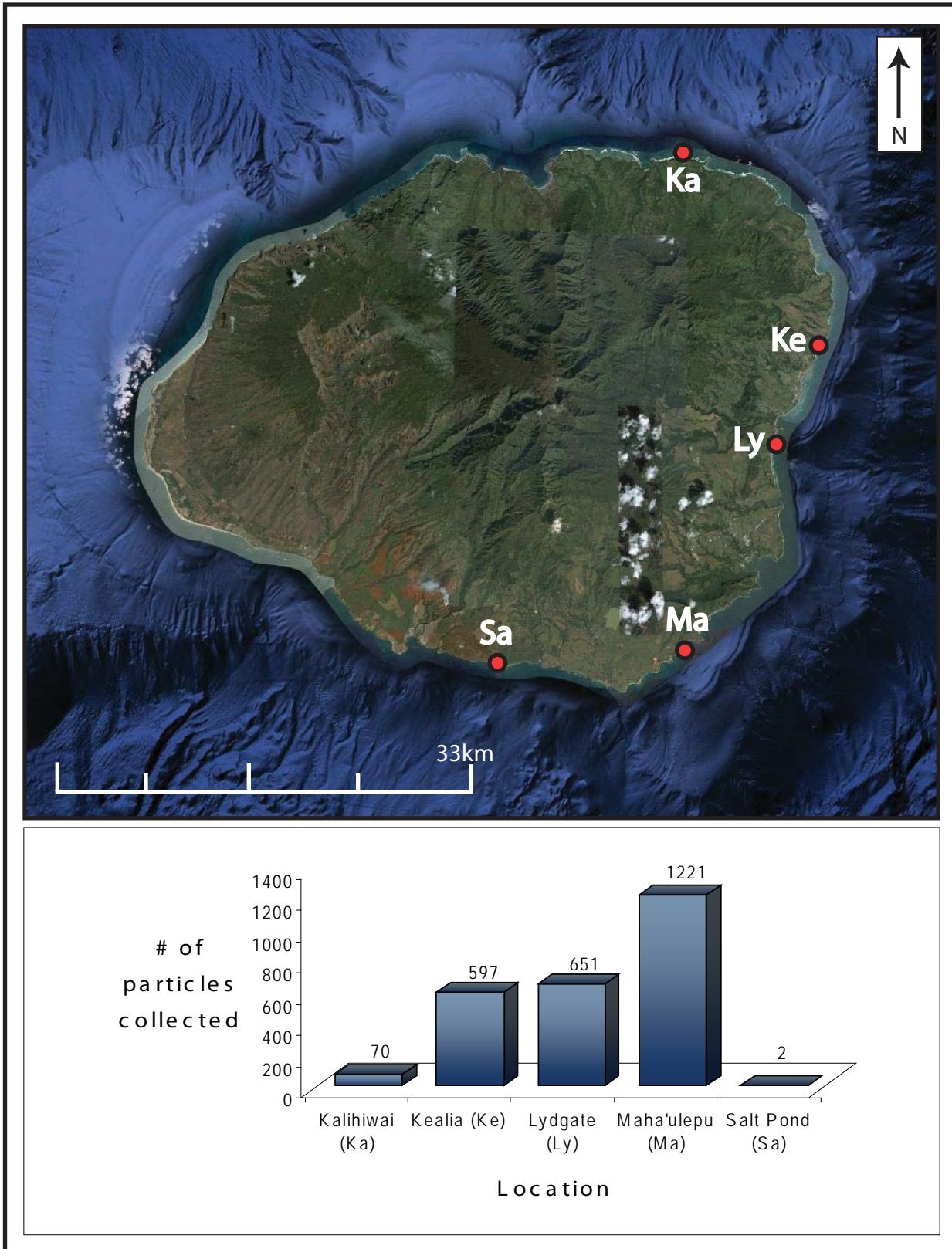


Figure 5.1 Satellite image (Google Earth) of Kauai. Red dots indicate location of sampling sites. Graph displays amount of plastic debris collected at each beach.

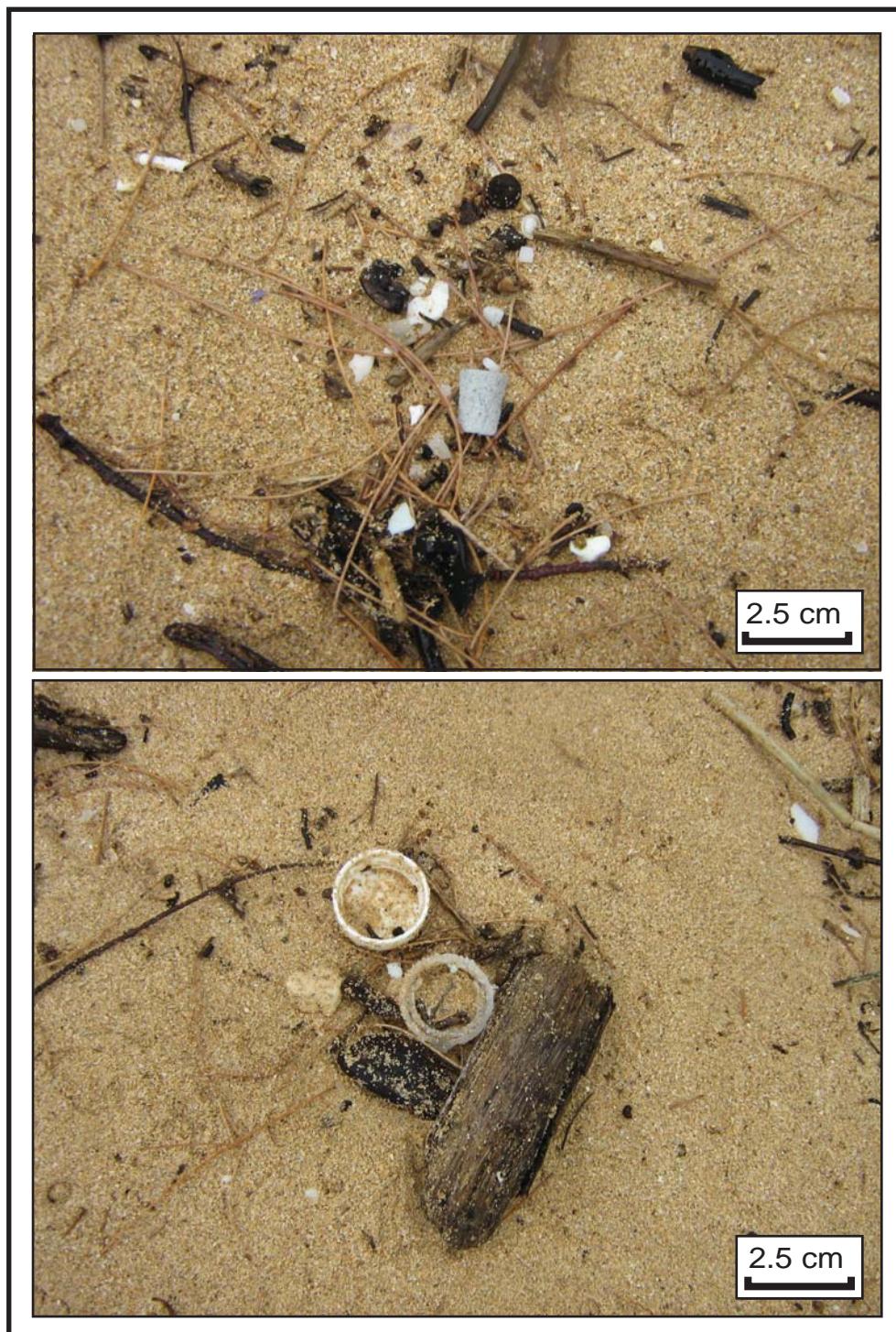


Figure 5.2 Photographs of plastic fragments intermixed with organic debris along the strandline on Maha'ulepu beach.

debris. Areas below the strandline contained little to no fragments and areas above contained fewer particles relative to the strandline. This is an indication that particles suspended in the water are being deposited during storm events and/or during each receding tide (McDermid and McMullen 2004; Cooper and Corcoran 2011). During sampling, we noted several rounded particles and plastic resin pellets being blown up the beach, suggesting that wind transport may be another process of deposition at the high tide line where particles are caught in organic material. At each sampling locality, plastic debris was primarily macroscopic (<5 mm) and limited to the top 3 cm of beach sediment.

Quantity, size and distribution of plastic debris on Kauaiian beaches can be attributed to an abundance of plastic within the North Pacific Gyre, depositional patterns of long-shore currents around the Hawaiian Islands, prevailing western trade winds, and trash left by beach-going residents and tourists. The relative abundance of microscopic to macroscopic debris is a result of Kauai's location within the North Pacific Gyre where large quantities of virgin resin pellets and fragmented pieces of larger items occur at a ratio of 6:1 plankton to plastic mass (Moore et al. 2001). No intact or partially intact debris was collected on Kauaiian beaches, as a result of regular beach clean up efforts conducted by area residents and organized volunteer groups.

5.2 Gros Morne National Park, Newfoundland, Canada

Plastic debris was present on all beaches sampled within, and near Gros Morne National Park (Figure 5.3). However, small fragments ($<5\text{cm}^2$), when compared to similar studies conducted in subtropical climates (see Corcoran et al. 2009; Cooper and Corcoran 2010), constituted a smaller portion of debris relative to the overall plastic load. High energy beaches with coarse sediment grades contained larger organic debris, such as tree branches and kelp, and this type of debris was dispersed throughout the beach but concentrated at the high water line (strandline). Plastic fragments were scattered across the beaches, but the greatest amount of plastic was located at the strandline where plastics were intermixed with organic debris.

Beaches with coarse sediment, including cobbles and boulders, primarily contained intact or partially intact plastic items (Table 5.1). Items such as shotgun shell casings, lobster tags, plastic bottles and tampon applicators were most common and in most cases displayed little visual sign of degradation. Fragmented debris were the predominant form of plastic present on finer-grained sandy beaches. However, shotgun shells and lobster tags were found on every beach sampled. Sandy beaches contained less organic material than coarse grained beaches.

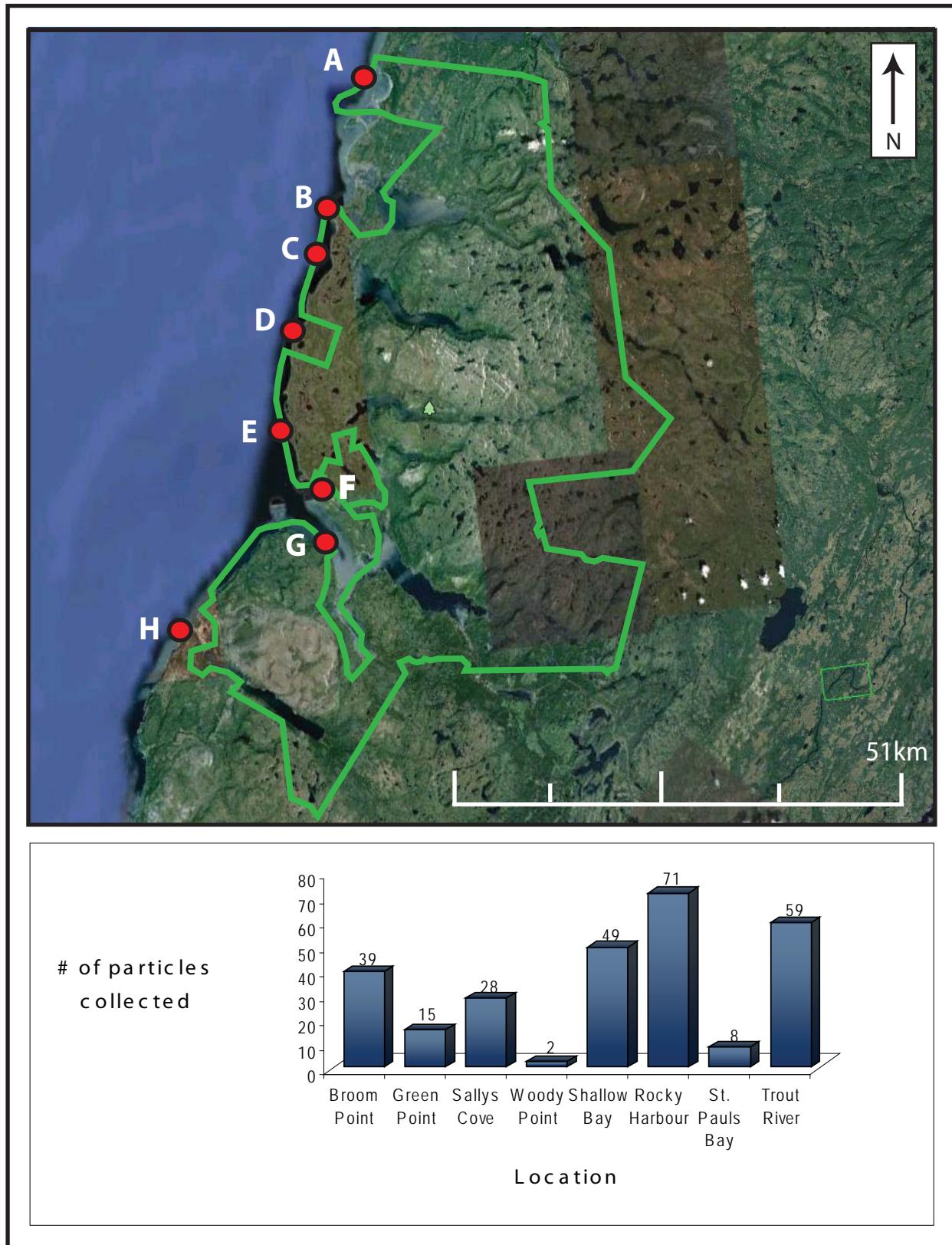


Figure 5.3 Satellite image (Google Earth) of Gros Morne National Park. Green line indicates the park boundary. Red dots indicate beaches where plastic debris was collected. Graph displays relative abundance of plastic debris collected at each sampling locality. A) Broom Point, B) Green Point, C) Sallys Cove, D) Woody Point, E) Shallow Bay, F) Rocky Harbour, G) St. Pauls Bay, H) Trout River.

Table 5.1 Plastic debris types sampled from Newfoundland localities. Mixed beach grain size refers to beaches with both coarse and fine sediment.

Beach Location	Average Beach Grain Size	Intact items	Partially intact items	Large fragmented debris >5 cm ²	Small fragmented debris <5 cm ²	Total debris on beach	% of Total (All beaches)
Shallow Bay	Fine Sand	6	6	12	25	49	18.0
St. Pauls	Coarse Gravel	3	2	3	0	8	2.2
Broom Point	Cobble	14	6	14	5	39	14.6
Sally's Cove	Mixed	0	2	12	14	28	10.1
Green Point	Cobble	6	3	5	1	15	5.6
Rocky Harbour	Fine Sand	5	2	12	52	71	26.6
Woody Point	Coarse Gravel	0	2	0	0	2	0.75
Trout River	Mixed	11	3	24	21	59	22.1
Total		45	26	82	118	271	100
% of Total		16.12	9.46	30.3	43.5	100	

The distribution of plastic debris closely follows patterns similar to the deposition of natural beach sediments. Intact, partially intact and large fragmented debris characterize high energy beaches such as those near Green Point and Broom Point. These beaches also contain greater quantities and larger varieties of organic debris. Smaller fragmented particles were most prevalent on lower energy beaches such as those near Shallow Bay and Rocky Harbour, which are more sheltered from strong winds and waves (see figure 4.6). The relationship between beach energy, sediment size and particle distribution was particularly evident on beaches containing a variety of sediment grades.

CHAPTER 6

COMPOSITION AND OXIDATION OF SAMPLES

6.1 Composition

6.1.1 Kauai, Hawaii, U.S.A

Compositional analysis of plastic debris sampled from Hawaiian beaches indicated that PE and PP were the only polymer types collected. PE constituted a much greater proportion of debris relative to PP, with results indicating a ratio of 80:20. The composition of sampled PE was indicated by characteristic peaks at wavenumbers 2916, 2849, 1471, and 718 cm⁻¹. PP samples produced five distinct peaks between 2723 and 2950 cm⁻¹, which are characteristic of the material (Figures 6.1-6.3, Appendix 1). Debris collected from Kauaiian beaches were primarily small fragmented pieces (<11mm) of larger items (Table 6.1).

6.1.2 Gros Morne National Park, Newfoundland, Canada

Beaches in and near Gros Morne National Park followed a similar trend to Hawaiian beaches with compositions of analyzed plastics being 86% PE and 14% PP (Table 6.2). Fragmented pieces of larger items represent the main component of debris.

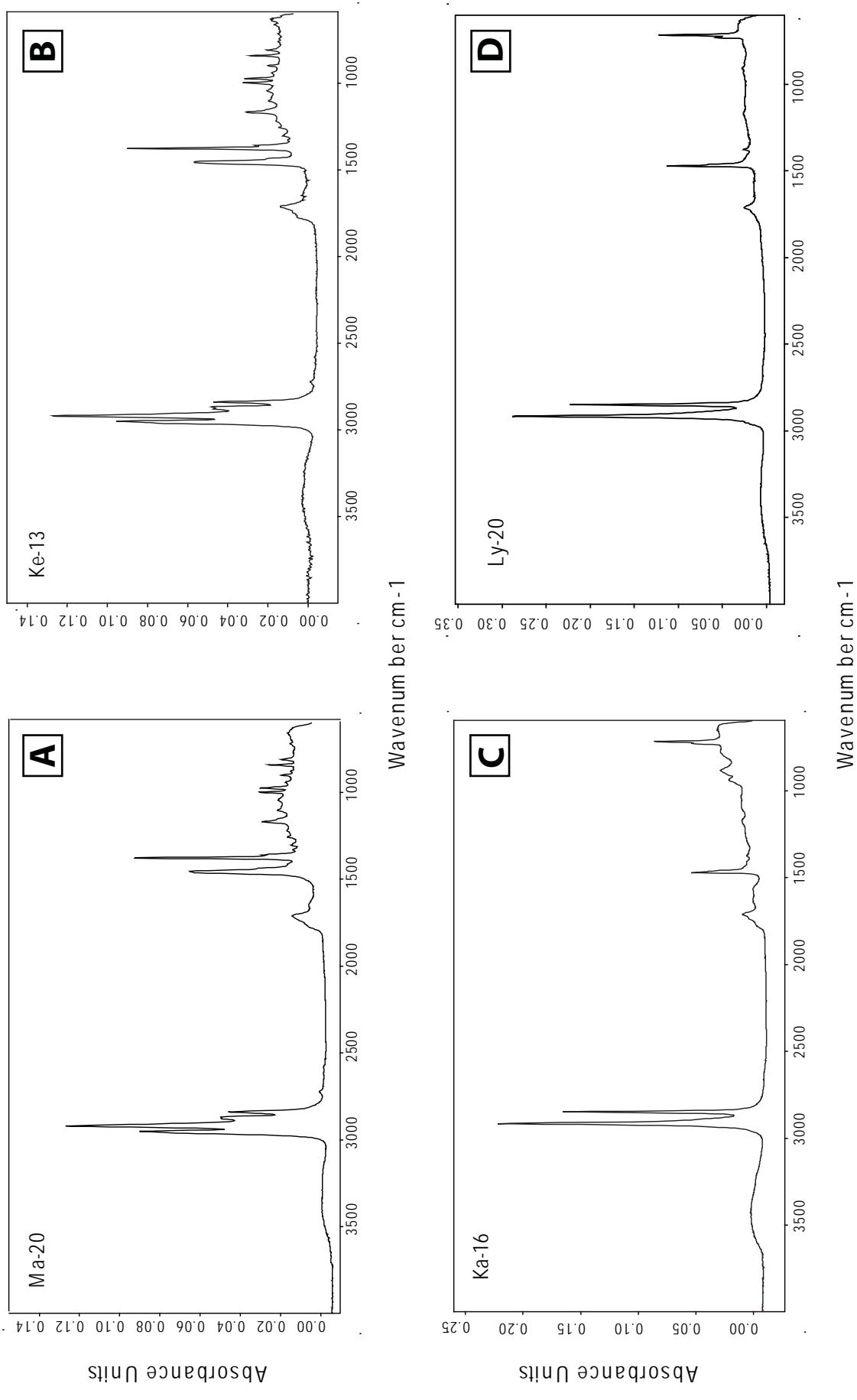


Figure 6.1 FTIR spectra of samples collected from Kauai beaches, indicating high levels of oxidation based on peak height at approximately 1700 cm^{-1} wavenumber relative to characteristic polyethylene peak heights at 1471 cm^{-1} . A), B) Samples Ma-20, Ke-13 are polypropylene, C), D) Samples Ka-16, Ly-20 are polyethylene.

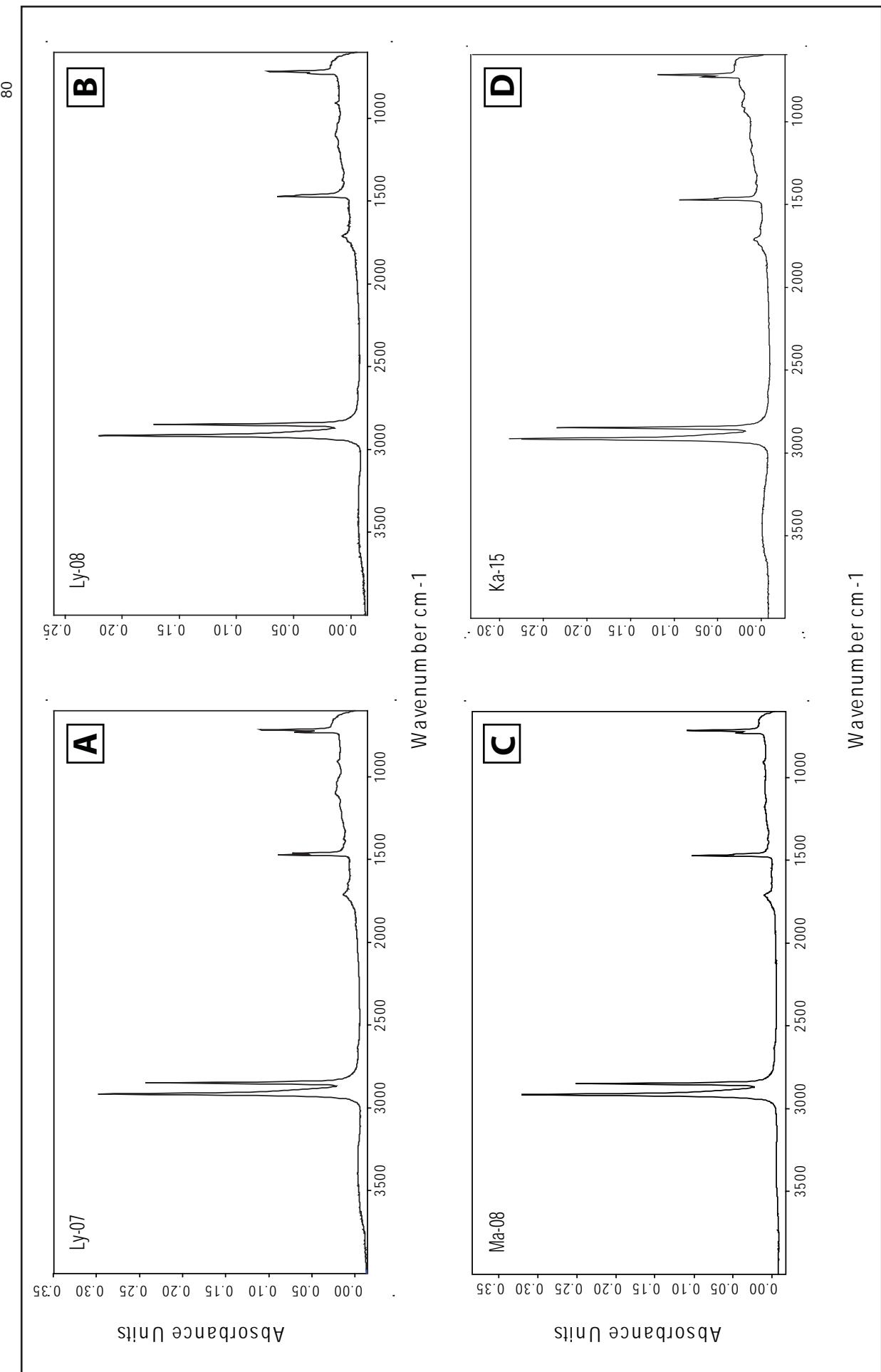


Figure 6.2 FTIR spectra of samples collected from Kauai beaches indicating medium levels of oxidation based on peak height at approximately 1700 cm^{-1} wavenumber relative to characteristic polyethylene peak heights at 1471 cm^{-1} . All samples are polyethylene.

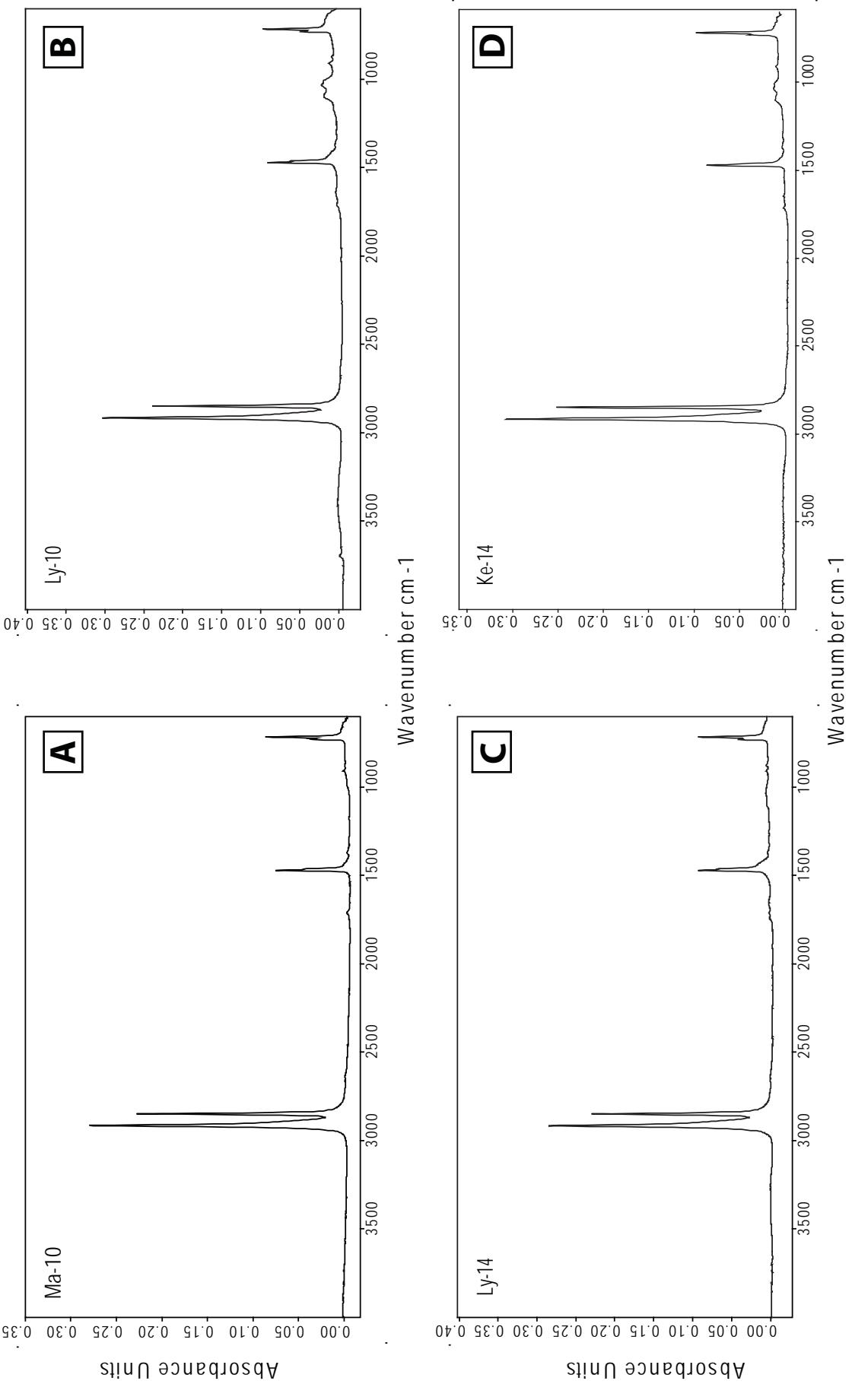


Figure 6.3 FTIR spectra of samples collected from Kauai beaches indicating low levels of oxidation based on peak height at approximately 1700 cm^{-1} wavenumber relative to characteristic polyethylene peak heights at 1471 cm^{-1} . All samples are polyethylene.

Table 6.1 Representative samples selected for FTIR and SEM analysis illustrating composition, size and oxidation level of debris from Kauaiian beaches. Oxidation levels were calculated using OPUS software, low 0-0.15, medium 0.16-0.30, high >0.31. PE- polyethylene, PP- polypropylene. (Modified from Cooper and Corcoran 2010).

Particle	Composition	Size (mm)	Oxidation (OPUS)	Oxidation (FTIR)
KE02	PE	10	0	low
KE03	PP	6	n.d.	high
KE04	PE	9	0	low
KE06	PE	10	0.20	med
KE08	PE	5	0.15	low
KE09	PP	7	n.d.	low
KE10	PE	6	0.06	low
KE13	PP	6	n.d.	high
KE14	PE	4	0	low
KE16	PE	5	0.18	low
KE17	PE	11	0.05	low
KE18	PE	7	0.21	med
KE19	PE	3	0.22	med
KE20	PE	9	0.21	med
KE21	PE	4	0.28	med
LY01	PE	4	0	low
LY03	PP	7	n.d.	low
LY04	PE	7	0.23	med
LY06	PP	9	n.d.	high
LY07	PE	9	0.19	med
LY08	PE	5	0.22	med
LY09	PE	4	0	low
LY10	PE	5	0.09	low
LY12	PE	5	0.18	med
LY14	PE	4	0.10	low
LY16	PE	3	0.13	low
LY18	PE	6	0.16	med
LY20	PE	4	0.39	high
LY21	PE	5	0.02	low
MA01	PE	10	0	low
MA02	PE	4	0	low
MA03	PE	6	0.01	low
MA04	PP	5	n.d.	high
MA05	PE	5	0	low
MA06	PE	8	0.26	med
MA07	PP	9	n.d.	low
MA08	PE	5	0.19	med
MA09	PE	4	0.02	low
MA10	PE	6	0	low
MA13	PE	6	0.14	low
MA14	PP	7	n.d.	med
MA15	PE	5	0.33	med
MA16	PE	5	0.30	med
MA18	PE	5	0.31	med
MA20	PP	4	n.d.	high
MA21	PE	7	0.24	med
KA05	PE	7	0.12	low
KA09	PE	7	0	low
KA10	PE	3	0	low
KA12	PE	4	0	low
KA13	PP	11	n.d.	med
KA15	PE	3	0.21	med
KA16	PE	4	0.38	high
KA17	PE	4	0	low
KA18	PP	6	n.d.	high
KA19	PE	4	0	low

Table 6.2 Representative samples selected for FTIR and SEM analysis illustrating composition, surface texture features, type of debris, and oxidation level of debris from Newfoundland beaches. Oxidation levels were calculated using OPUS software, low 0-0.15, medium 0.16-0.30, high >0.31. PE- polyethylene, PP- polypropylene, PS-polystyrene.

Sample	Composition	Oxidation Level (FTIR)	Oxidation Level (OPUS)	Surface textures	Debris type
NL-01	PS	ND	n.d	Linear fractures	Bottle cap
NL-02	PP	Low	n.d	Cracks, adhering particles	Lobster trap tag
NL-03	PE	Low	0.02	Cracks	Fragment
NL-04	PP	Low	n.d.	Fractures	Lobster trap tag
NL-06	PE	High	0.38	Fractures, granular oxidation	Fragment
NL-07	PE	Low	0.10	Grooves	Fragment
NL-10	PE	Low	0.02	Flakes, granular oxidation	Lobster trap tag
NL-13	PE	Low	0.05	Flakes, granular oxidation	Pellet
NL-14	PE	Med	0.19	Porous	Shotgun shell
NL-15	PE	Low	0.14	ND	Fragment
NL-16	PE	Low	0.09	Cracks	Cigar tip
NL-18	PE	Low	0	Flakes, adhering particles	Bottle
NL-19	PE	Low	0	Grooves, flakes	Lobster trap tag
NL-22	PE	Low	0.14	Adhering particles, grooves	Toy shovel
NL-23	PE	med	0.22	Flakes	Fragment

Composition of sampled debris was indicated by characteristic peaks at wavenumbers 2916, 2849, 1471, and 718 cm⁻¹ for PE, and characteristic peaks between 2723 and 2950 cm⁻¹ for PP (Figures 6.4-6.5, Appendix 1). The high proportion of intact, nearly intact and large fragmented debris provided for easier identification of debris type relative to Kauaiian samples (Table 6.2). Based on composition and visual assessment, sources of plastic debris collected from Newfoundland beaches were disseminated into five categories, including i) Hunting/Fishing gear, ii) Food packaging, iii) Medical/Sanitary, iv) Consumer goods, and v) Indeterminate (fragments) (Figure 6.6).

6.2 Oxidation of samples

Increased absorption peaks in FTIR spectra near wavenumber 1711 cm⁻¹ are indicative of oxidation. Oxidation levels were classified as low, medium or high, (see table 6.1) based on increased peak height at 1711 cm⁻¹ relative to the characteristic peak height at 1471 cm⁻¹ when compared against standard blanks (Figure 6.7). Samples collected from the islands of Kauai and Newfoundland display varying levels of oxidation with relative increase of absorption peaks as indicated in figures 6.1-6.5, tables 6.1, 6.2, Appendix 1). Eleven PP samples from Kauaiian beaches were examined, 58% of these samples exhibited high oxidation levels, compared to 45 PE samples with just 0.04% being classified with high oxidation levels. This is consistent with data collected from experimentally degraded plastics, which indicate that PP is more conducive to photo-oxidative degradation relative to PE.

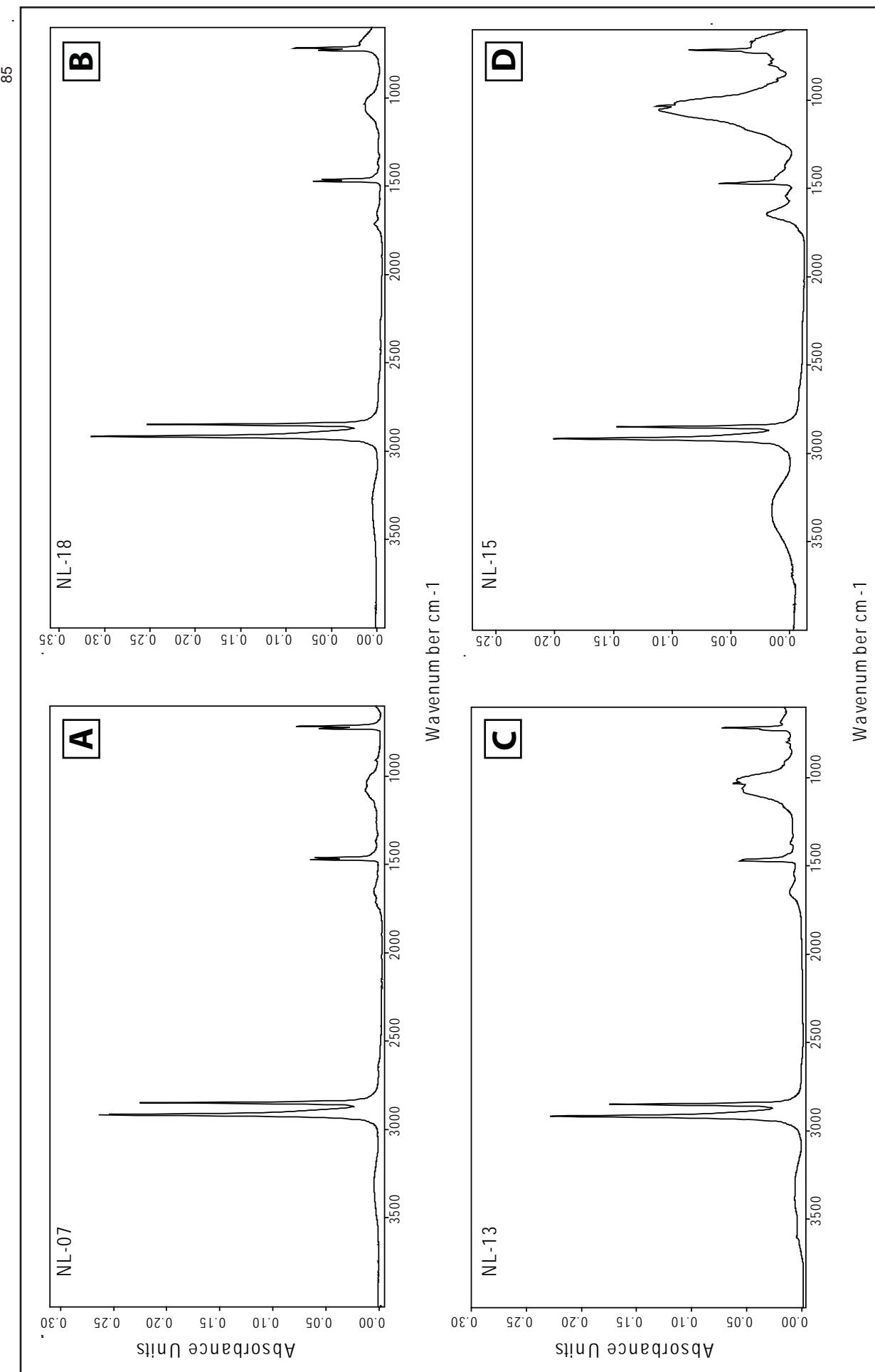


Figure 6.4 FTIR spectra of polyethylene samples collected from Newfoundland beaches indicating low, medium, and high levels of oxidation based on peak height at approximately 1700 cm^{-1} wavenumber relative to characteristic polyethylene peak heights at 1471 cm^{-1} .
 A), B) Samples NL-07 and NL-18, with low levels of oxidation, C) Sample NL-13 displays a medium level of oxidation and D) Sample NL-15 displays a high level of oxidation.

Figure 6.4

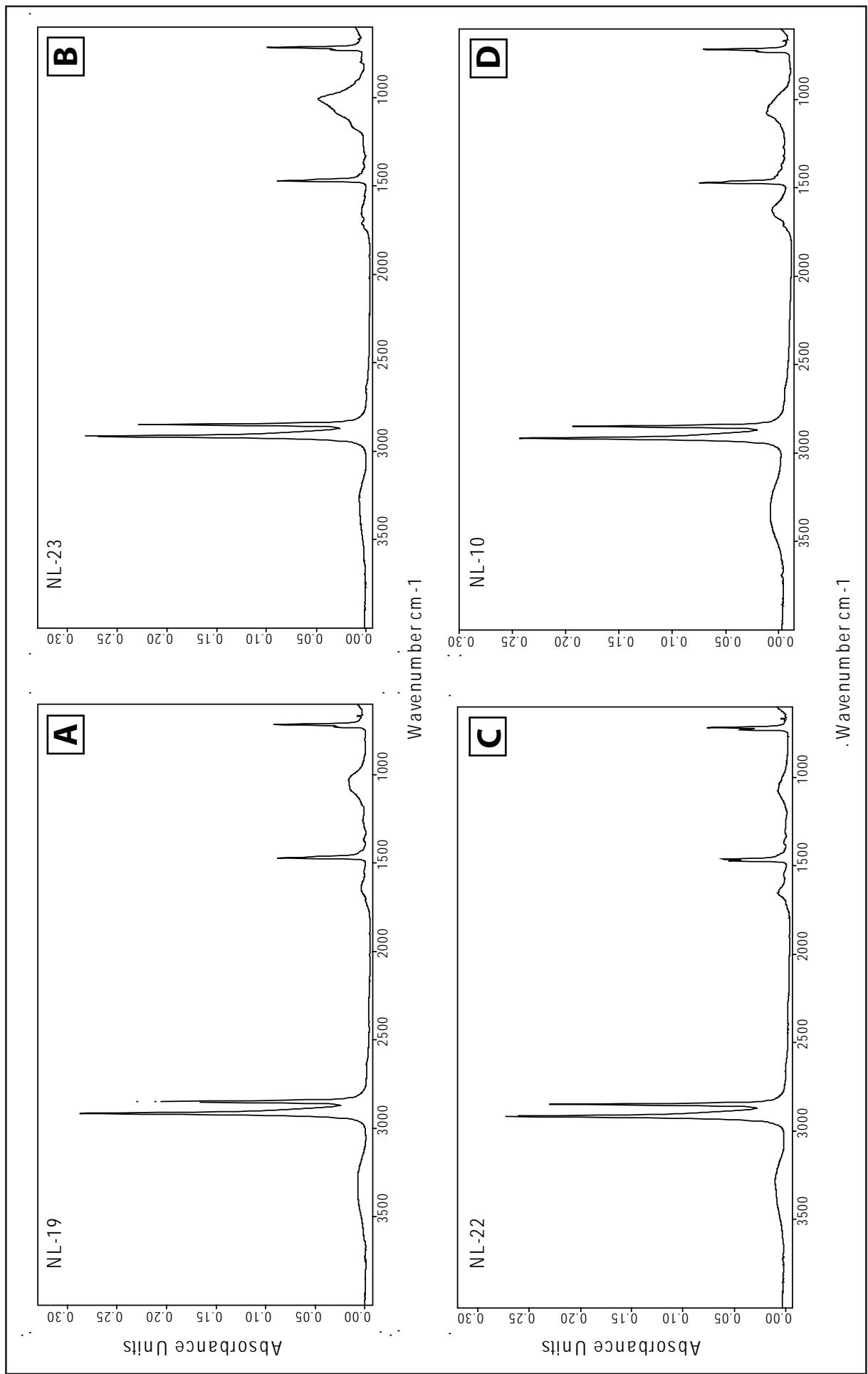


Figure 6.5 FTIR spectra of polyethylene samples collected from Newfoundland beaches indicating low, medium, and high levels of oxidation based on peak height at approximately 1700 cm^{-1} wavenumber relative to characteristic polyethylene peak heights at 1471 cm^{-1} .
 A), B) Samples NL-19 and NL-23, with low levels of oxidation, C) Sample NL-22 displays a medium level of oxidation and D) Sample NL-10 displays a high level of oxidation.

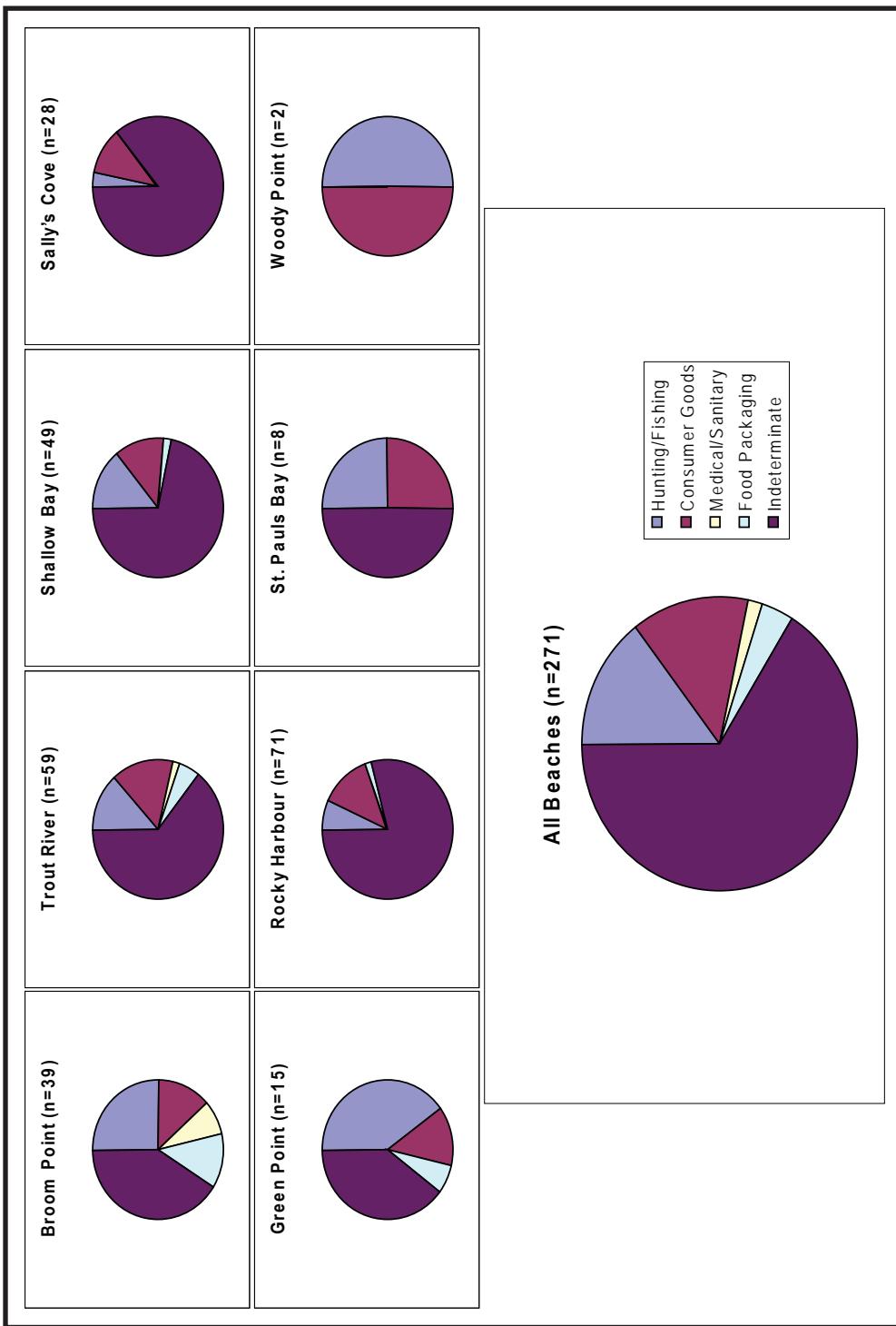


Figure 6.6 Pie graphs indicating sources of various debris types at each sampling location, as well as all beaches combined.

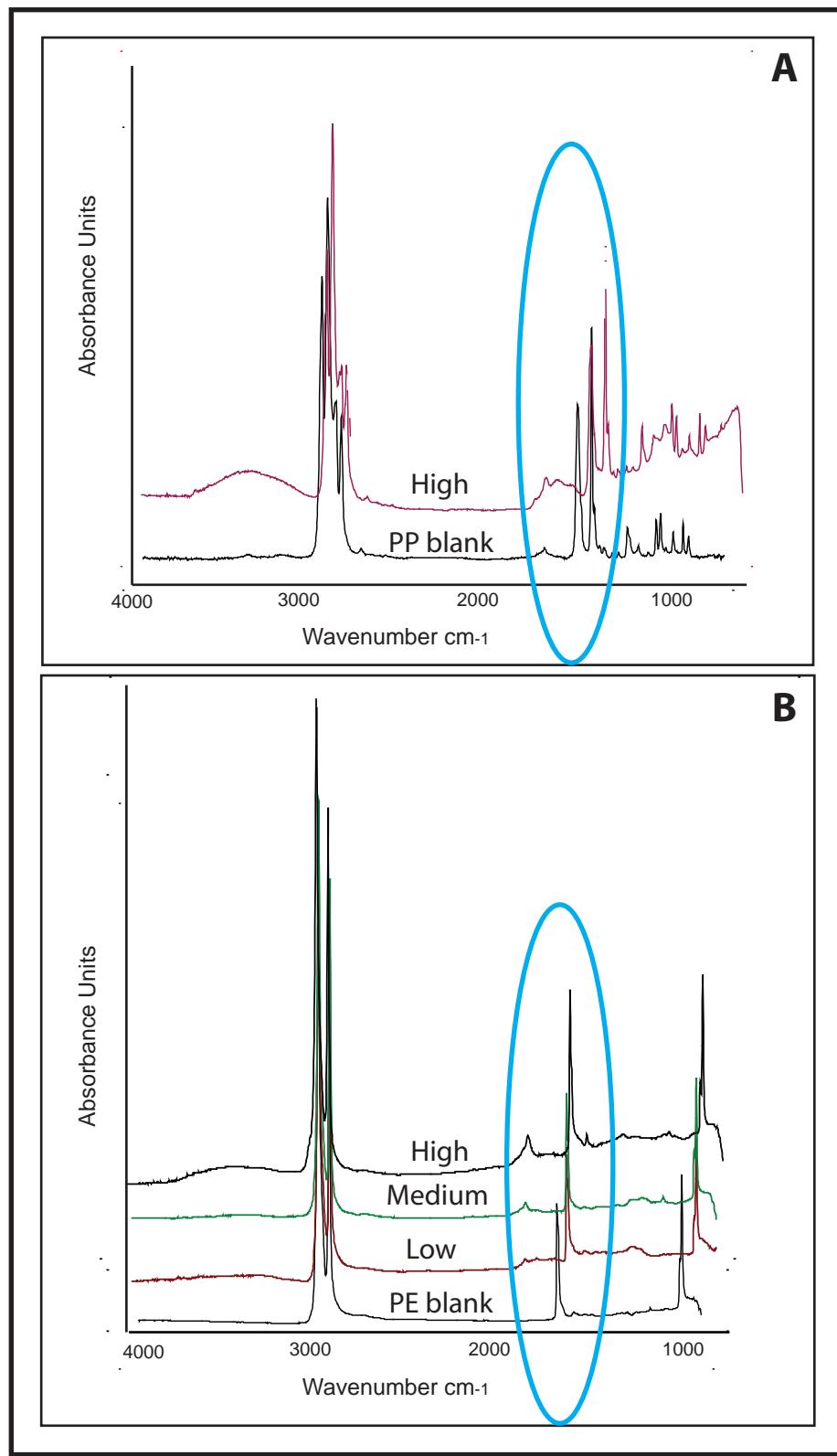


Figure 6.7 FTIR spectra illustrating increasing levels of oxidation of samples relative to pure untreated blanks at approximately 1711 cm^{-1} wavenumber region as indicated by blue circles, A) PP, B) PE.

CHAPTER 7

DEGRADATION OF SAMPLES

7.1 Chemically Produced Surface Textures

7.1.1 Flakes

Flaking involves the formation of a brittle surface area or layer on the polymer surface. This area or layer resembles a skin with a finite thickness that can become very brittle and subsequently detach from the polymer surface when exposed to natural weathering conditions (Kulshreshtha 1996). Flaking of a polymer can be facilitated by mechanically produced features, including fractures and cracks, which provide an ideal site for flaking to propagate (Figures 7.1-7.3, Appendix 2).

7.2 Mechanically Produced Surface Textures

7.2.1 Grooves

Grooves result from traction processes when plastic particles are dragged over harder materials, such as sand, granules or pebbles. Conversely they may also form when sediment grains are transported over stationary plastic debris. Grooves can be either curved or straight and are defined as deep elongate depressions or troughs caused by

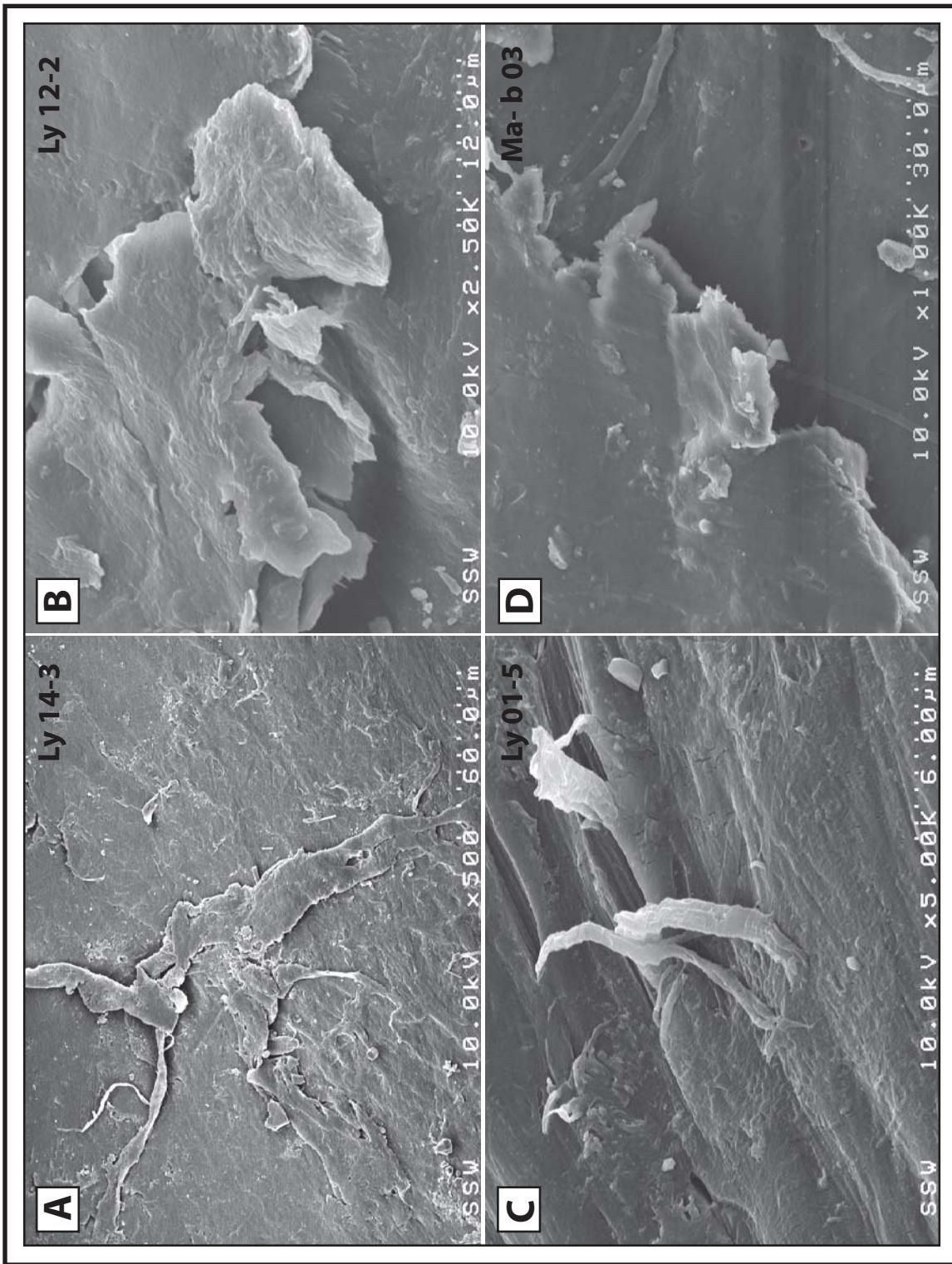


Figure 7.1 SEM images of chemically induced flakes on polymer surfaces sampled from Kauaiian beaches. A), B), C) collected from Lydgate Beach, D) collected from Maha'ulepu Beach.

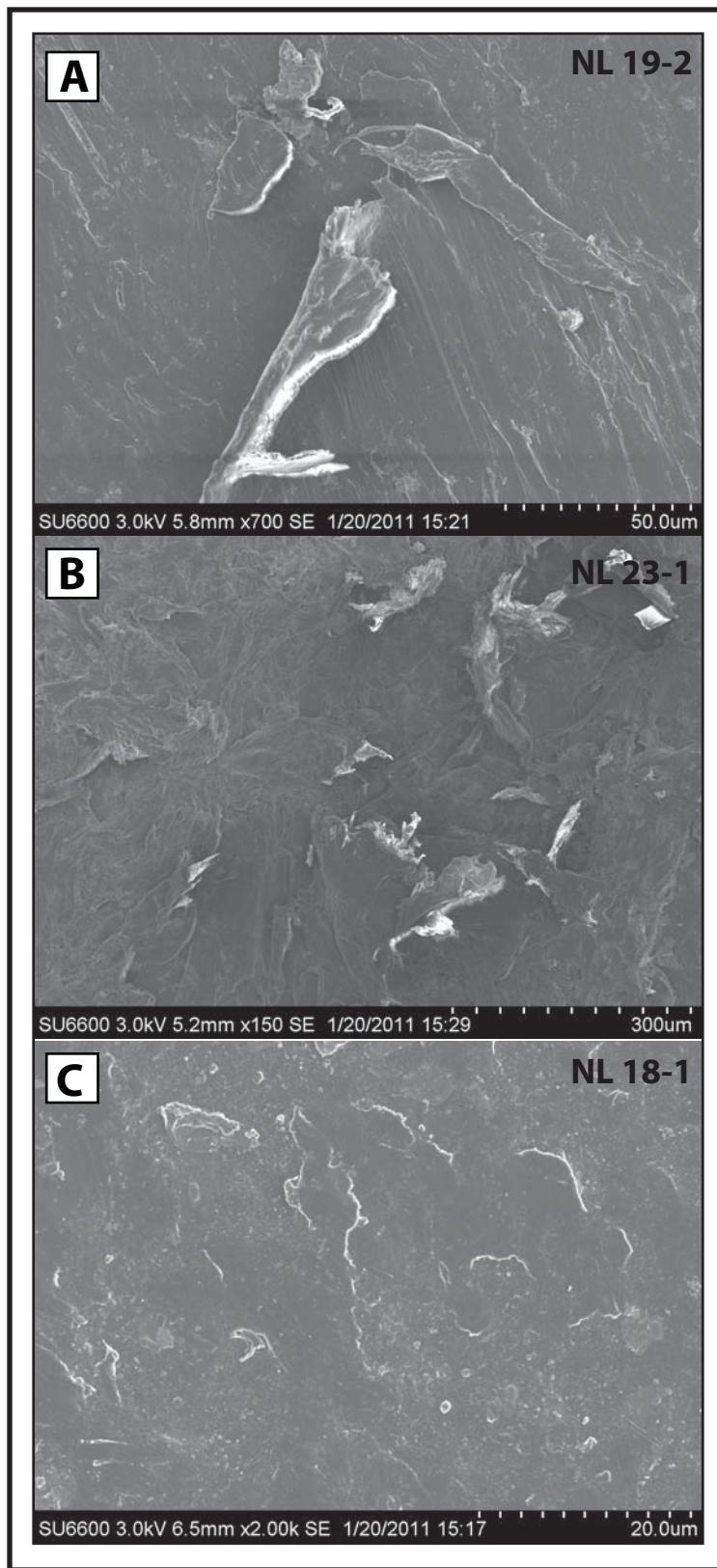


Figure 7.2 SEM images of chemically induced flakes identified on polymer surfaces sampled from Newfoundland beaches. A), C) collected from St. Pauls Bay, B) collected from Shallow Bay.

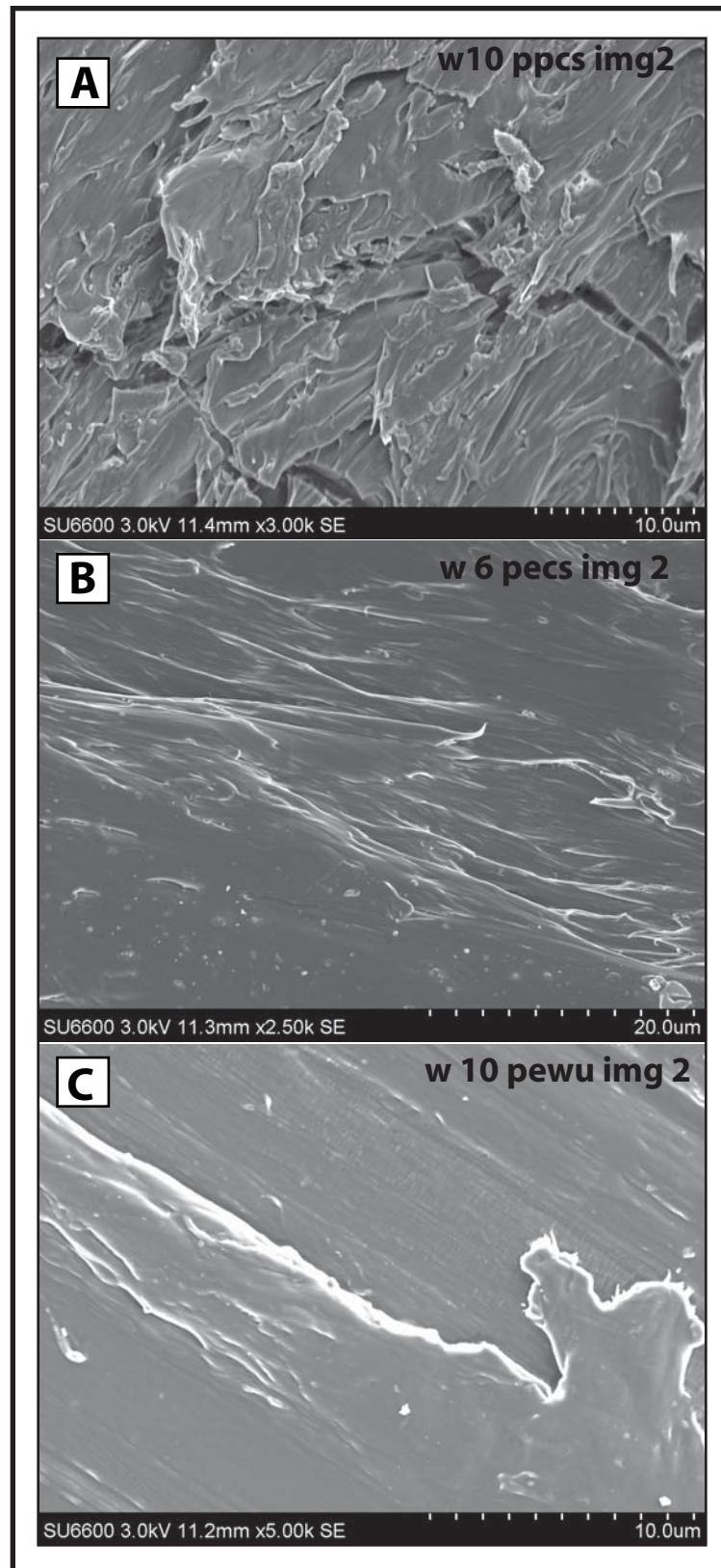


Figure 7.3 SEM images of chemically induced flakes on surfaces of experimentally degraded polymers. A) Polypropylene, B), C) Polyethylene.

some type of stylus (engraving tool). Straight grooves are deeper and distinctly linear relative to curved grooves (Mahaney 2002). Surface textural analysis indicates that the grooves on samples from both localities vary in width and length, are >100 μm long and >3 μm wide, are randomly oriented, and may be smooth or contain vertical notching (Figure 7.4, Appendix 2).

7.2.2 Fractures

Fractures can be shallow or deep and may occur in linear or conchoidal formations. Linear fractures locally grade into conchoidal fractures which are curved and have a ribbed appearance similar to that of conch shells (Mahaney 2002). Examination of samples from both localities show fractures which are long and thin ($1\mu\text{m} \times 5\text{-}75\mu\text{m}$) occurring in a linear formation. These surface textures may be an early indication of stresses occurring on particles which have been embrittled through photo-oxidative processes (Figure 7.5, Appendix 2).

7.2.3 Cracks

Analysis of samples from both Kauai and Newfoundland indicate that large, deep cracks occur in both linear and random orientations (Figure 7.6, Appendix 2). Average sizes ranged from 3-5 μm wide, and 10-250 μm long, however, crack size is dependent

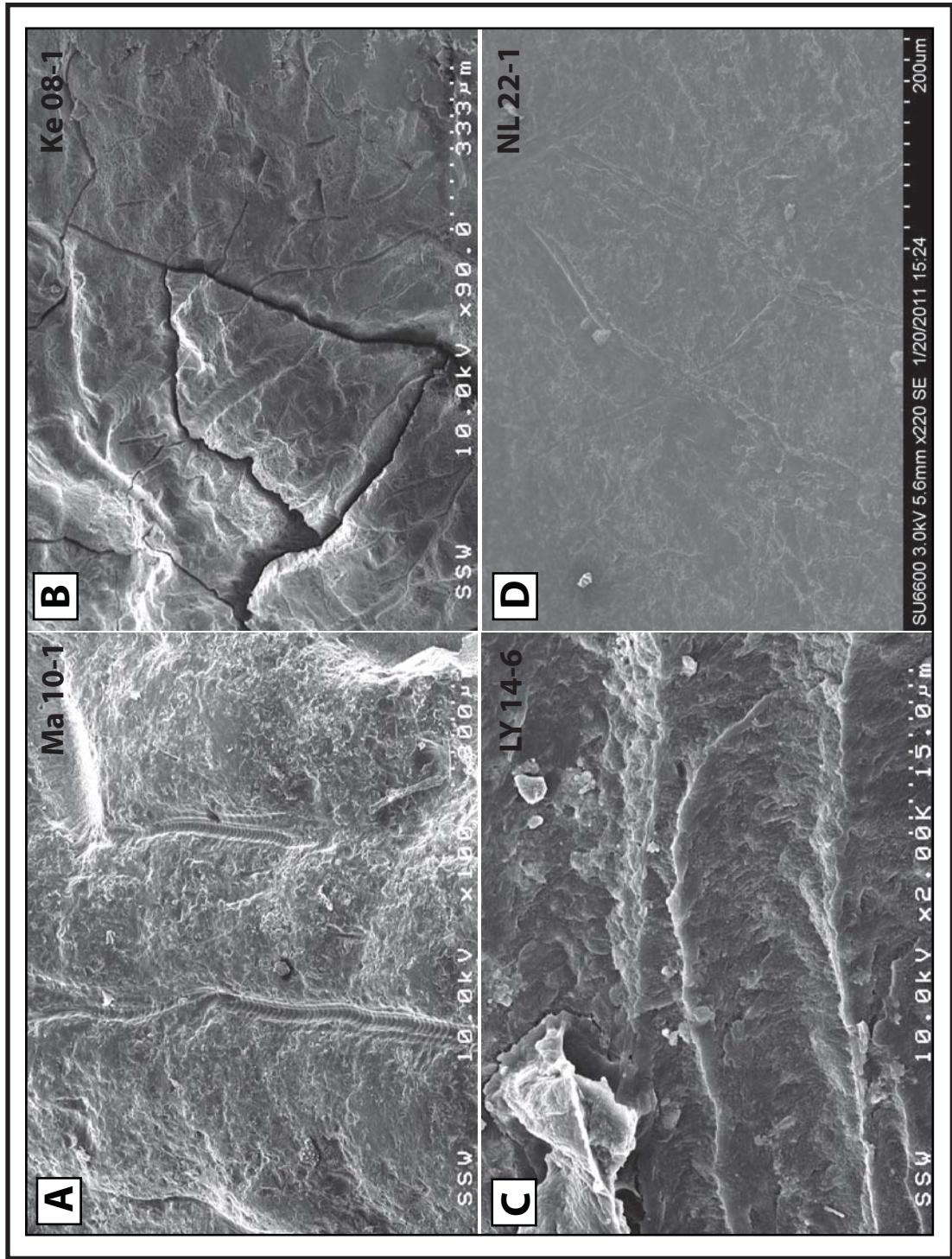


Figure 7.4 SEM images of grooves on polymer surfaces sampled from Kauaian and Newfoundland beaches. A) Sample Ma 10-1 collected from Maha'ulepu Beach, Kauai, B) Sample Ke 08-1 collected from Kealia Beach, Kauai, C) Sample LY 14-6 collected from Lydgate Beach, Kauai, and D) Sample NL 22-1 collected from Shallow Bay, Newfoundland.

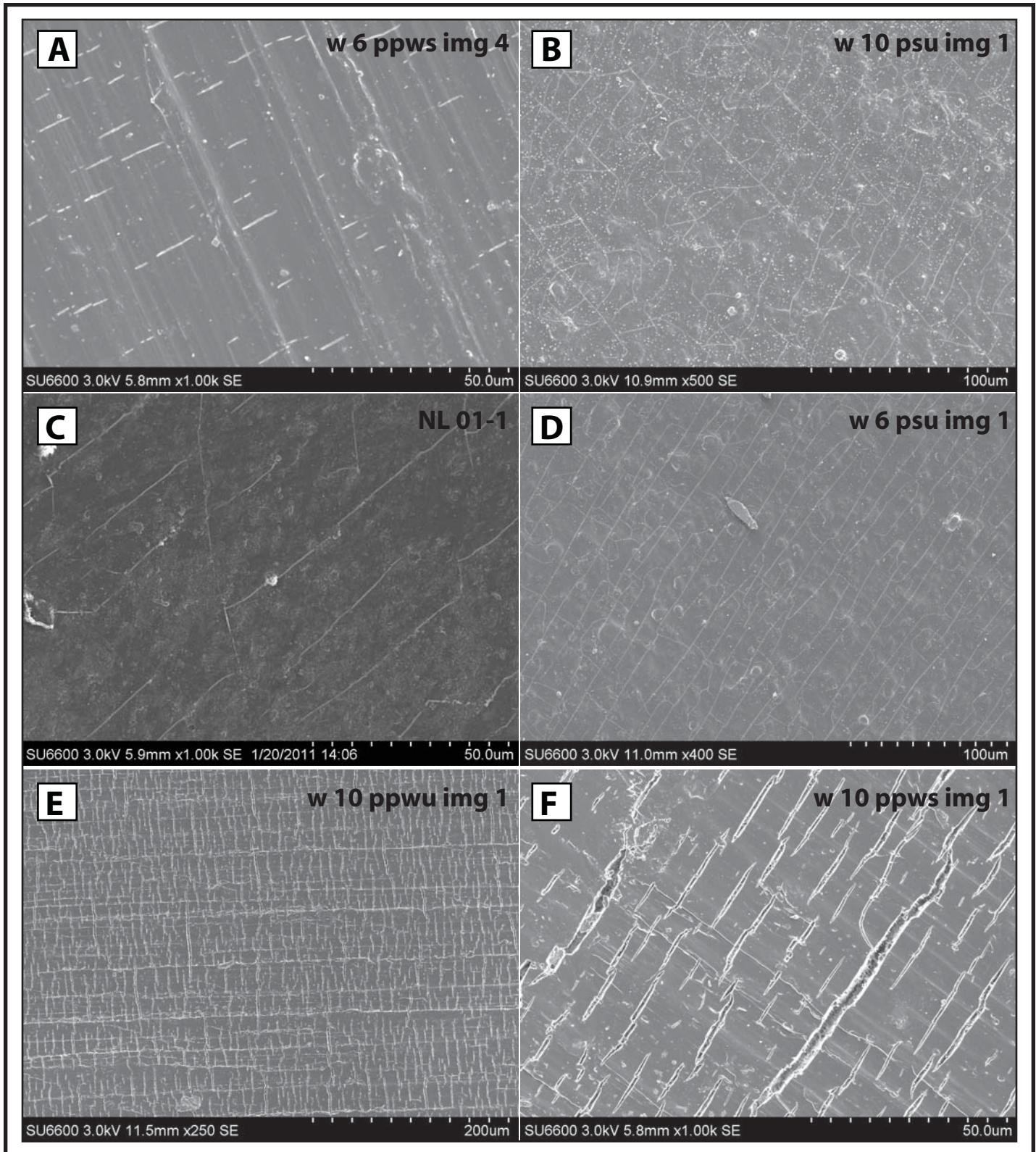


Figure 7.5 SEM images of small fractures forming on polymer surfaces. A), B), D), E), and F), are images of polymers degraded experimentally, C) Sample NL 01-1 was collected from Woody Point, Newfoundland.

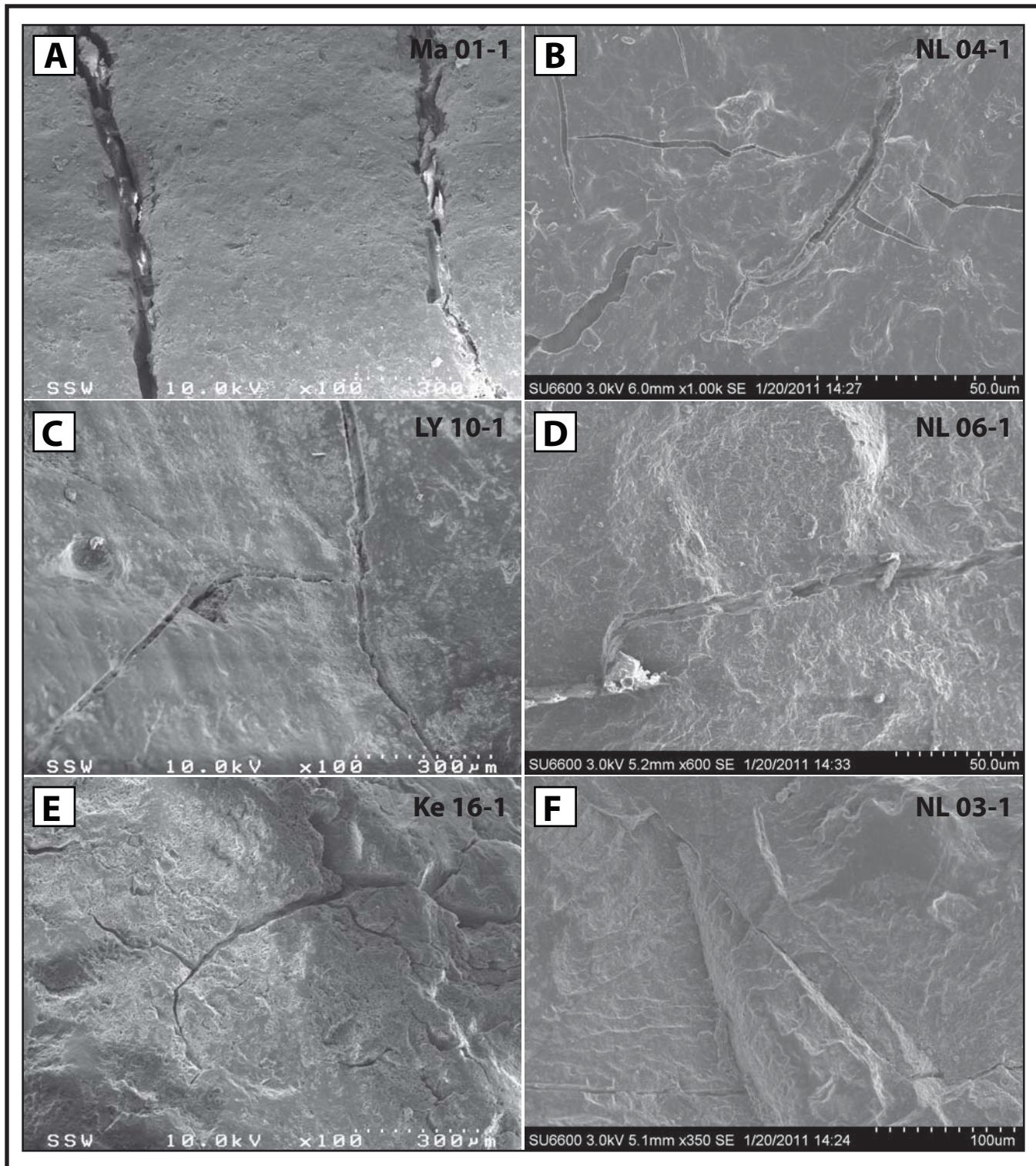


Figure 7.6 SEM images of cracks forming on the surfaces of various polymer samples. A), C), and E) Samples collected from Maha'ulepu, Lydgate, and Kealia beaches on the island of Kauai. B), D), Samples collected from Green Point, Newfoundland and F) Sample collected from Broom Point, Newfoundland.

on fragment size therefore these values represent ranges only. Cracks represent extended exposure to degradative processes, primarily photooxidation, and are an extension of fractures, which act as stress concentrators and fracture loci (Rabek 1996). Tensile stresses are placed on surfaces when polymers are exposed to moisture (e.g. humid air, direct rain or dew) and as the absorption of water causes swelling of plastic components. Desiccation of the surface layer leads to contraction which is hindered by the swollen layers below. This process may result in cracking due to the tensile stresses on the polymer surface (Rabek 1996). The growth of cracks can be limited by tie-molecules (fibrils) which were most prominent in samples degraded experimentally (Figure 7.7 A,C,D, Appendix 2), but were also identified on samples collected from Kauai (Figure 7.7 B, Appendix 2). Tie molecules induce plasticization when mechanical stresses are applied and can contribute to necking and elongation of the polymer (Kulshreshtha 1992).

7.2.4 Adhering Particles

Adhering particles are fragments or particles of other substances, either natural or synthetic, which have agglutinated to larger items (Mahaney 2002). The adhesion to plastic particles is a result of the cohesiveness of the surfaces. Examination of plastic debris from both sampling localities shows that adhering particles were prominent on many samples, occurred in random orientations, and were <20 µm in size (Figure 7.8, Appendix 2).

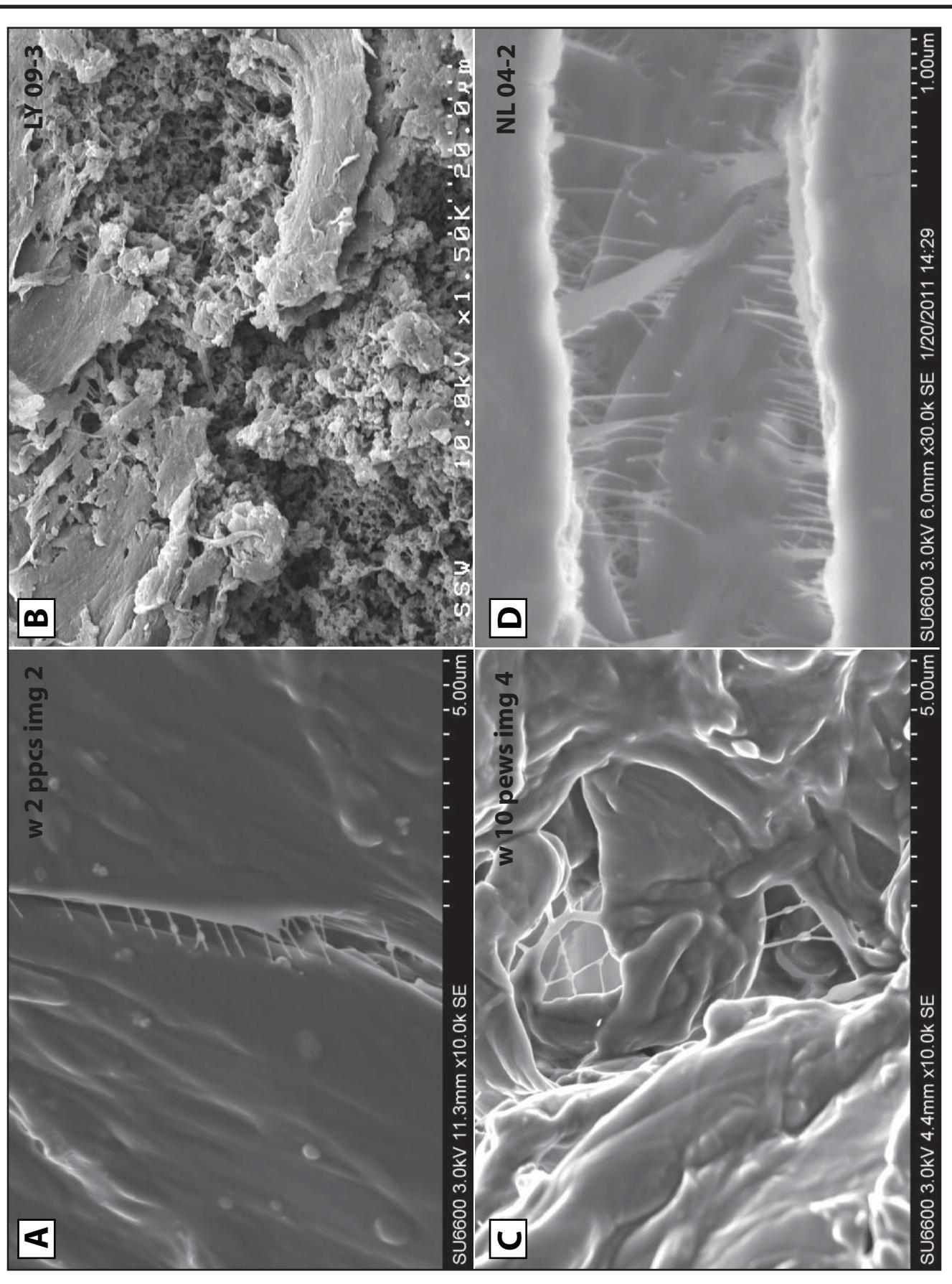


Figure 7.7 SEM images of tie molecules (fibrils) which limit the propagation of cracks in the polymer surface. A), C) Samples of experimentally degraded polymers, B) Sample collected from Lydgate Beach on the island of Kauai, D) Sample collected from Broom Point, Newfoundland.

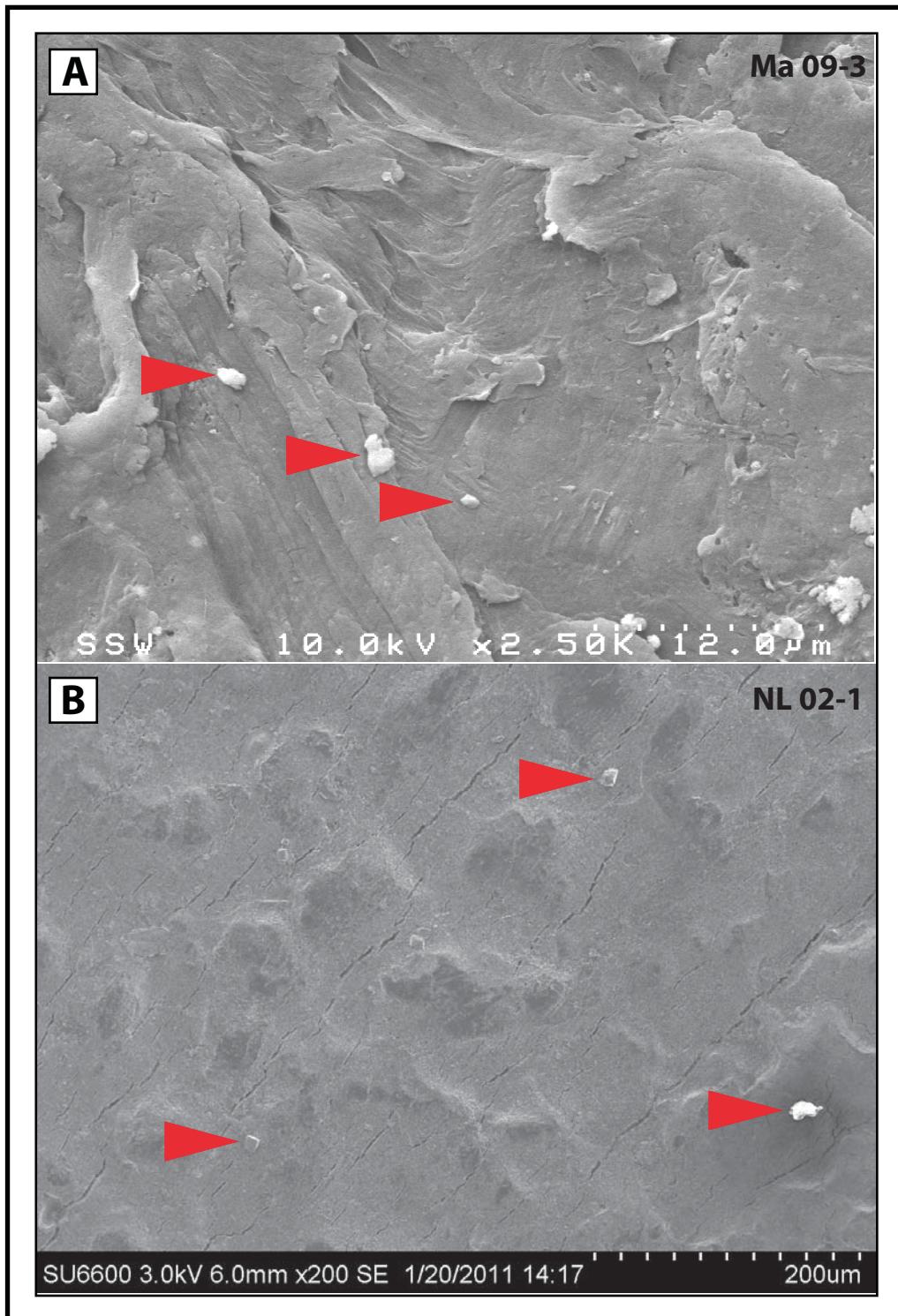


Figure 7.8 SEM images of adhering particles on polymer surfaces indicated by red arrows. A) Sample collected from Maha'ulepu Beach on the island of Kauai, B) Sample collected from Woody Point, Newfoundland.

7.2.5 Pits

Pits are small impact sites on the polymer surface caused by mechanical forces exerted on the particle while at sea, in the surf zone, or once deposited on the beach. Pits can form when plastics are hit by hard objects such as hail or sand grains. Analysis of sampled debris shows that impact sites are potential areas for increased oxidation, and/or mechanisms for transport of biological organisms (Figure 7.9, Appendix 2). Pits were identified only on samples from Kauai and were between 40 and 80 μm in diameter.

7.2.6 Vermiculate textures

Vermiculate textures have a burrow-like surface which may extend deeper into cracks and crevices. The visual characteristics of this surface texture suggest that it may be produced from a biological source, but this could not be confirmed. Vermiculate textures were present only on PE particles sampled from beaches on Kauai, Hawaii (Figure 7.10, Appendix 2).

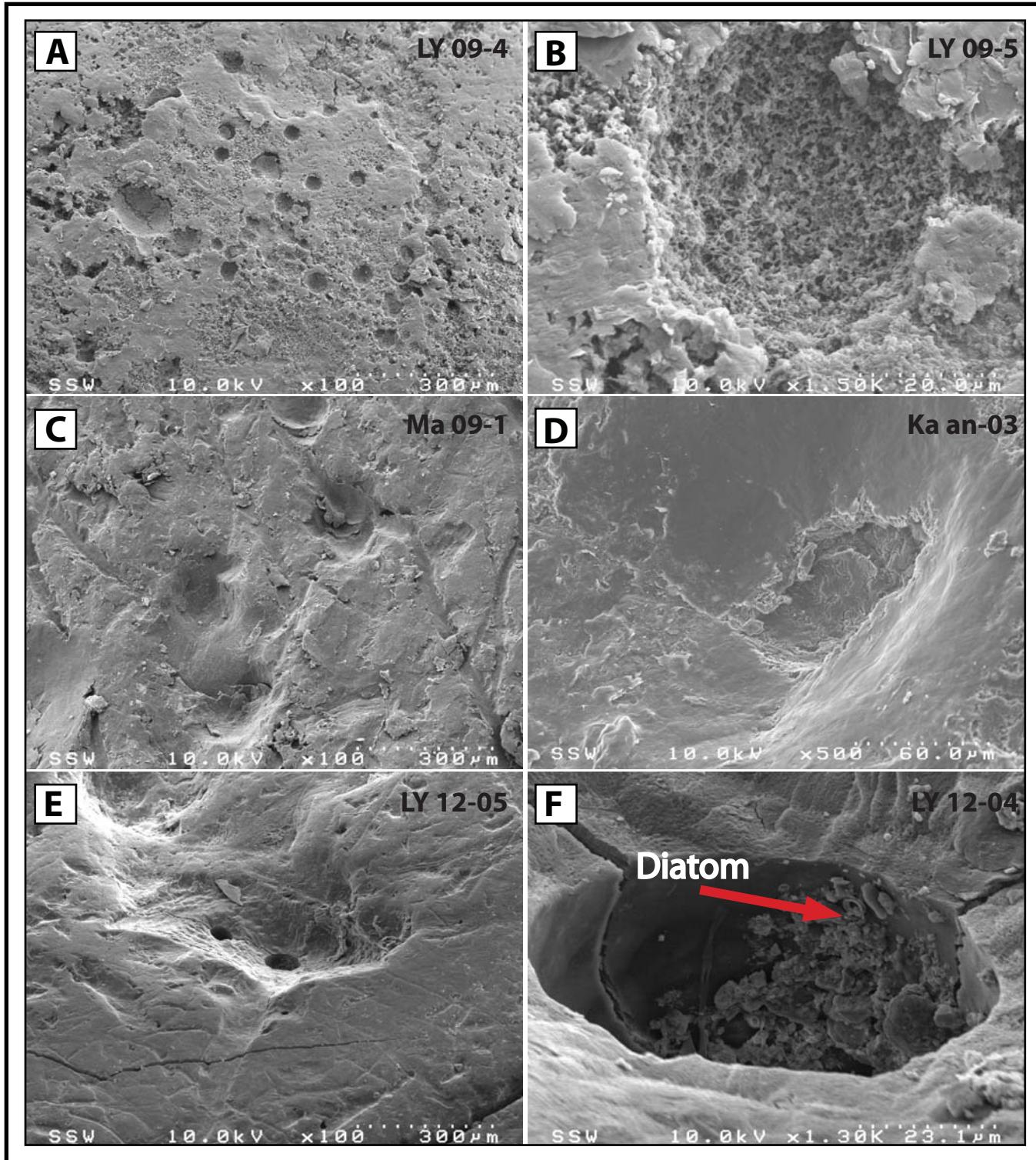


Figure 7.9 SEM images of pits formed on polymer surfaces of samples collected from Kauaiian beaches. A), B), E), F) Samples collected from Lydgate Beach, C) Sample collected from Maha'ulepu Beach, D) Sample collected from Kalihiwai Beach. Sample LY 09-5 displays how pits provide sites for oxidation to occur, sample LY 12-4 displays how pits may facilitate transport of microorganisms.

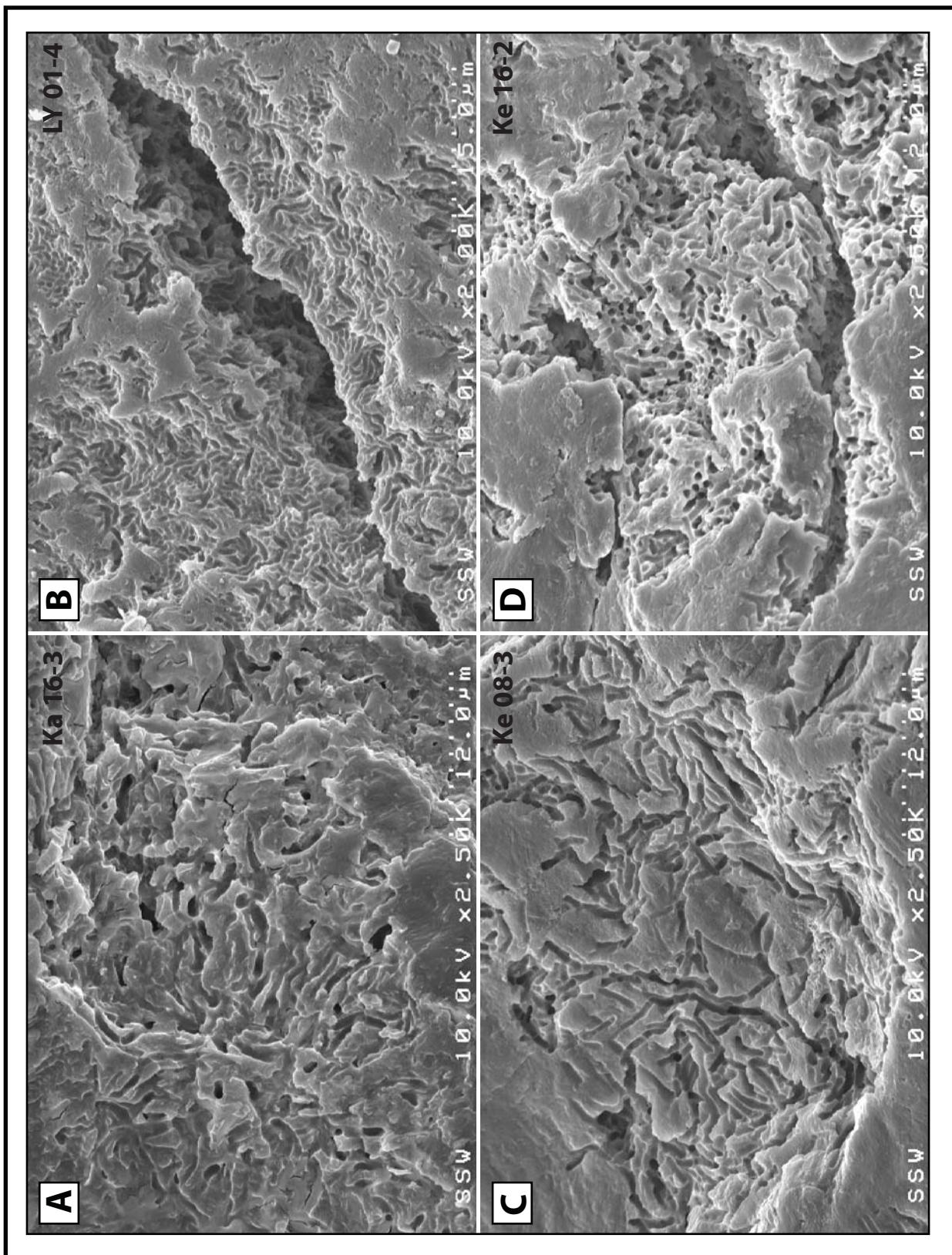


Figure 7.10 SEM images of vermiculate textures on polymer surfaces sampled from Kauaiian beaches. A) Sample Ka 16-3 collected from Kaliihiwai Beach, B) Texture extending into crack on sample LY 01-4 collected from Lydgate Beach, C), D) Samples Ke 08-3 and Ke 16-2 collected from Kealia Beach.

CHAPTER 8

EXPERIMENTAL CHAMBER STUDY

Three commonly used polymer types with various characteristics (Table 8.1) were compared and analyzed to clarify which surface textures form through chemical weathering in the absence of mechanical erosion. Samples included small (1 cm x 1 cm) particles of PE, PP and PS obtained from common household food packaging, as well as virgin plastic pellets from Nova Chemicals (Ontario, Canada). Ten pieces of each plastic type were placed on a sand base within a chamber maintaining a constant temperature of 26° C. The samples were irradiated with 366 nm of long wave ultraviolet radiation from a Mineralight Multiband hand held ultraviolet wand and were removed at weeks 2, 6, and 10. A second suite of samples was placed in a Kelvinator chest freezer at -16° C for ten weeks. The samples were then analyzed using FTIR and SEM (methods as outlined in chapter 4).

8.1 Effects of Composition and Time

We examined the effects of UV irradiation on PE fragments, PP fragments, PS fragments, and PE pellets over a period of 10 weeks. Exposure time was shown to be an important factor in the degradation of plastic, as evidenced from the gradual increase in crazing (cracking network) from weeks 0 to 10 (Figures 8.1-8.2). White PP and PS

Table 8.1 Polymer types and products used in the experimental chamber study.
 PP, polypropylene; PE, polyethylene; PS, polystyrene.

Polymer Type	PP (yogurt tub)	PE (yogurt lid)	PS (bread tag)	PE (pellet)
Characteristic	White unscored White scored Coloured unscored Coloured scored	White unscored White scored Coloured unscored Coloured scored	Scored Unscored Coloured unscored Coloured scored	Scored Unscored Unscored

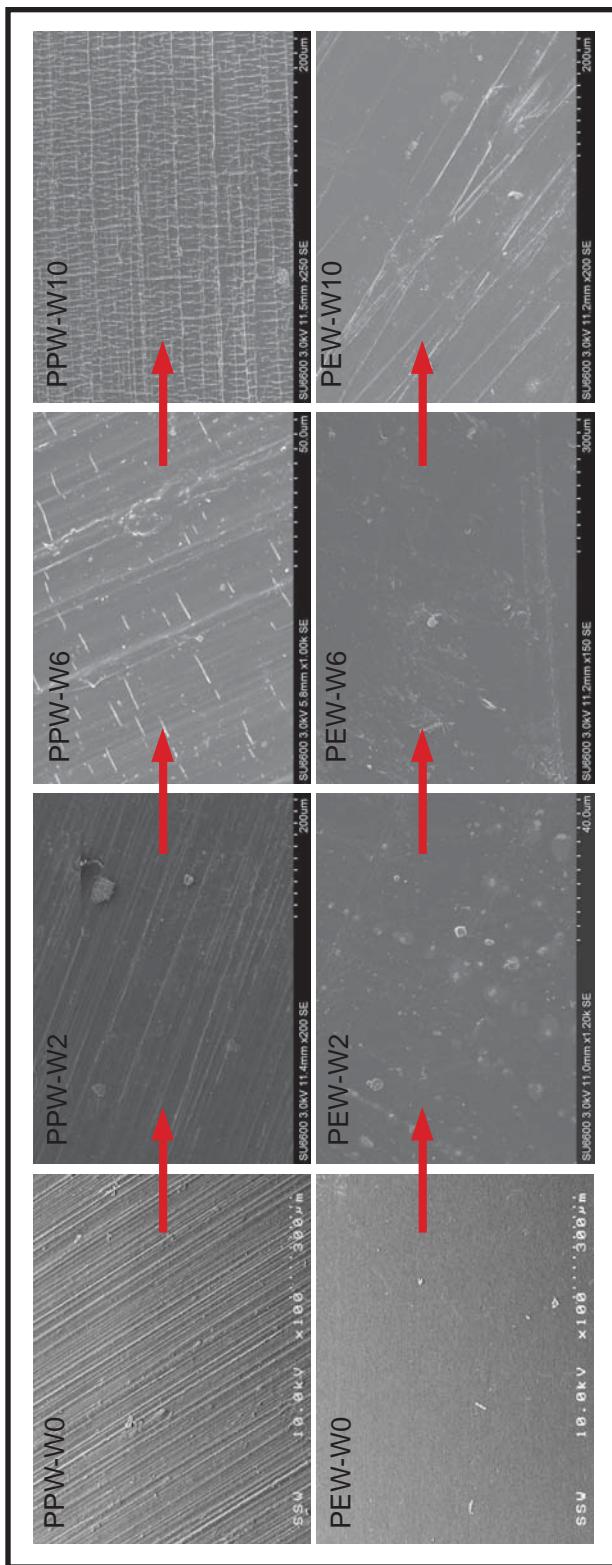


Figure 8.1 SEM images showing the effects of time on plastics degradation. W0, W2, W6, and W10 refer to the number of weeks during the experiment. Red arrows point to the gradual increase in surface textures within the same plastic type over time. PPW, white polypropylene fragment; PEW, white polyethylene fragment.

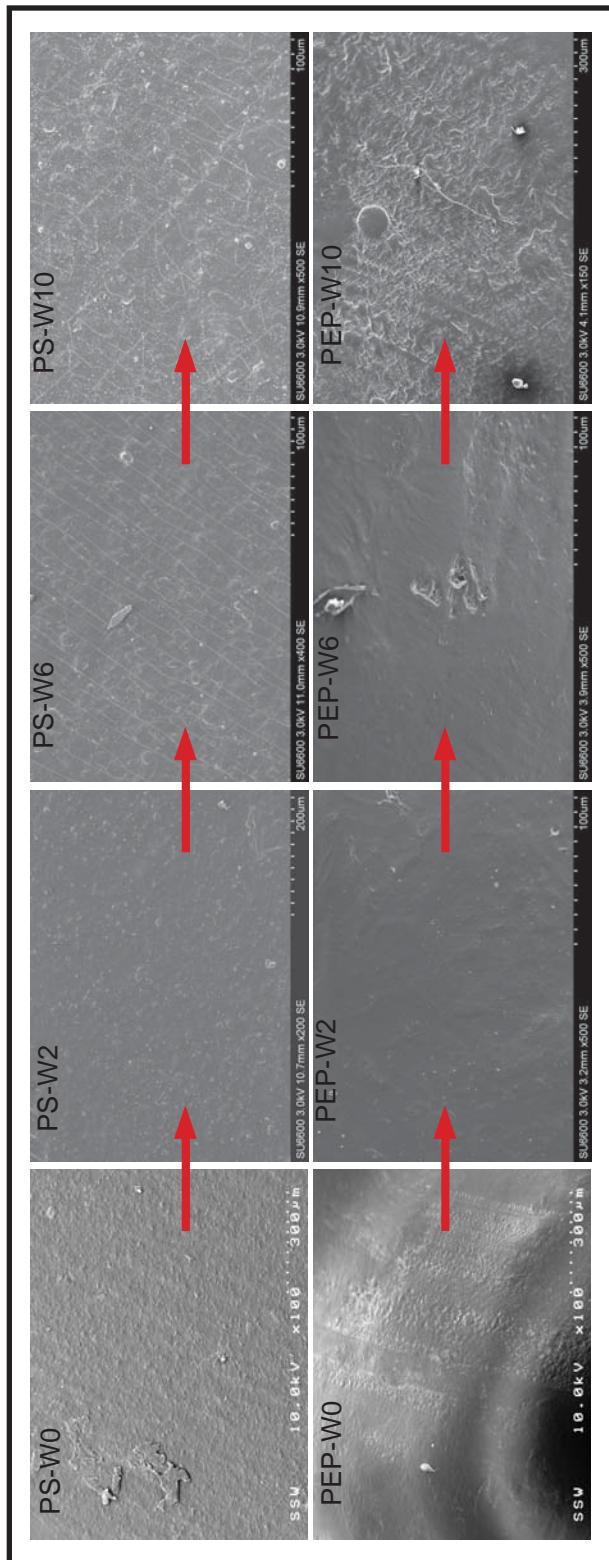


Figure 8.2 SEM images showing the effects of time on plastics degradation. W0, W2, W6, and W10 refer to the number of weeks during the experiment. Red arrows point to the gradual increase in surface textures within the same plastic type over time. PS, polystyrene fragment; PEP, polyethylene pellet.

exhibited the highest textural degree of degradation, which is supported by the successive increase in the level of oxidation as indicated by increased absorption peaks around the 1713 cm^{-1} wavenumber region on FTIR spectra (Figure 8.3). SEM imagery of PE fragments and pellets showed minimal textural changes. Zhao et al. (2007) demonstrated that pure PE samples irradiated with UV light for 100 hours undergo little alteration. FTIR spectra from this study were determined for PE pellets exposed to 1680 hours of UV light and we also found no significant increase in oxidation level. Previous research conducted by Cooper and Corcoran (2010) suggested that plastic debris sampled from subtropical beaches showed PE to be more conducive to chemical weathering relative to PP, however SEM imagery of the plastics in our experimental study clearly indicate that this is not the case. Instead, the more abundant weathering features in PE fragments from the sampled beaches must have experienced greater residence times at sea and/or on the beach than the PP types.

8.2 Effects of Colour

Both PE and PP fragments were used to determine the effects of color on degradation. The results indicate that the coloured fragments display minimal crazing compared with the white fragments (Figure 8.4). Coloured PE and PP showed very little change in surface textures over 10 weeks of UV exposure. FTIR spectra of coloured samples are affected by the paint on the surface of the plastic and therefore these samples were excluded from oxidation analysis.

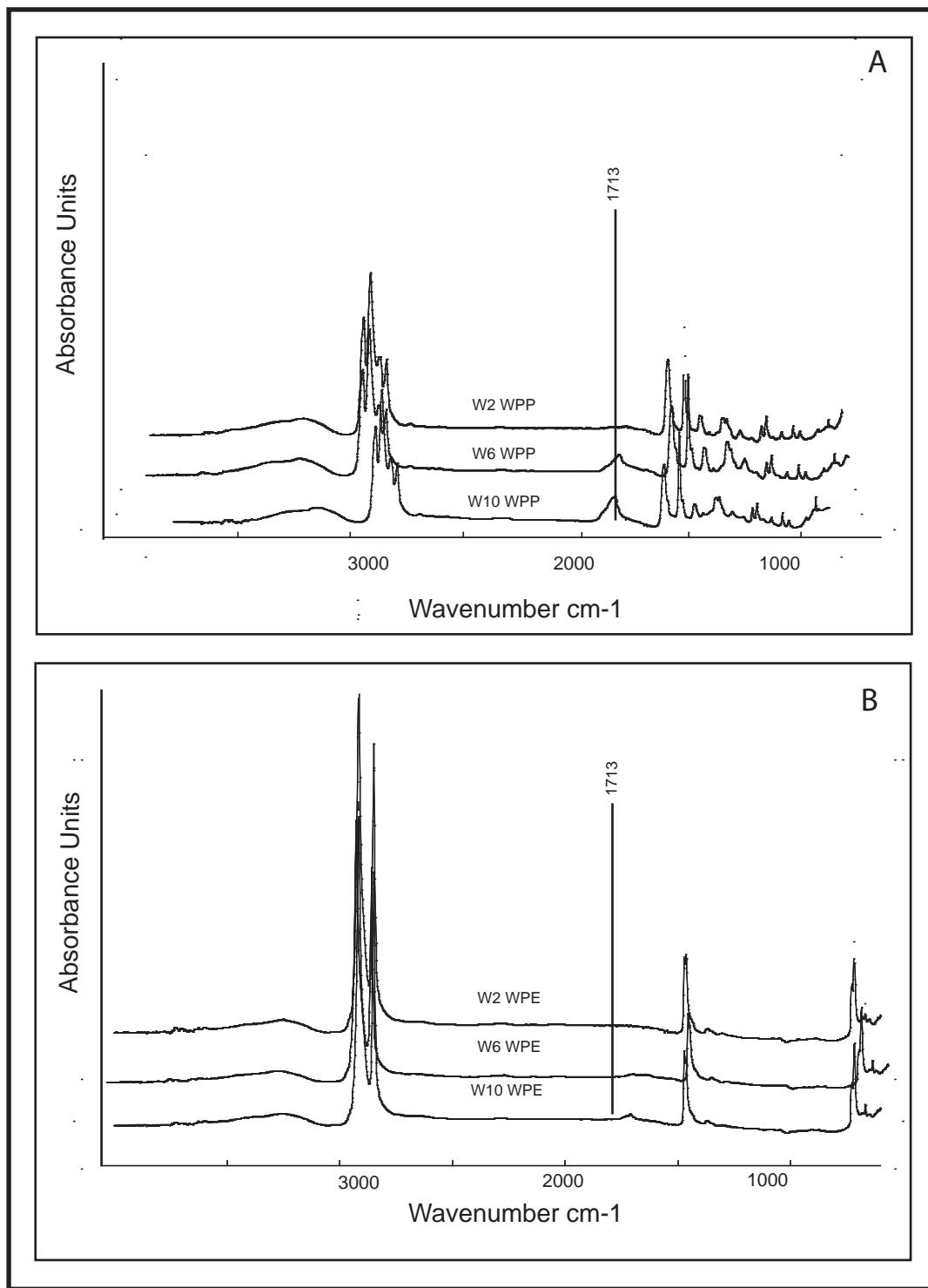


Figure 8.3 FTIR spectra for representative samples of A) white polypropylene (WPP) and B) white polyethylene (WPE) samples from weeks 2, 6, and 10. Note the increase in peak height at the 1713 cm⁻¹ wavenumber region, which indicates the level of surface oxidation.

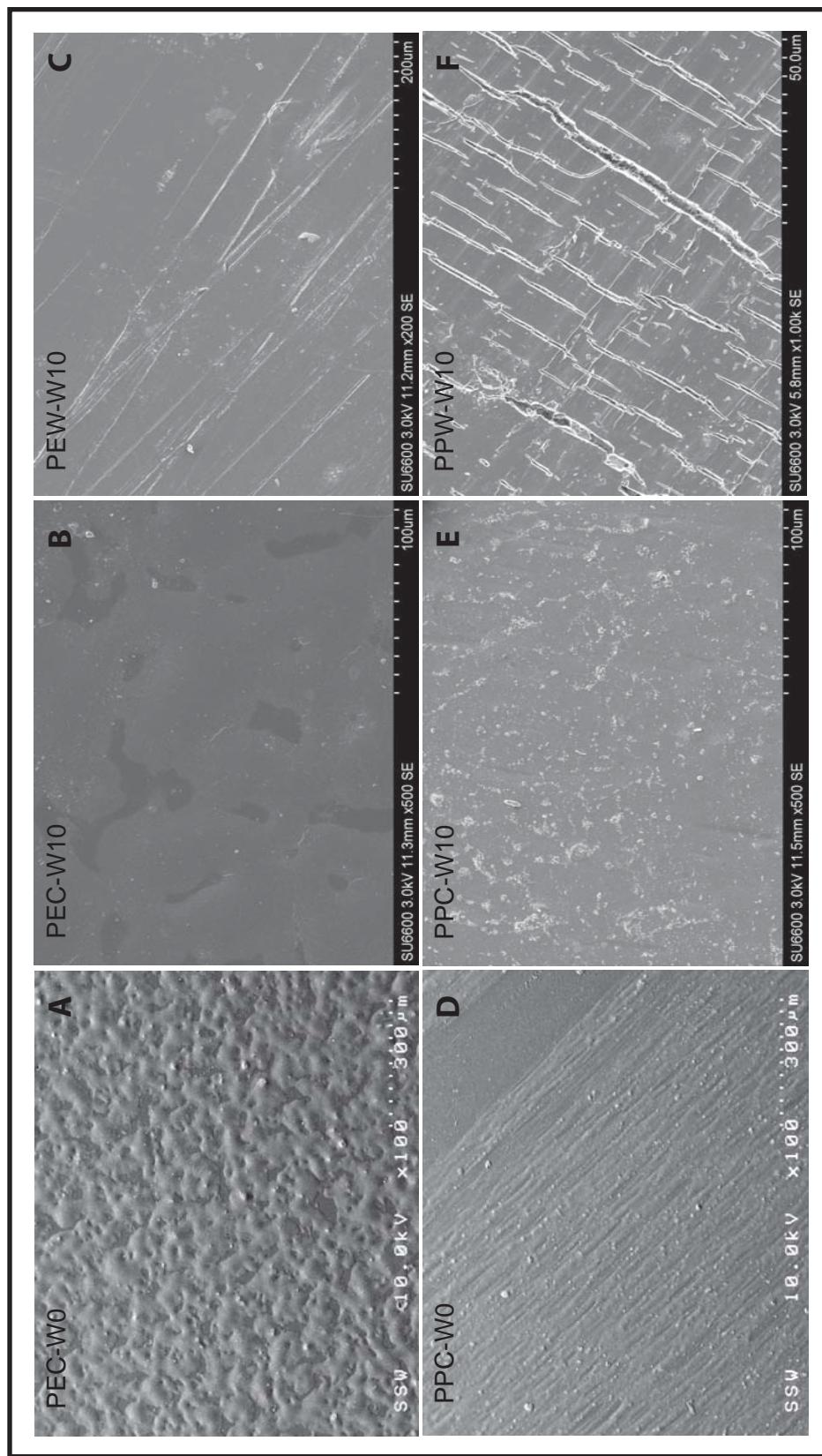


Figure 8.4 SEM images showing the effects of colour on plastics degradation. A) coloured polyethylene at week 0, B) coloured polyethylene at week 10, C) white polyethylene at week 10, D) coloured polypropylene at week 0, E) coloured polypropylene at week 10, F) white polypropylene at week 10. Note the abundance of fractures in samples PEW-W10 and PPW-W10 compared with the coloured samples.

8.3 Effects of Scoring

Certain plastic fragments were scored (incised) in order to simulate the effects of mechanically-produced fractures on the rate of chemical weathering (Figures 8.5-8.6). Previous research conducted by Corcoran et al. (2009) and Cooper and Corcoran (2010) indicated that mechanically produced fractures and cracks are favourable sites for oxidative processes to occur. Artificially scored white PE exhibited little difference in degradation relative to non-scored samples (Figure 8.5A), as a result of its chemical weathering-resistant nature. However, both white PP and PS show extensive degradation within the fractures compared with the non-scored surface (Figure 8.5 B,C). The results also indicate that coloured PP and PE, which are preferentially resistant to chemical weathering, readily degrade within the incisions (Figure 8.6 D,E). PE pellets are homogenous in their composition and, as expected, showed no significant difference in degradation within the incision compared with the surface.

8.4 Effects of Cold Temperatures

Cold temperatures in the absence of UV radiation for 10 weeks had little effect on surface textures of the different plastic types. White PP, white PE, PE pellets and PS displayed little to no degradation from week 0 to week 10. Analysis of SEM images displayed only minor degradation in specific areas. Coloured PE and PP experienced minor flaking as a result of cold exposure (Figure 8.7). Similarly, FTIR spectra of samples exposed to cold exhibit no noticeable difference in the level of oxidation.

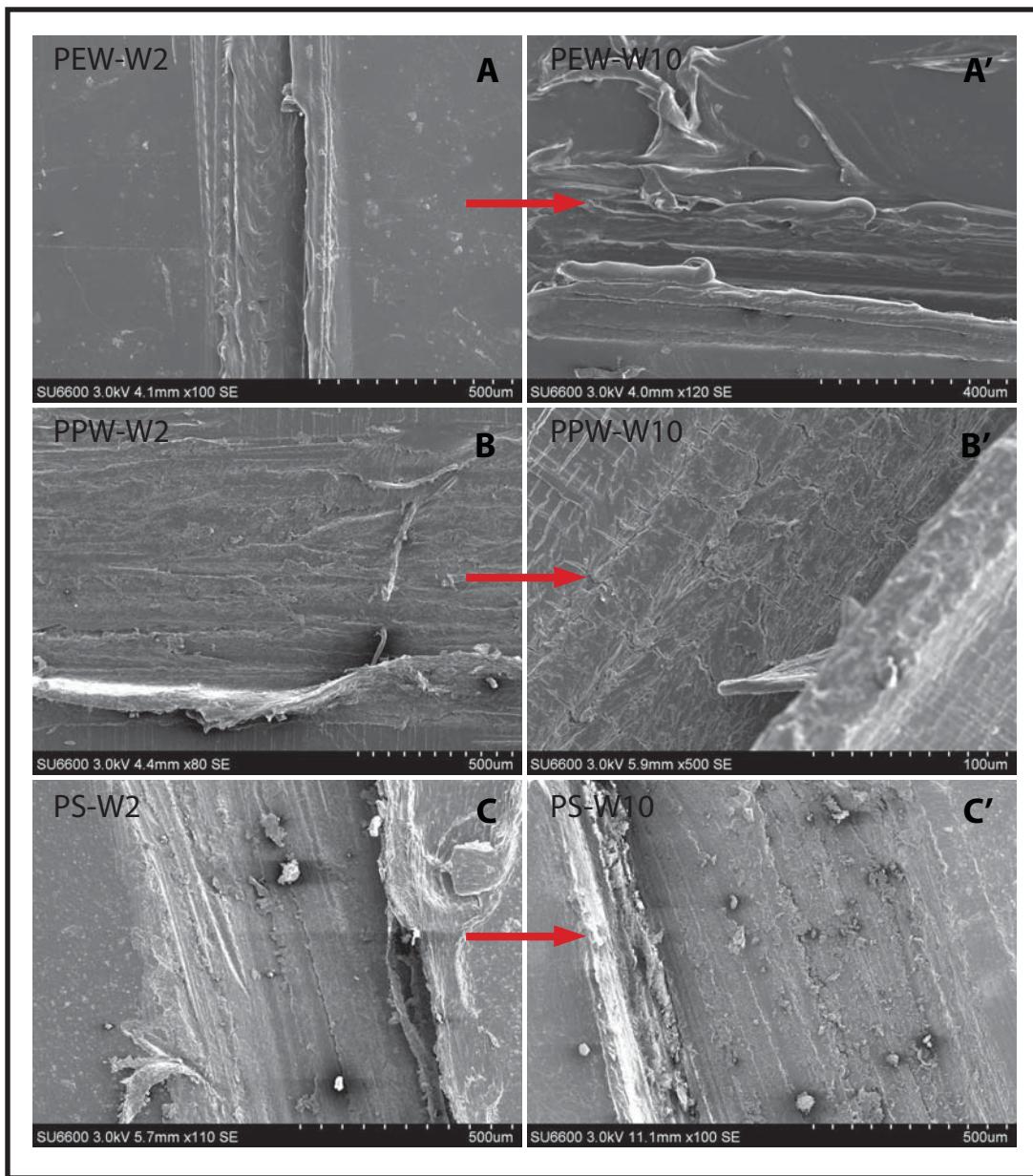


Figure 8.5 SEM images showing the effects of scoring on plastics degradation. A-A') white polyethylene at weeks 2 and 10, B-B') white polypropylene at weeks 2 and 10, C-C') polystyrene at weeks 2 and 10. Red arrows point to the gradual increase in surface textures over time. Note that there is no notable difference between white polyethylene between weeks 2 and 10.

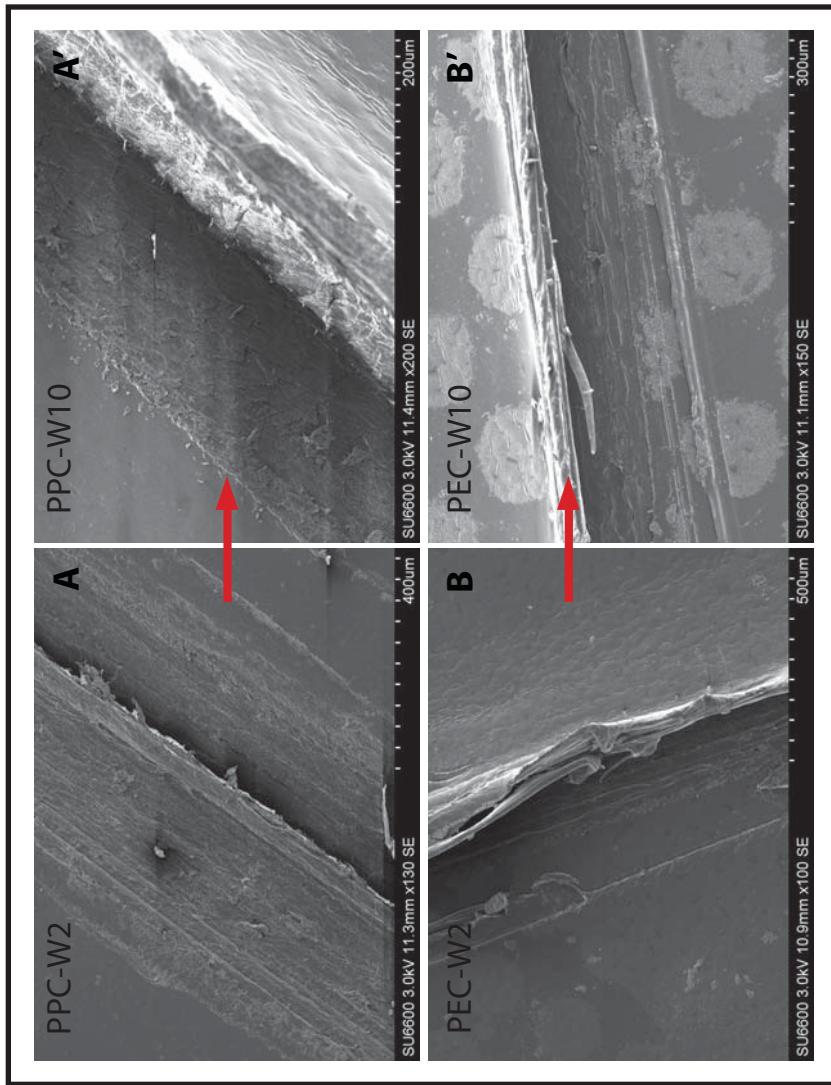


Figure 8.6 SEM images showing the effects of scoring on plastics degradation.
A-A') coloured polypropylene at weeks 2 and 10, B-B') coloured polyethylene at weeks 2 and 10. Red arrows point to the gradual increase in surface textures over time.

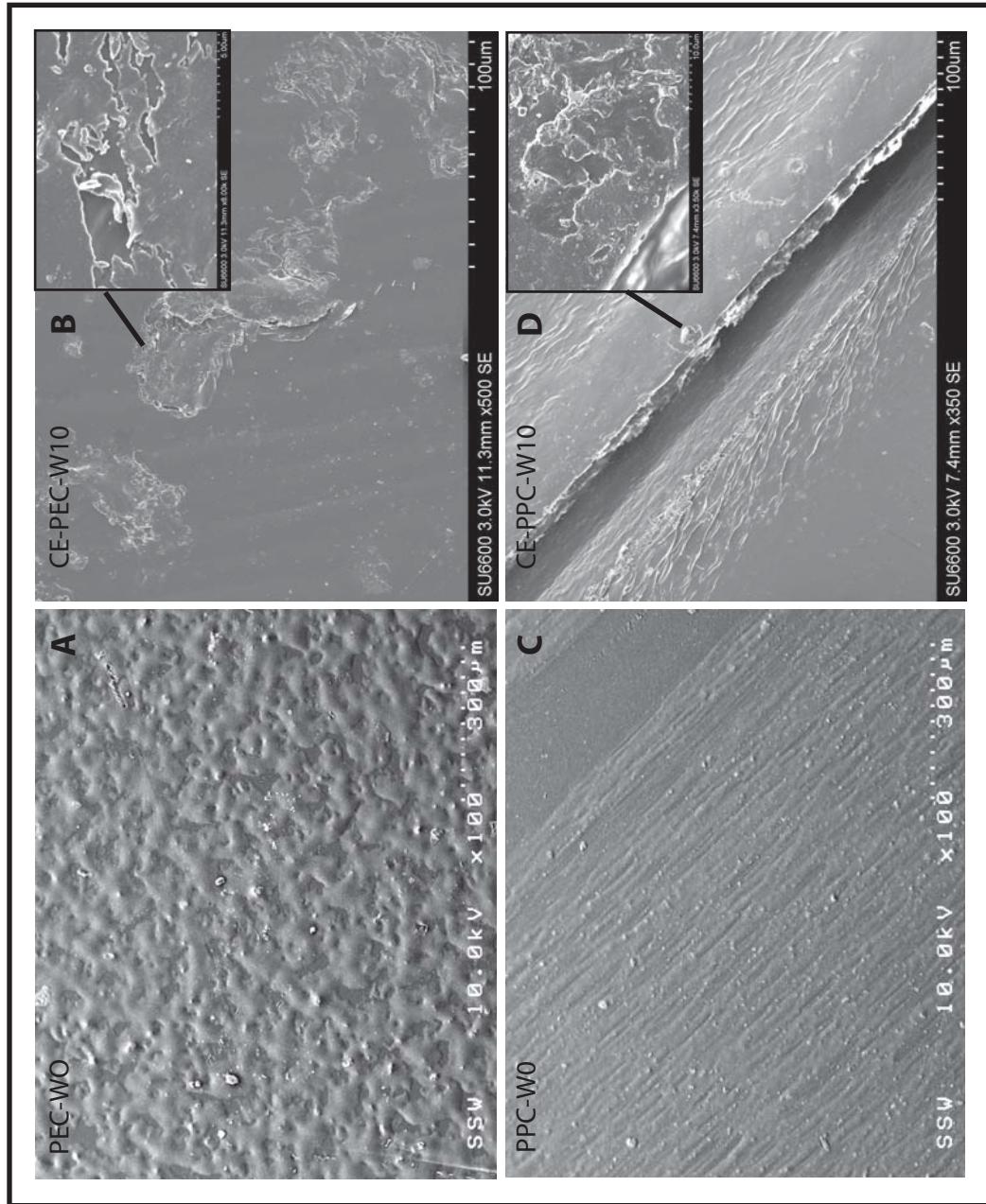


Figure 8.7 SEM images showing the effects of cold on plastics degradation. A) coloured polyethylene at week 0, B) cold exposure coloured polyethylene at week 10, C), coloured polypropylene at week 0, D) cold exposure polypropylene at week 10. Note flaking associated with coloured samples.

CHAPTER 9

DISCUSSION

9.1 Plastic Beach Debris

Kauai is located within the North Pacific Tropical Gyre and the combination of geographical location, wind and ocean currents, and the great accumulation of debris within the gyre, result in steady deposition of plastic debris on Kauaiian beaches (Cooper and Corcoran 2010). Heaviest accumulation of debris occurs on the eastern side of the island due to the relationship between longshore ocean currents and northeast trade winds (Corcoran et al. 2009; Cooper and Corcoran 2010). Gros Morne National Park is located on the western side of Newfoundland and deposition of debris on beaches is primarily controlled by winds blowing in from the Gulf of St. Lawrence, and the Labrador Current which travels south between Labrador and Newfoundland (Table 9.1).

Plastic debris deposited on beaches originates from both land and water-based sources, however the majority of plastic ocean debris (>80%) is derived from land-based sources (Derraik 2002, Gregory and Andrade 2003). Kauai has a population of 58,000 people, and approximately one million more visit each year (Kauai Highlights 2010), however, large quantities of intact or nearly intact debris from beachgoers is minimal. The majority of plastics being deposited on Kauaiian beaches are plastic resin pellets and small (<1 cm) fragmented pieces of larger items, which is indicative of debris with longer

Table 9.1 Summary of climate, debris characteristics, surface textures, and composition of plastics collected from both sampling localities as well as plastics degraded experimentally.

	Kauai	Newfoundland	Experimental
Climate			
Primary wind direction	W-SW	SW	N/A
Average precipitation/year	1200 mm	1316 mm	N/A
Average temperature	27°C yearly	13.3°C summer -6.4°C winter	26°C
Winter/Summer temperature diff.	8°C	20°C	N/A
Plastic Debris			
# of beaches sampled	5	8	N/A
# of beaches with plastic present	5	8	N/A
Most prevalent type identified	PE	PE	N/A
# of particles collected	2541	271	N/A
Intact debris	0	45 (16.6 %)	N/A
Nearly intact debris	0	26 (9.6 %)	N/A
Large fragments >5 cm	124 (4.9 %)	82 (30.3 %)	N/A
Small fragments <5 cm	2142 (84.3 %)	118 (43.5 %)	N/A
Pellets collected	143 (5.6%)	1 (0.4 %)	N/A
Other (Styrofoam, etc.)	132 (5.2 %)	0	N/A
Textures present on samples			
Flakes	✓	✓	✓
Grooves	✓	✓	X
Fractures	✓	✓	✓
Cracks	✓	✓	✓
Pits	✓	✓	X
Tie molecules	✓	✓	✓
Adhering particles	✓	✓	X
Vermiculate	✓	X	X
Composition			
# of particles examined	56	15	N/A
# of PE	45 (80.4 %)	12 (80.0 %)	N/A
# of PP	11 (19.6 %)	2 (13.3 %)	N/A
# of PS	0	1 (6.7 %)	N/A
# of high oxidation	8 (14.3 %)	4 (28.5 %)	N/A
# of medium oxidation	19 (33.9 %)	3 (21.4 %)	N/A
# of low oxidation	29 (51.8 %)	7 (50.0 %)	N/A

residence times in the environment, and more distant sources (Moore 2008). Plastic resin pellets are commonly found on beaches around the world (Carpenter et al. 1972; Moore 2008; Costa et al. 2010; Zbyszewski and Corcoran 2011), and comprise a large portion of plastic debris collected from Kauai, however, only one pellet was identified on Gros Morne beaches (Table 9.1). Beach cleanups on Kauai are organized by several volunteer groups including The Kauai Group Sierra Club and The Surfrider Foundation who routinely clear the beach of large plastic debris and derelict fishing gear. The regular removal of large debris may explain the relative abundance of small particles and pellets on the beaches as these items are more difficult to detect, they are present in larger quantities, and they are less cost effective to remove.

The proportion of small particles relative to larger items on Kauaiian beaches is in contrast to debris types sampled from Gros Morne National Park beaches (Table 9.1). Sampling of beaches in, and near the park, displayed a large proportion of intact and nearly intact debris which suggests that plastics originate from more local sources. The large proportion of macroscopic debris including shot gun shells and lobster trap tags suggests plastic waste is being deposited into the waters from nearshore activities such as fishing and hunting. Other clearly identifiable debris included tampon applicators and food packaging which are likely washed into local ocean waters through streams, rivers and storm drains located near more highly populated areas (Figure 9.1).



Figure 9.1 Satellite image (Google Earth) of Trout River, showing the proximity of the population to the water, and two rivers feeding into the bay, which result in the deposition of intact and nearly intact debris on the beach.

Newfoundland has a population exceeding 500,000 people and another 500,000 people visit the island each year. Annual cleanups of beaches within Gros Morne National Park are conducted by Parks Canada as well as other organizations such as The Protected Areas Association of Newfoundland and Labrador. Notwithstanding the efforts put forward by environmental groups, plastic debris continues to accumulate, due in large part to the high rate of deposition. Plastic debris was present on every beach visited in both study areas (Table 9.1). Polyethylene and PP are the most widely used polymer types, and consequently have become the most prominent polymer types found in the natural environment (Arutchelvi et al. 2008, Corcoran et al. 2009; Cooper and Corcoran 2010; Zbyszewski and Corcoran 2011). Analysis of plastic debris sampled from Kauaiian and Newfoundland beaches confirmed the abundance of PE and PP compared with other polymer compositions.

Kauaiian beaches are primarily composed of calcareous sands made up of mainly coralline algae and coral fragments, which results in a relatively uniform sediment size (Blay and Siemers 2004). Plastic debris was evenly distributed along each sampling site on Kauai, with the exception of Salt Pond where only two particles were collected. Beach sediment on Newfoundland beaches ranges from fine sand to boulders. Plastic debris on Newfoundland beaches closely mimicked the deposition of natural sediment with large debris and coarse sediment being located on high energy beaches, and smaller fragmented debris and finer sediment on low energy beaches. Accumulation of plastics at Kauai and Newfoundland sampling locations was most abundant along the high water mark where plastics were intermixed with organic debris. The retention of plastics along

strandlines indicates that plastics are being deposited when wind and waves are strongest, such as at high tide or during storm events. When plastics are deposited at the high water mark they are, at least temporarily, removed from the water making them susceptible to increased UV irradiation and subsequently increased thermal and photo oxidative processes. Return of the particles to the water may occur through many avenues such as wind, waves, or rain. Subsequently, the chemically embrittled particles are made more susceptible to mechanical degradation processes that occur in the littoral zone.

9.2 Plastics Degradation

All synthetic polymers will degrade when exposed to the natural environment, however the rate of degradation is dependant on environmental conditions such as sunlight intensity and temperature as well as polymer type (Gijsman et al. 1999). The textural investigations of this study indicate that polymers in the natural environment exhibit many of the same surface textural characteristics as natural beach sediments. Mechanical erosion processes produced distinct surface textures on debris collected from both sampling localities, confirming that mechanical degradation of plastics operates comparably in both subtropical and temperate climates (Table 9.1). Chemical degradation characteristics were less prominent on Newfoundland samples which may be a result of less time at sea, cooler water, air and beach temperatures, and/or decreased exposure to UV radiation.

Vermiculate textures present on PE particles collected from Kauai were not identified on experimentally degraded PE, nor samples collected from Newfoundland. The presence of a unique surface texture suggests that polymers in subtropical climates may be susceptible to different modes of degradation caused by water salinity and/or temperature, biological activity, day length/amount of sunlight, or some combination of these factors.

Biological degradation of polymers may take several hundred years, however, chemical and mechanical degradative processes appear to facilitate degradation of plastic by biological organisms (Arutchelvi et al. 2008). In addition, the adhesion of the organism to the polymer may initiate or promote degradation (Figure 9.2). Conversely, the presence of a biofilm on debris surfaces may hinder chemical oxidation of the polymer surface by blocking harmful UV radiation (Figure 9.3). Samples collected by Dr. Patricia Corcoran near Punta Maroma, Mexico ($20^{\circ} 44' 14''$ N / $86^{\circ} 57' 58''$ W) displayed a significant amount of biological fouling (see Figures 3.7, 3.8, Appendix 3 7-10). This is consistent with several Kauaiian samples which were also found to contain biological organisms (see Figure 7.9 F, Appendix 2 60-61). No biological organisms were identified on Newfoundland samples. Combined with the abundance of organisms associated with polymer samples collected from warmer climates, this indicates that air and water temperatures play a significant role in biological accumulation on, and degradation of, plastic ocean debris.

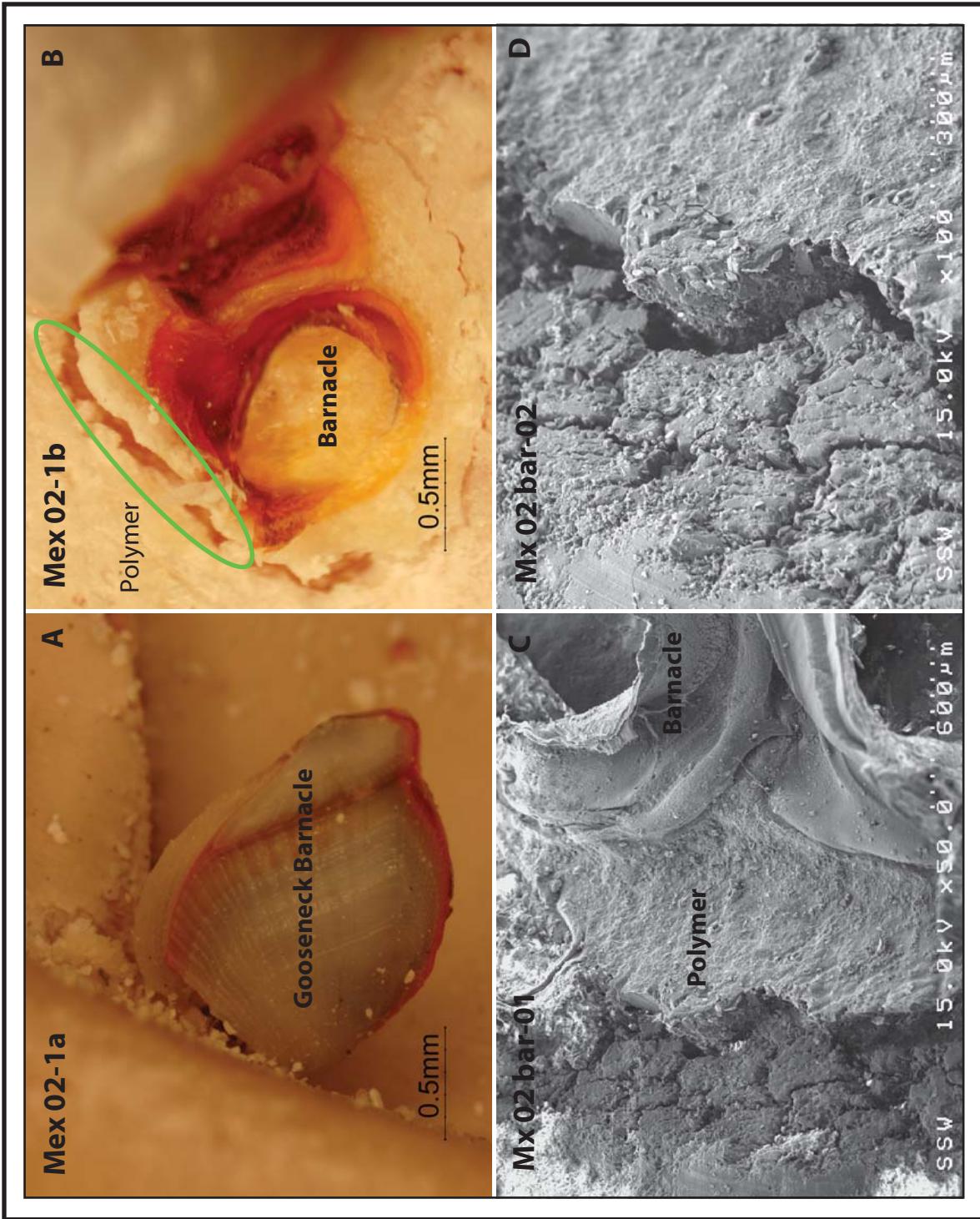


Figure 9.2 A),B) Digital photographs of a Gooseneck Barnacle attached to a polymer sample collected from a beach near Punta Maroma, Mexico. The green circle indicates a crack that has formed as a result of the barnacle attachment and growth. C),D) SEM images of the separated area at higher magnification.

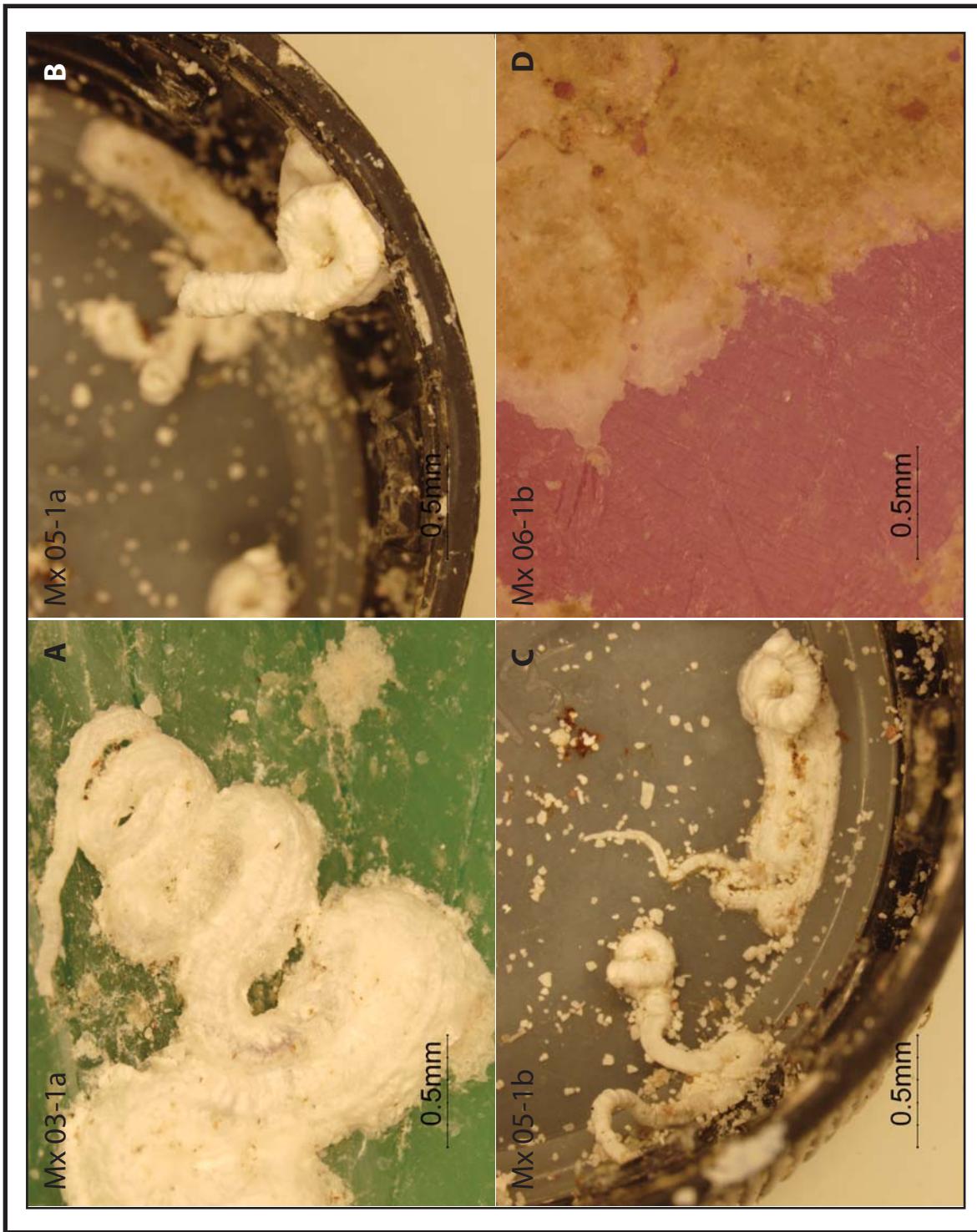


Figure 9.3 Digital photographs of plastic beach debris collected near Punta Maroma, Mexico. Growth of biological organisms may block UV light and inhibit oxidation processes.

Surface textures on PE samples such as grooves, vermiculate and flakes were not present on PP samples which displayed deeper, more well-defined cracks and fractures. Analysis confirms that in the natural environment, PE is preferentially degraded relative to PP; however, under experimental conditions PP was more susceptible to UV irradiation and displayed significantly higher levels of degradation over 10 weeks of exposure to UV light. White PP displayed the highest level of degradation whereas coloured PP displayed little cracking or fracturing, indicating that colourants are effective at protecting polymers from UV radiation. Artificially induced fractures (scoring) provided preferential sites for oxidation to occur, and/or propagate which is consistent with results obtained from analysis of polymers in the natural environment (see Cooper and Corcoran 2010). These factors confirm that mechanical degradation works with chemical oxidation to degrade plastic debris most efficiently on beaches, relative to other natural settings as suggested Corcoran et al. (2009) and Cooper and Corcoran (2010).

The surface textures of plastic fragments and pellets exposed to UV radiation over certain time periods varied extensively depending on polymer type, colour and presence of mechanically-induced fractures. White PS and PP samples displayed a significant increase in degradation between weeks 0, 2, 6 and 10 based on SEM imaging. FTIR spectra for these plastic types also show increasing oxidation with time. Smaller oxidation peaks produced by the white PE indicate that some chemical weathering occurred, but it was minimal compared with the PP and PS samples. The PE fragments and pellets display minimal surface textures in SEM images, indicating that they are not significantly altered by UV radiation. PP with colourants on the surface display little

effects of UV radiation when compared with white PP, suggesting that colourants protect polymers from chemical degradation. Crazing within the artificial incisions (scored surfaces) on both coloured and white PP was similar, supporting the hypothesis that mechanical erosion features promote more rapid chemical weathering. Our results show that exposure to cold temperatures over a 10 week period did not produce crazing, but some flaking occurred in specific spots on coloured PE and PP. Continuing research into the mechanical and chemical controls that contribute toward the breakdown of commonly used plastics will provide a clearer understanding of the polymers for which production and use should be avoided.

CHAPTER 10

SUMMARY AND CONCLUSIONS

This thesis presents the analysis of plastic debris from the beaches of Kauai, Hawaii, U.S.A. and Gros Morne National Park, Newfoundland, Canada, as well as experimentally degraded plastic samples of the two most commonly used polymer types. The data were used to illustrate which polymer types occur most in natural beach environments, the rate at which accumulation occurs, the level of degradation, both mechanical and chemical, from subtropical and temperate climates, as well as the distribution and deposition of plastic debris on beaches.

Composition and sources

- PE and PP are the dominant polymer types deposited on beaches. Both sampling locations indicate an approximate ratio of 4:1 PE to PP. The abundance of PE and PP is consistent with preferred production of these compositions in end-user products.

- The small size of plastic fragments and large proportion of pellets on Kauaiian beaches indicates longer sediment residence times and more distal sources.

Newfoundland beaches contain a large proportion of intact and nearly intact plastic debris which is consistent with debris derived from more local sources.

- Particles on Kauaiian beaches are sourced primarily from the North Pacific Tropical Gyre. Newfoundland beaches contain debris from several inland sources including fishing/hunting, consumer waste, medical/sanitary and food packaging.

Distribution and accumulation

- A total of 6082 pieces of plastic were collected from Maha'ulepu beach at an average rate of 484 pieces/day. The first day of sampling yielded 1243 plastic particles, and during the following 10 days, approximately 400-600 fragments were deposited on the beach daily.
- All sample locations on Kauai and Newfoundland contained some measurable amount of plastic debris, however, wind and wave patterns, ocean currents, proximity to sources and beach clean-up efforts play key roles in the size, distribution, accumulation and retention of plastic debris.
- Ocean currents, and wind and wave patterns around Kauai, are responsible for the distribution and accumulation of plastic debris along the eastern shoreline of the

island. Deposition of debris on Newfoundland beaches is controlled by easterly winds and the Labrador Current.

- Organic material along the strandlines in both study areas was responsible for trapping plastic debris. Lower energy beaches with finer sediment typically contained smaller organic material and plastic particles concentrated at the strandline. High energy beaches contained coarser sediment, and larger organic material and plastic debris. The concentration of plastic along the strandline is an indication that plastic debris is being deposited when winds are highest such as during storm events and/or when tides recede.
- Distribution patterns of plastic debris indicate that plastics follow similar depositional patterns as natural beach sediments. Plastic debris size on beaches is proportional to sediment size suggesting that as plastic degrades it may become a significant future component of the sedimentary deposit record.

Degradation

- Plastic debris in temperate climates produce less chemically weathered surface textures, relative to subtropical climates, which is possibly due to less time at sea, cooler water, air and beach temperatures, and/or decreased exposure to UV radiation.

- Plastic particles from beaches in subtropical and temperate climates exhibit similar mechanically produced surface textures.
- Plastics on beaches are more readily and efficiently degraded, relative to other natural settings, due to the combination of mechanical and chemical erosion processes.
- Experimentally degraded plastics exposed to UV radiation display increasing surface texture formation relative to exposure time. White PP particles display increased levels of degradation relative to other polymer types including coloured PP and PE, as well as virgin pellets.
- Paints and dyes on plastic surfaces provide protection from UV radiation and diminish the extent of photo-oxidation of polymers. Photo-oxidative processes, however, were found to degrade polymers when artificial fractures (scoring) were induced on coloured polymer surfaces.
- The adhesion of biological organisms to polymer surfaces may initiate or promote degradation. The presence of these organisms is more prevalent in areas with warmer water and air temperatures.

- The biofouling of polymer surfaces is more extensive in warmer climates and the growth of biological organisms may protect the plastic by restricting the amount of UV radiation reaching the polymer surface.
- Mechanically produced cracks, fractures and pits, formed under either natural or experimentally produced conditions, provide preferential sites for UV induced oxidation to progress. Chemically embrittled debris may be further degraded and fragmented through the mechanical degradation processes associated with the littoral zones of beaches.
- IR spectra of sampled and experimentally degraded polymers indicate that PP is more conducive to photo-oxidative degradation relative to PE.
- SEM indicates that the combined effects of chemical and mechanical degradation processes may degrade PE preferentially to PP.
- The calculated regeneration rate of plastics on Kauaiian beaches demonstrates that the continued misuse and improper disposal of synthetic polymers will not be resolved simply by switching to more rapidly-degrading polymer types.

The research conducted for this thesis takes a novel approach to understanding the fate of synthetic polymers in the natural environment. Most research in the scientific literature focuses on quantity and type of plastic debris, but our research group is the first to utilize FTIR and SEM technologies to better understand the effects of chemical and mechanical processes on the degradation of plastic debris. The results corroborate previous work conducted by our research group which indicates that beaches are the most optimal sites for the degradation of synthetic polymers in natural environments.

Future work should include further investigations into the adhesion of POPs on plastic surfaces and the subsequent effects of pollutant transport, as well as the biological implications of these chemicals to marine species. In addition, in-depth studies into the origins of the vermiculate textures may provide an understanding of other possible modes of degradation. Simulated mechanical and thermal degradation studies would provide valuable information into the roles these processes play in the ultimate degradation of plastic debris. Furthermore, determining the fate of microplastics in the environment will indicate the effects these particles have on thermal retention and distribution of heat, as well as the porosity and permeability of beach sands.

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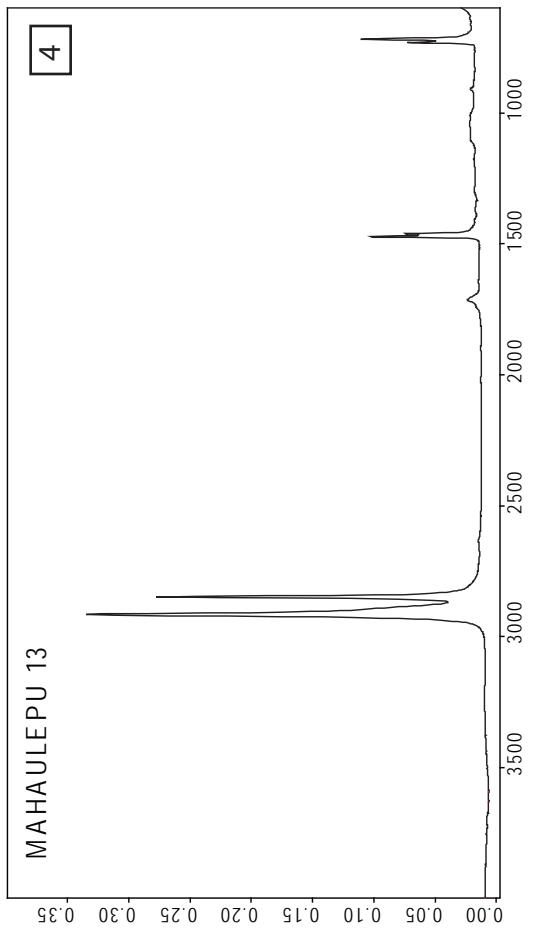
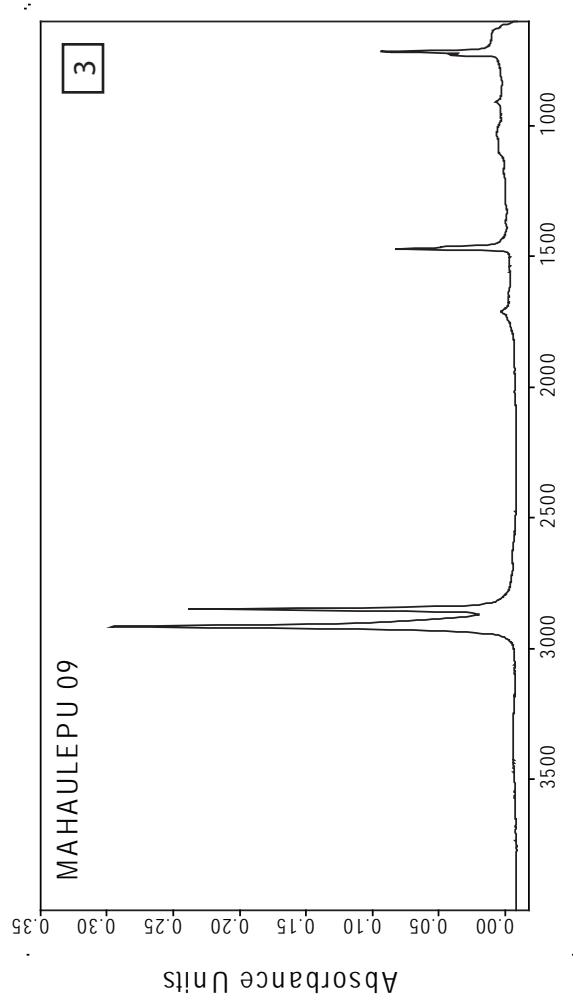
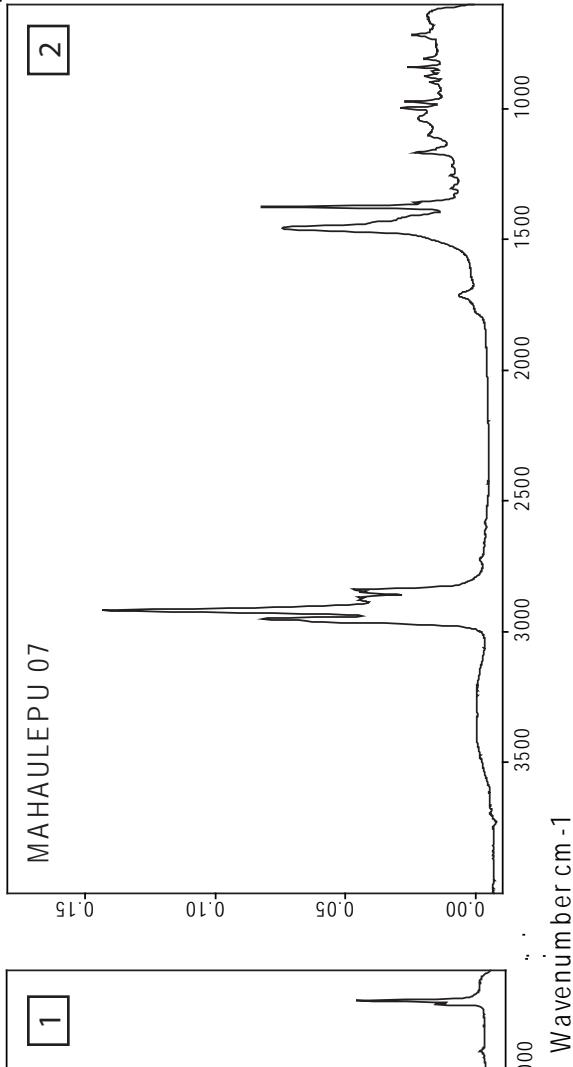
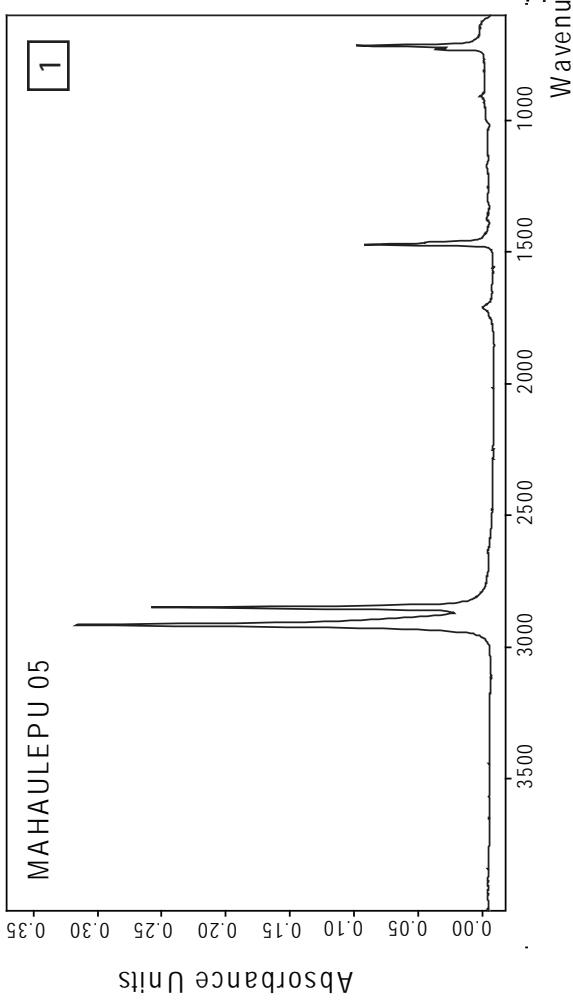
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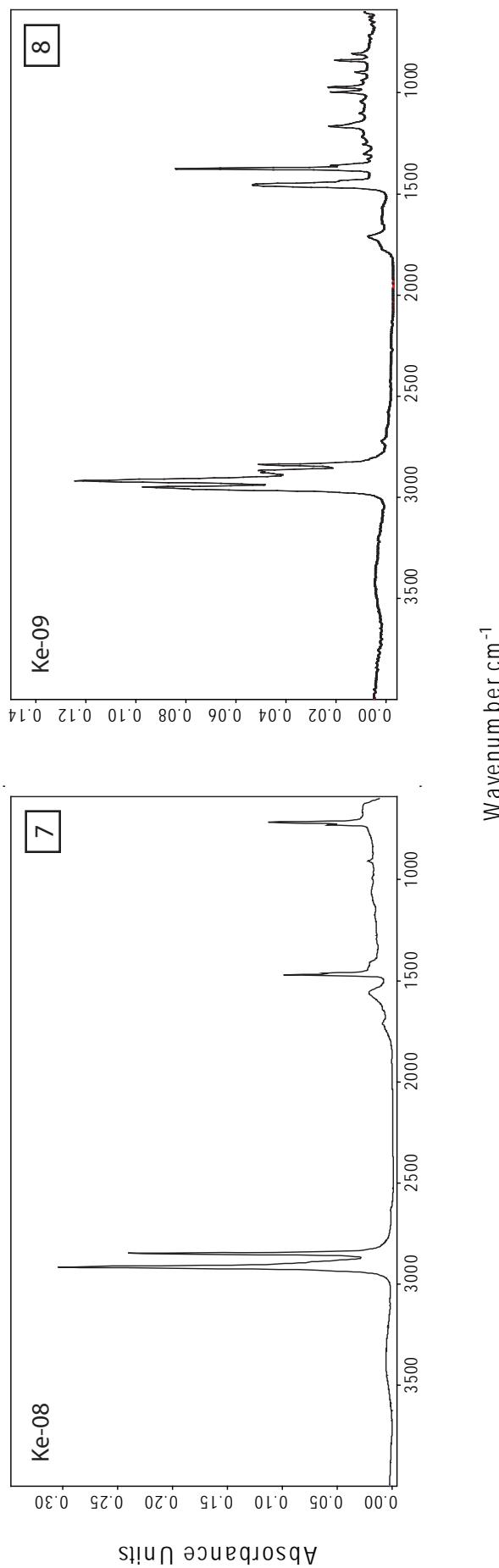
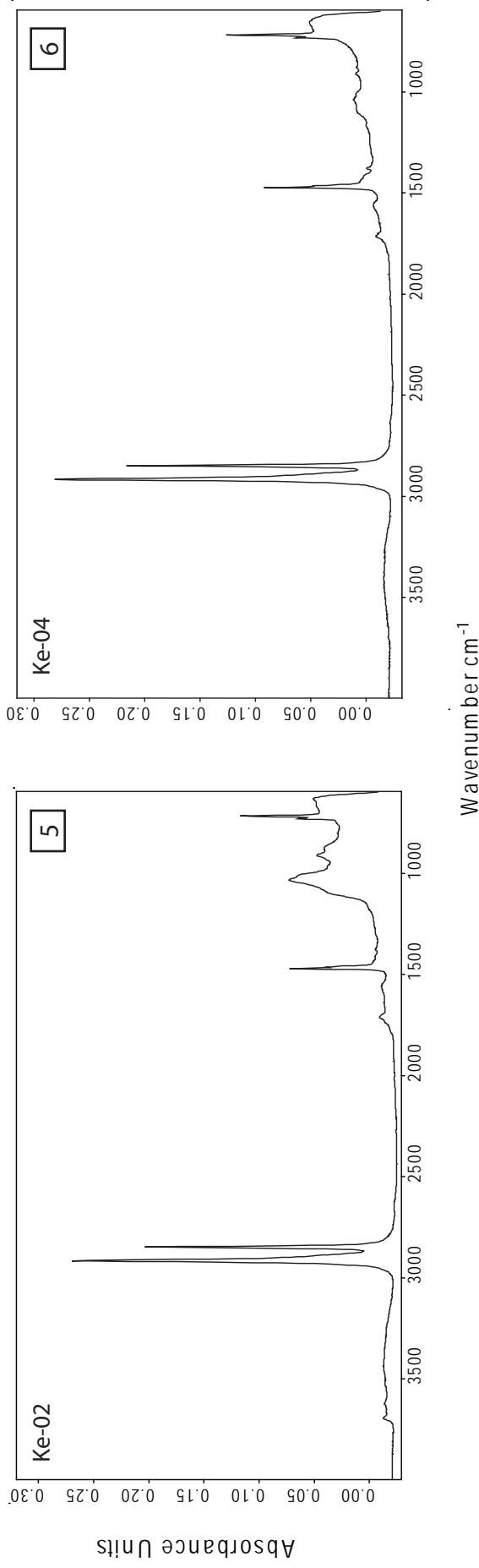
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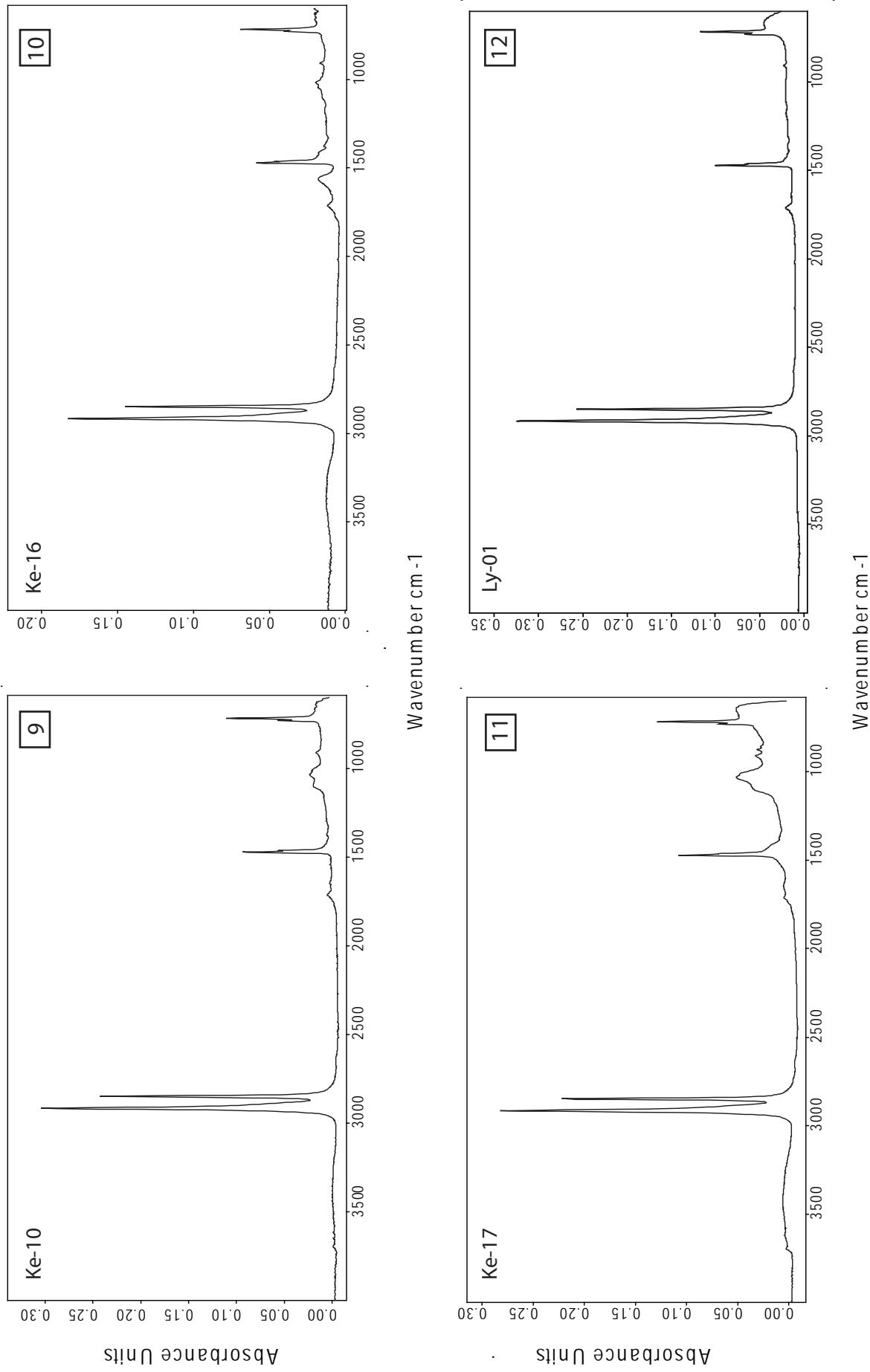
APPENDICES

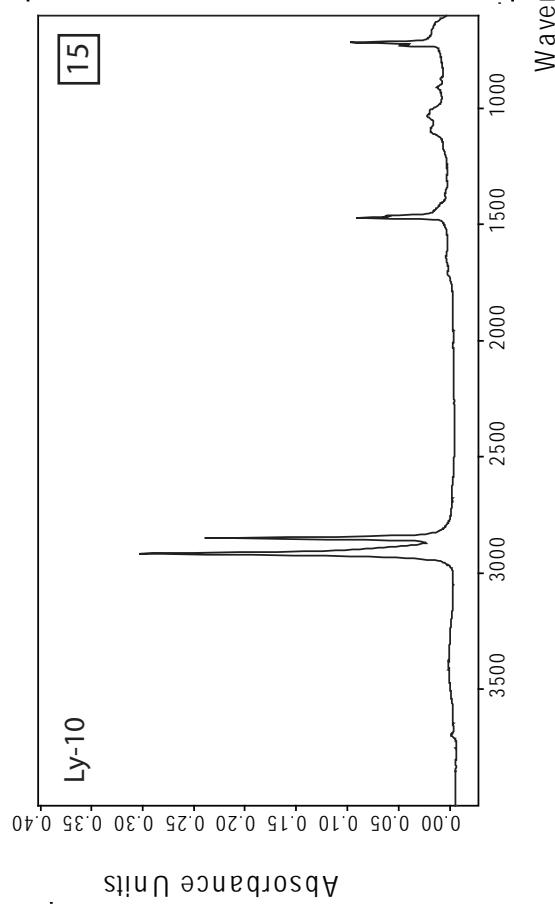
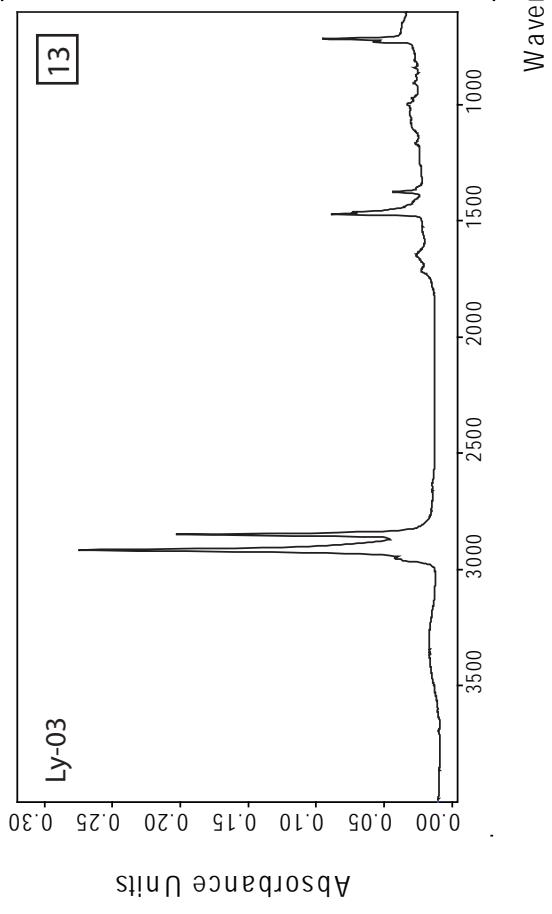
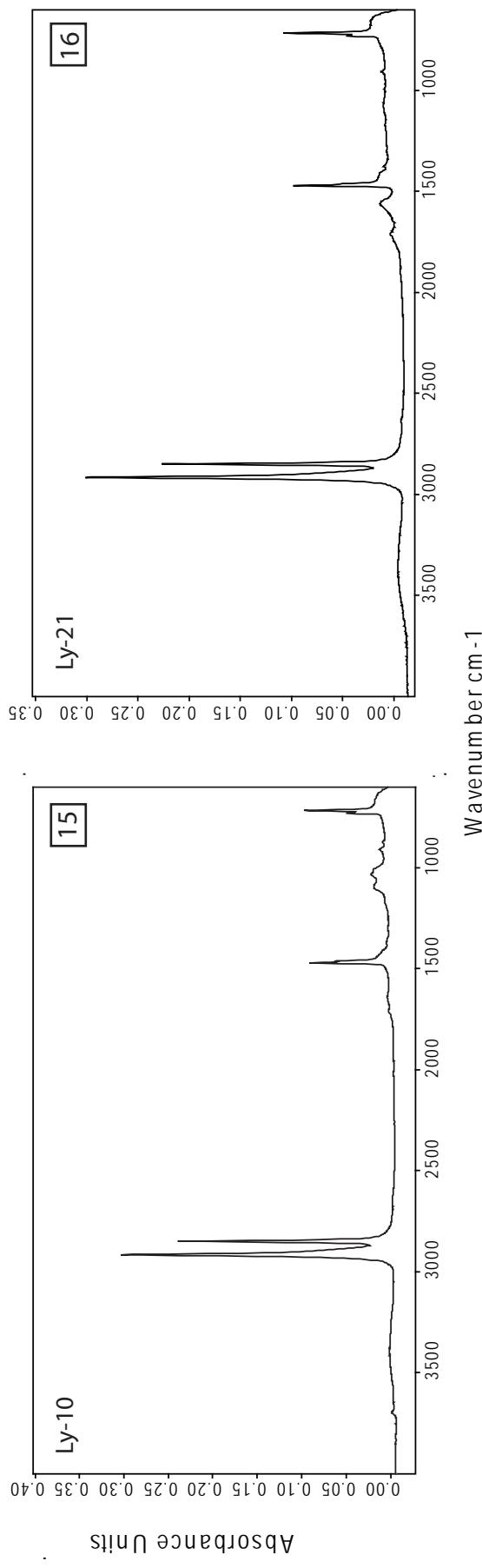
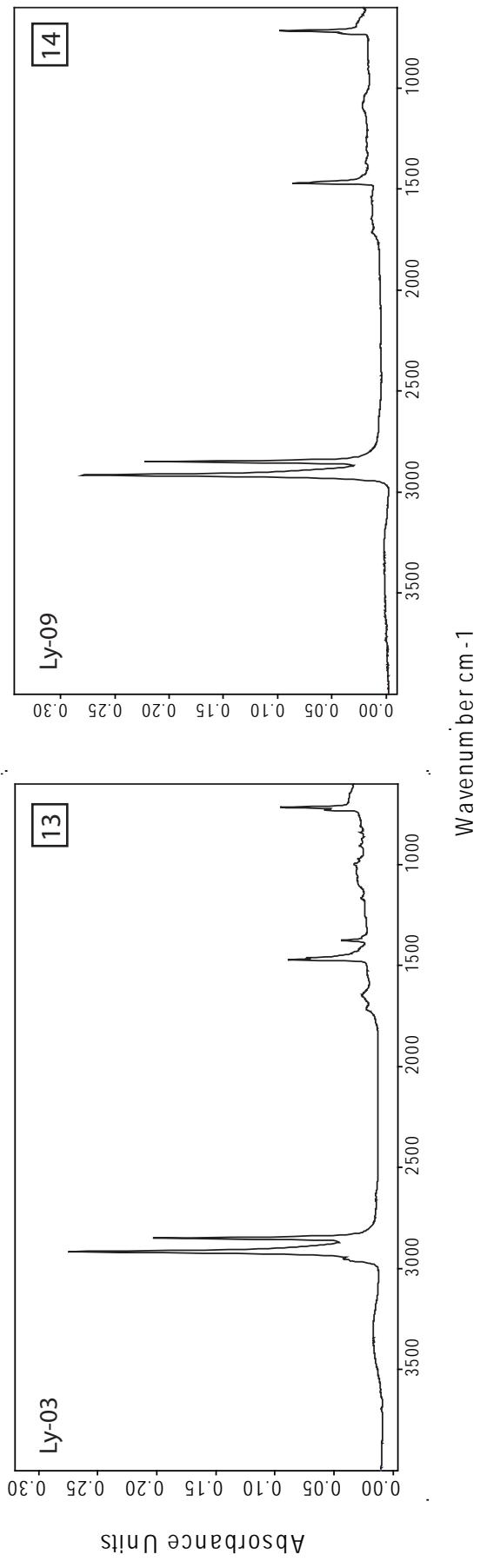
APPENDIX 1

FTIR Spectra of Kauaiian, Experimental chamber study, and Newfoundland samples. Spectra 1-44 are from Kauaiian samples, 1-25 have low oxidation, 26-40 have medium oxidation and 41-44 have high oxidation. Spectra 45-60 are from experimentally degraded samples, 45-58 have low oxidation, 59 has medium oxidation and 60 has high oxidation. Spectra 61-74 are from Newfoundland samples, 61-67 have low oxidation, 68-70 have medium oxidation and 71-74 have high oxidation.

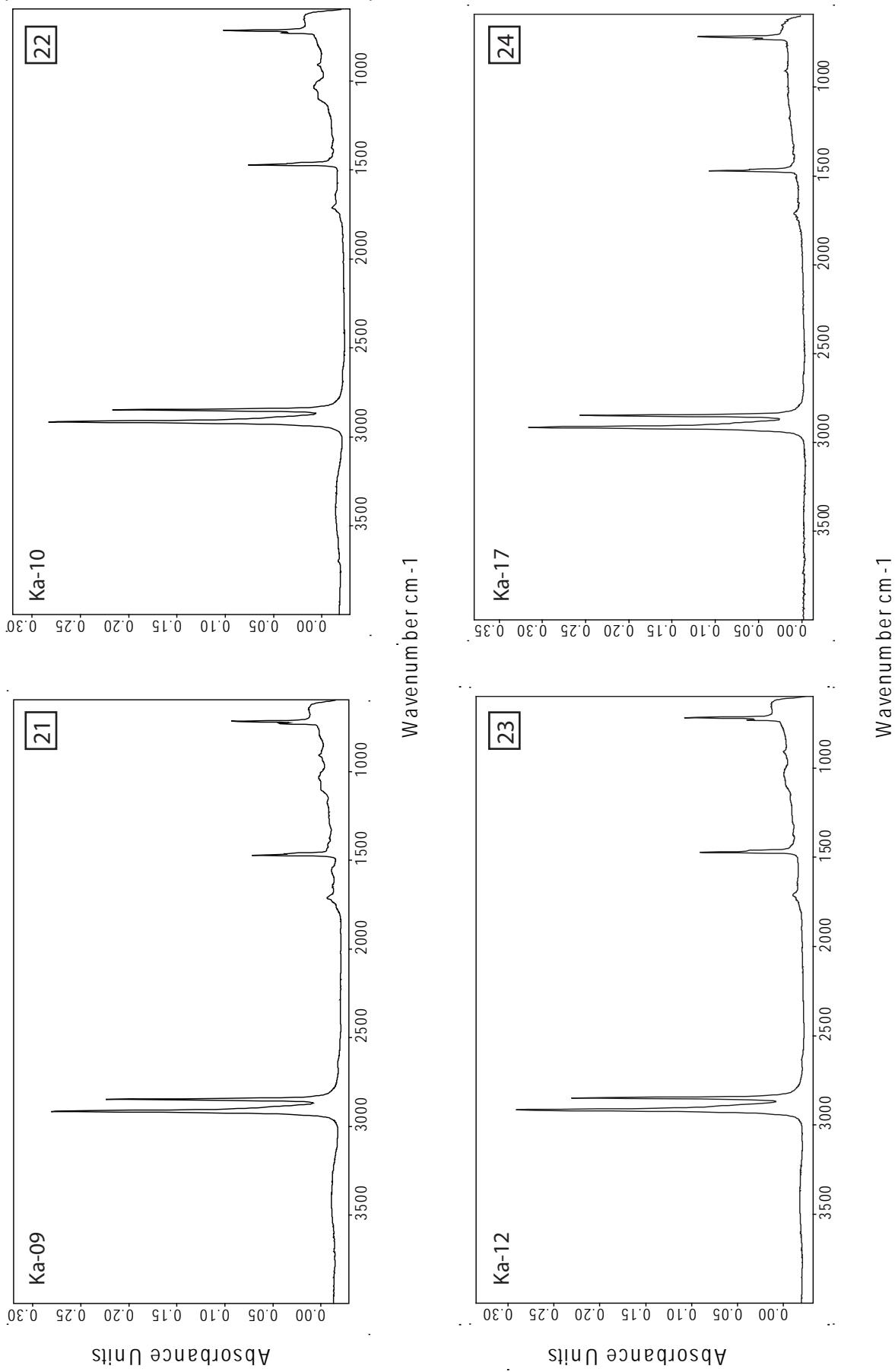


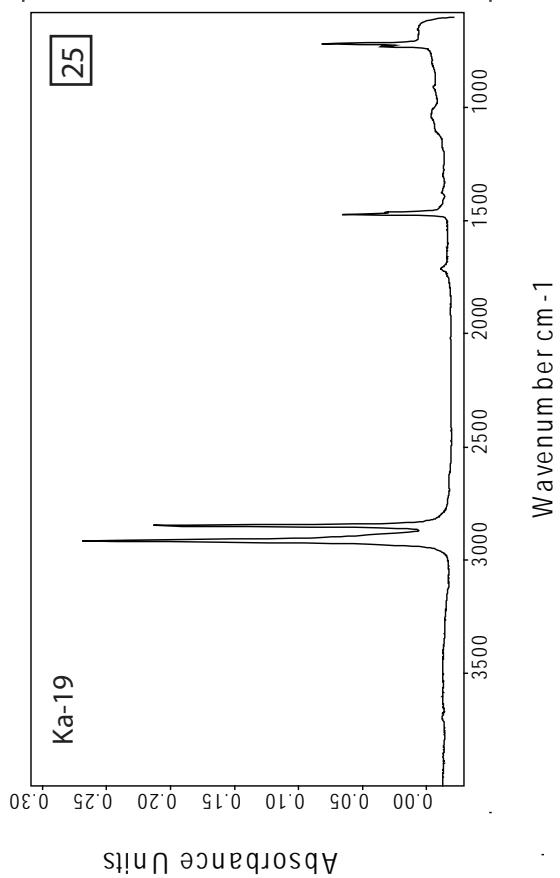


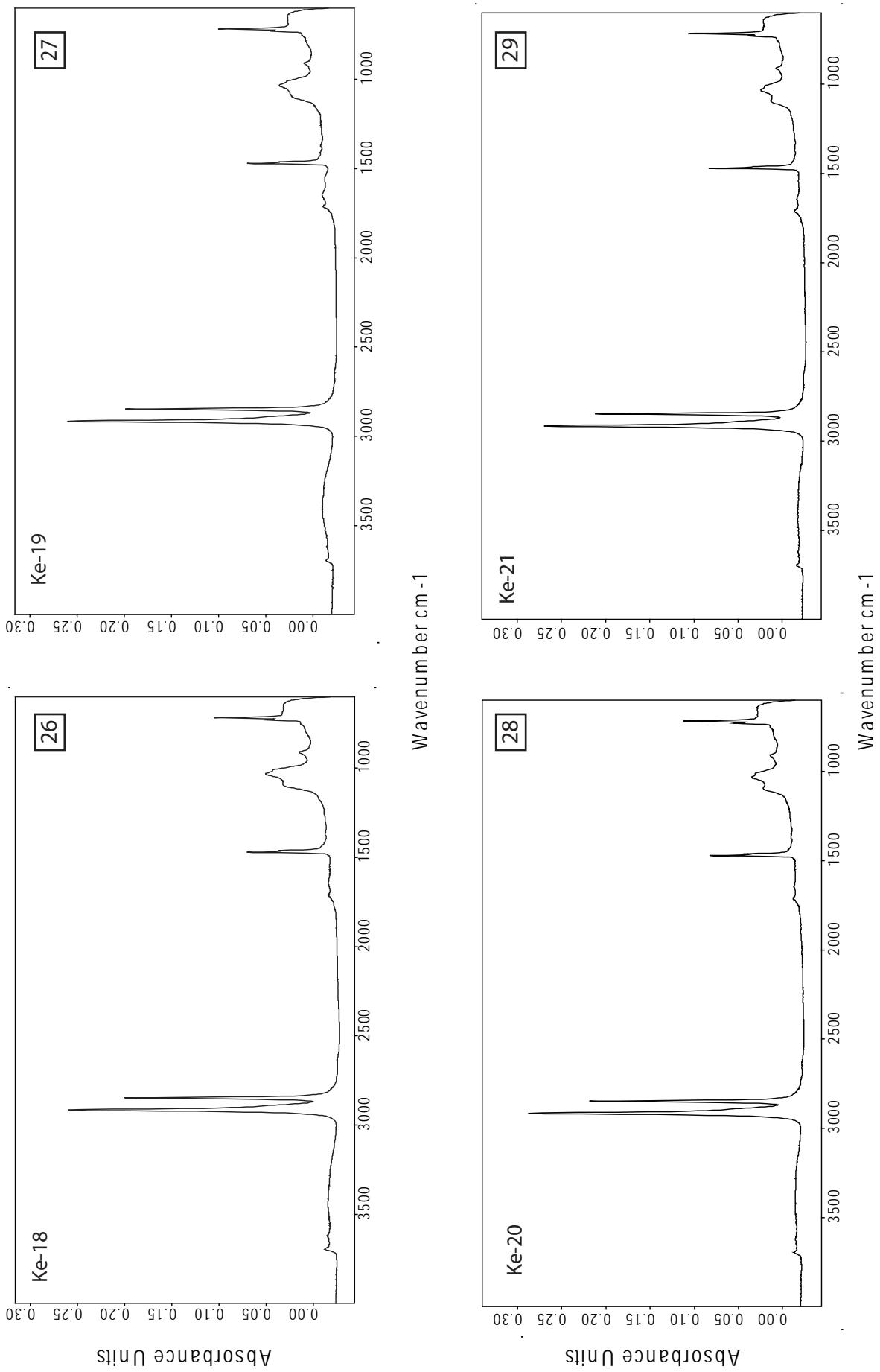




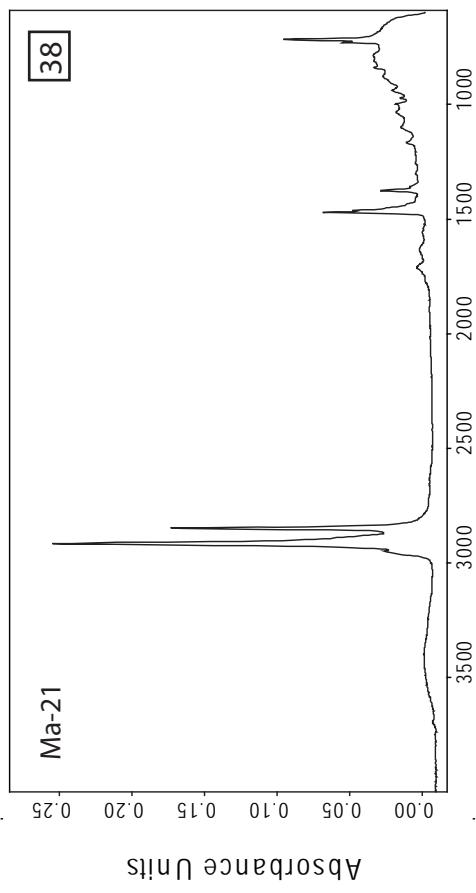
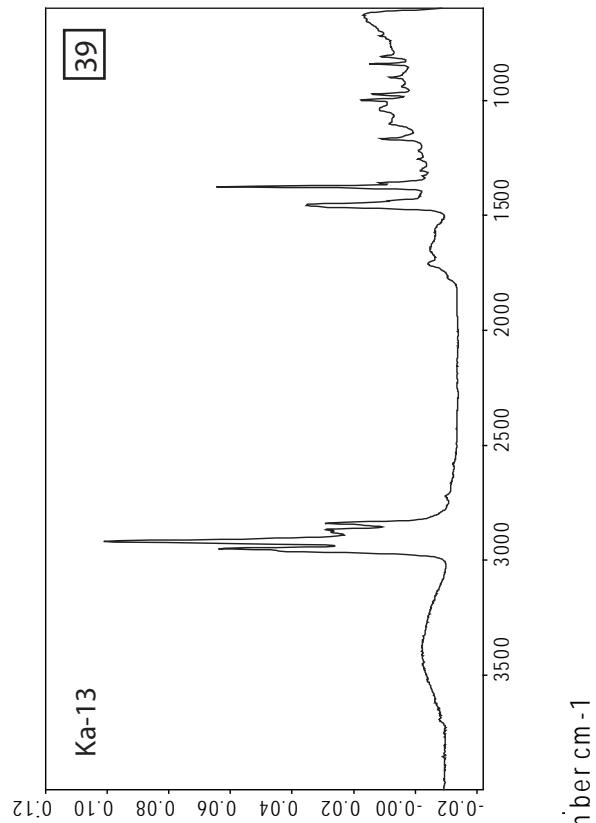
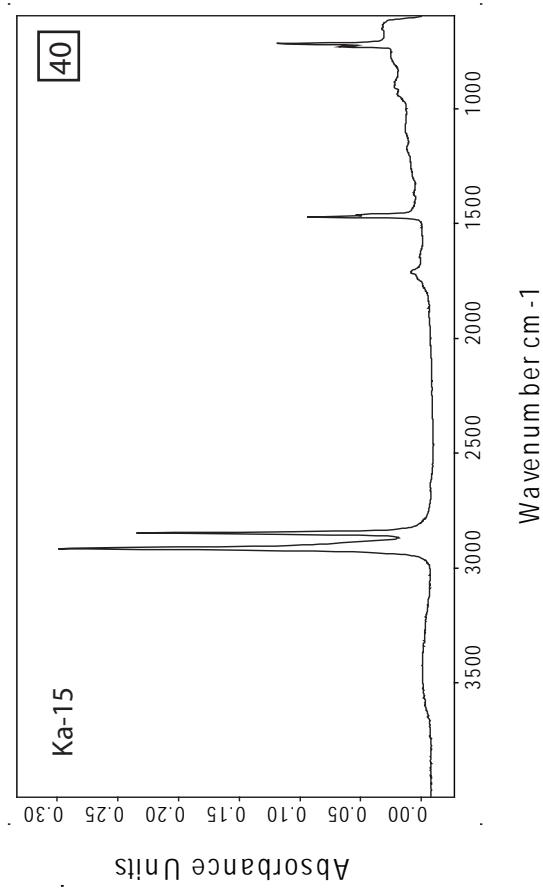


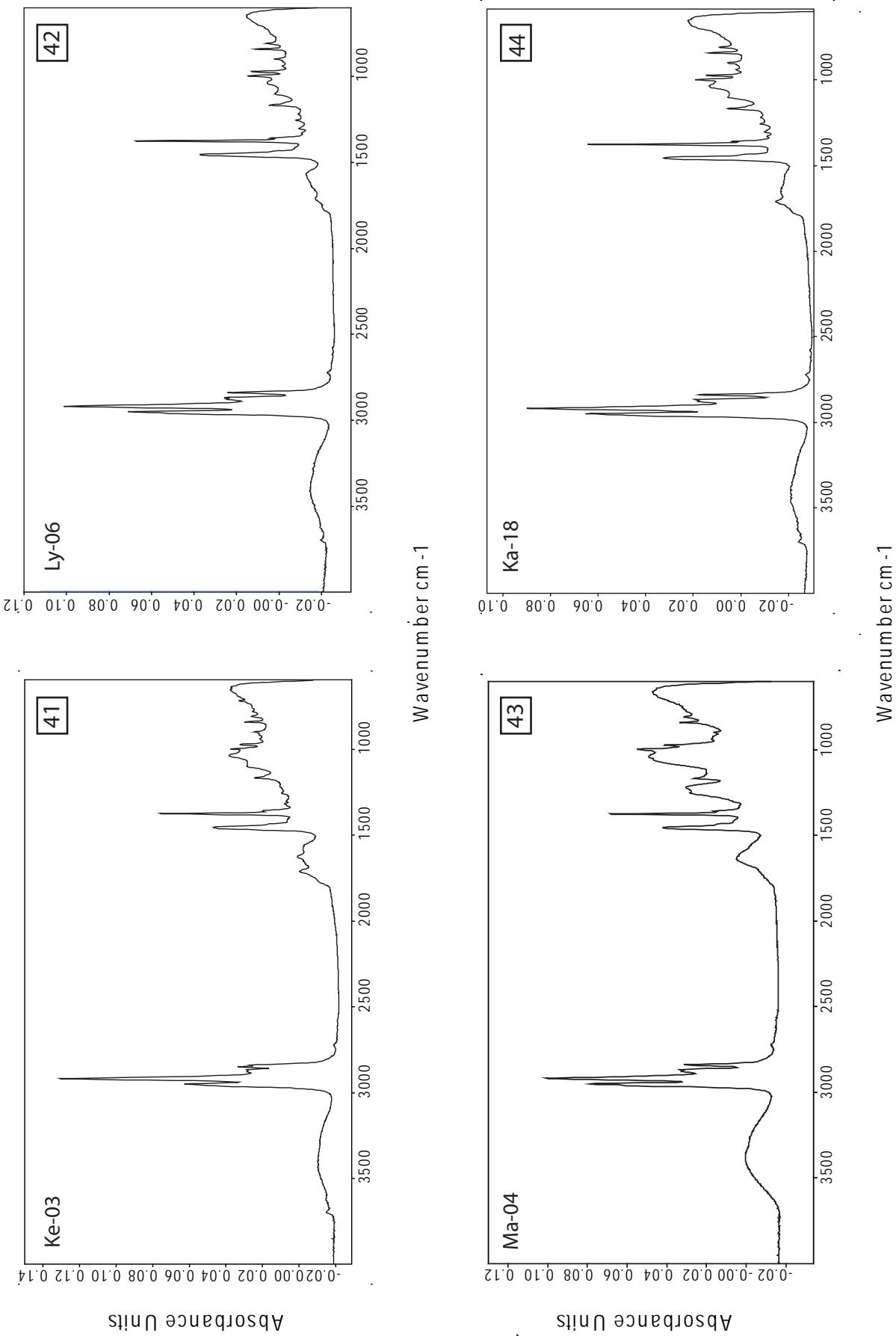


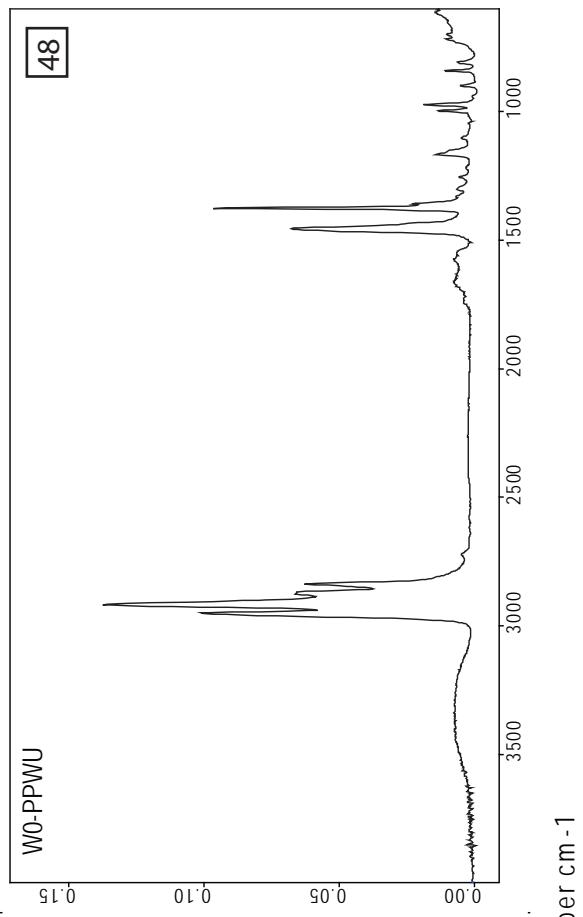
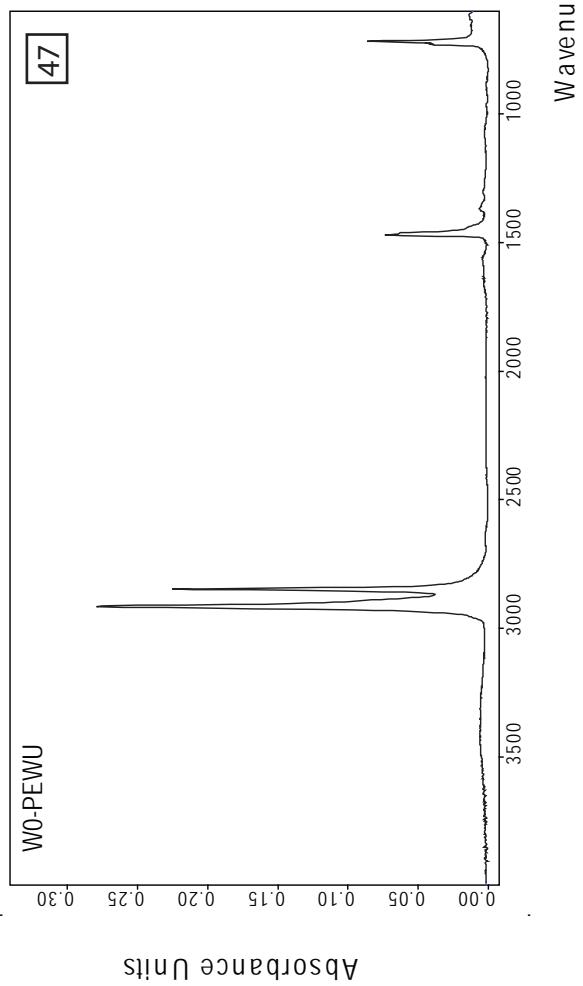
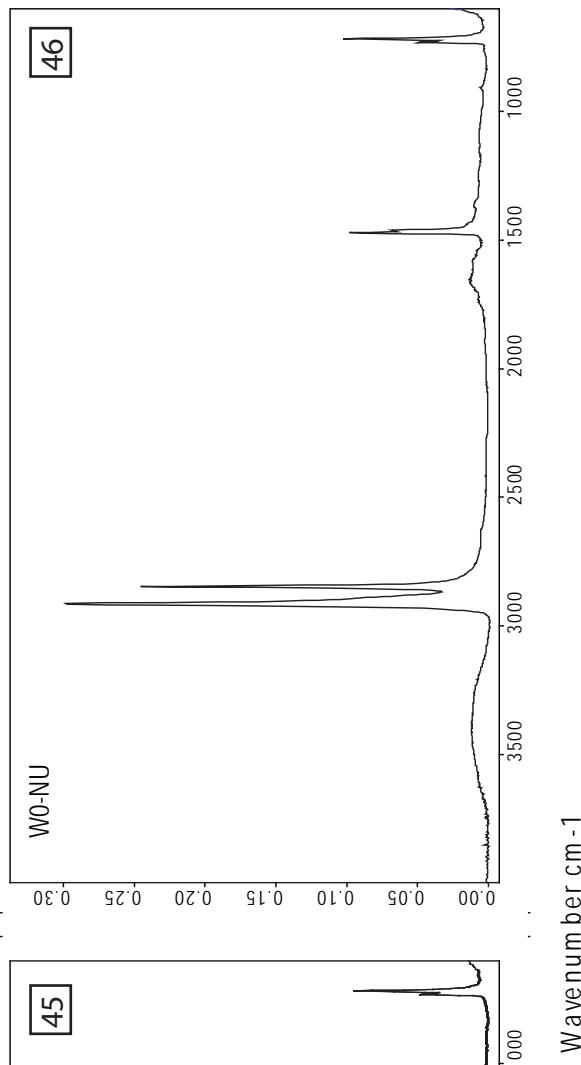
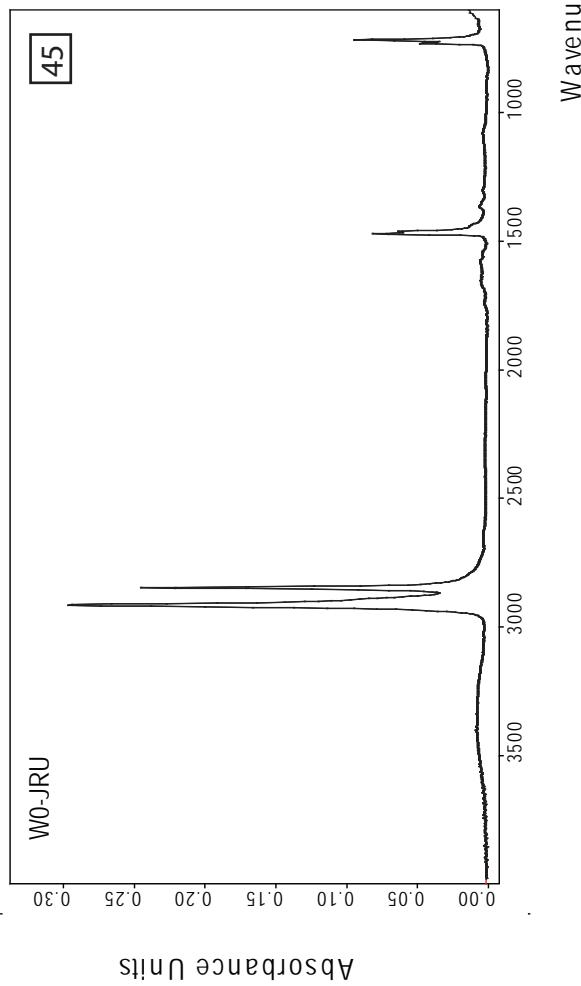


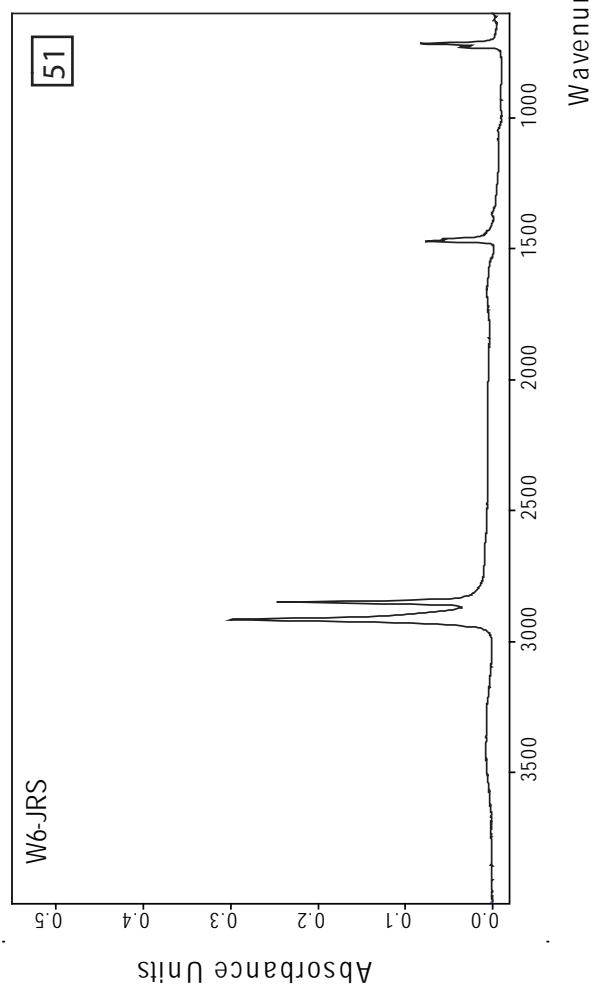
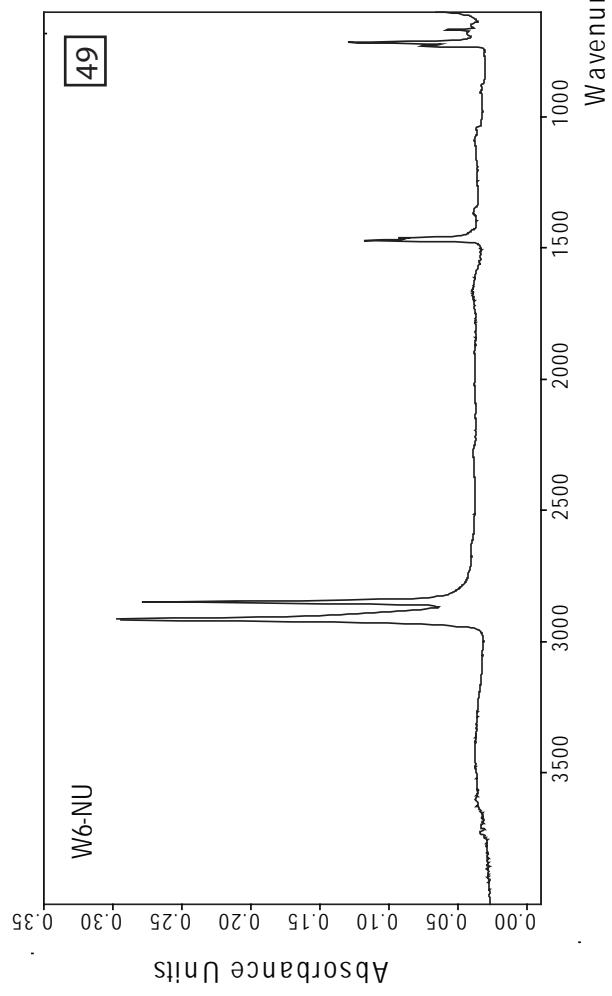
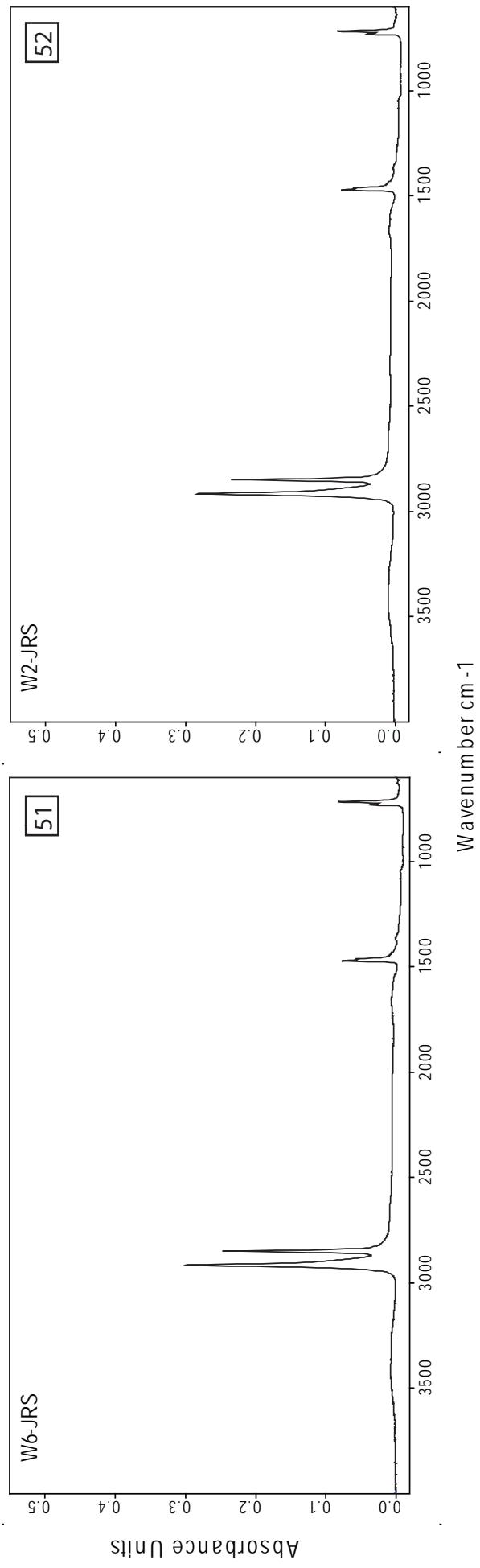
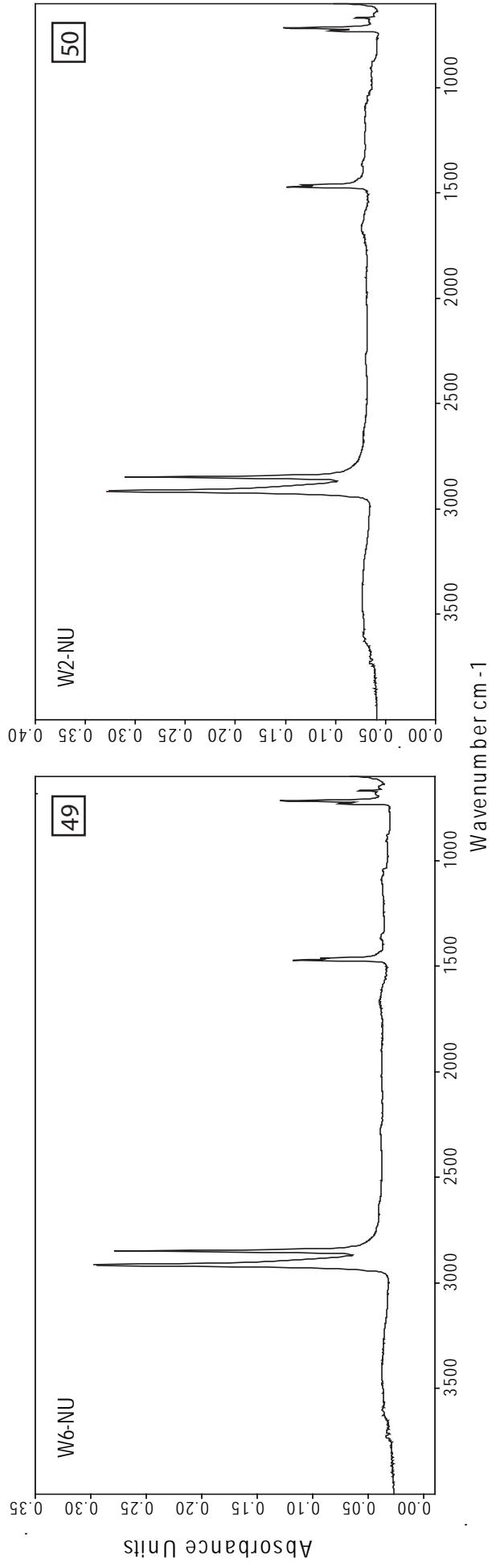


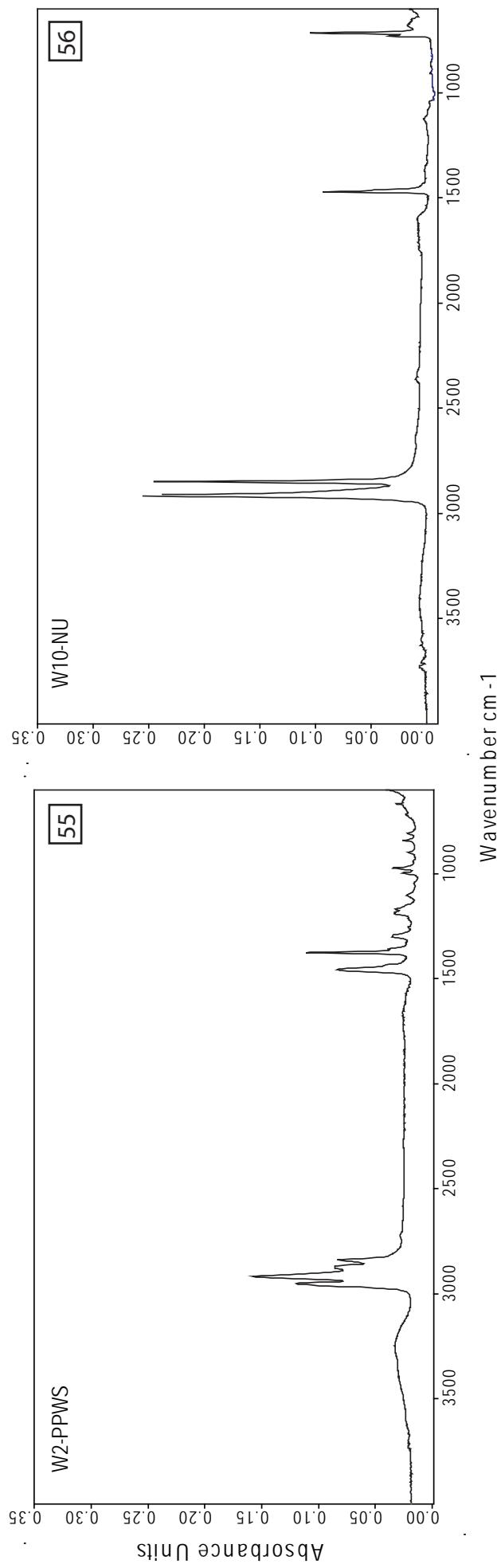
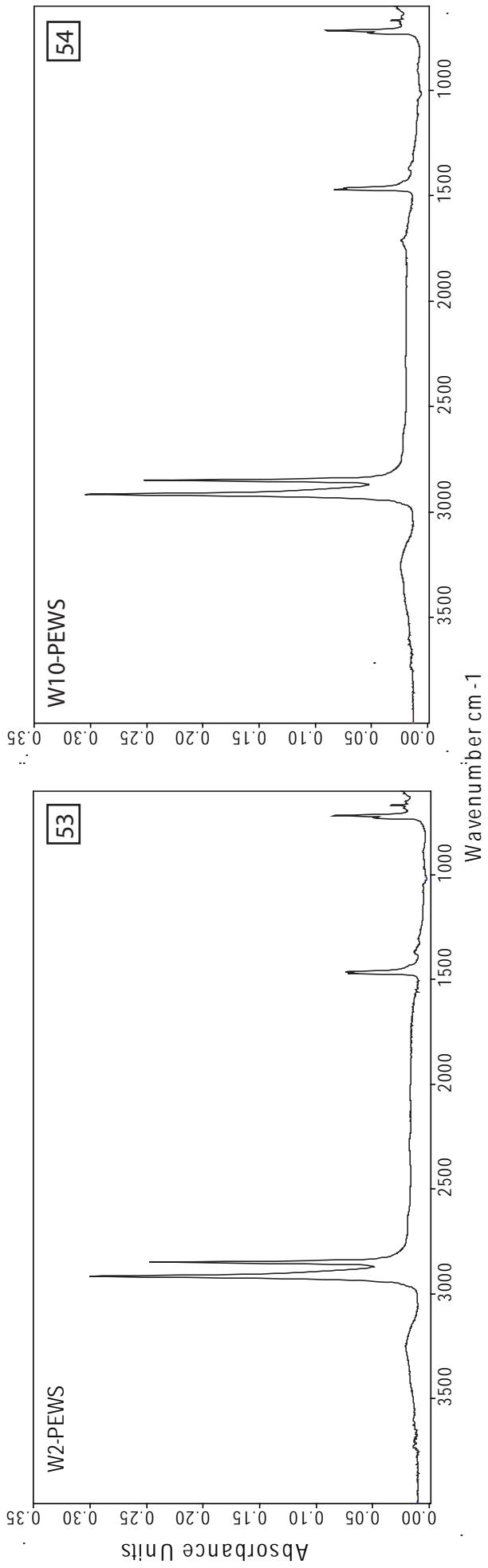


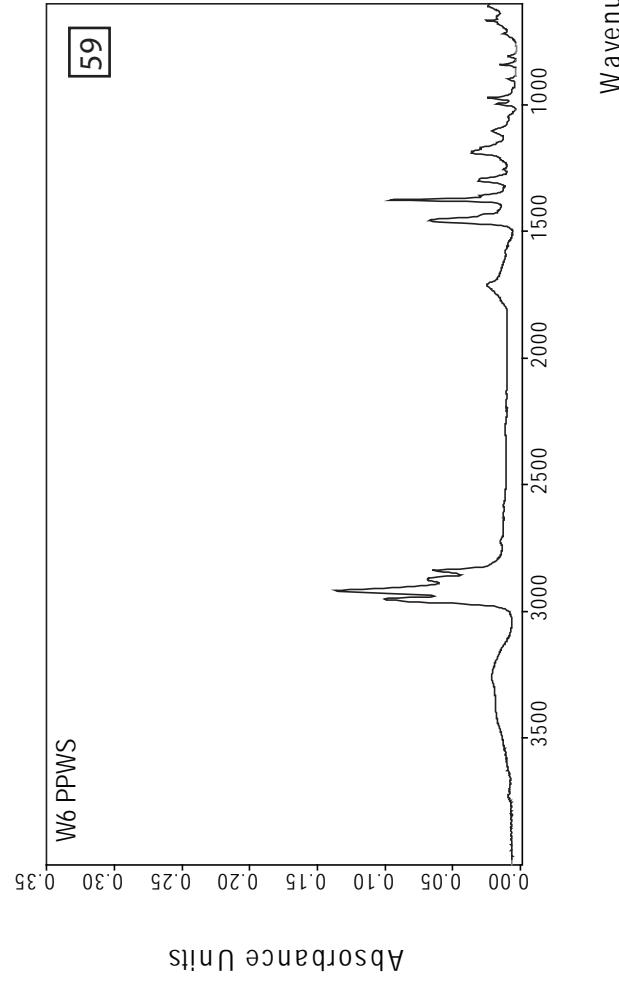
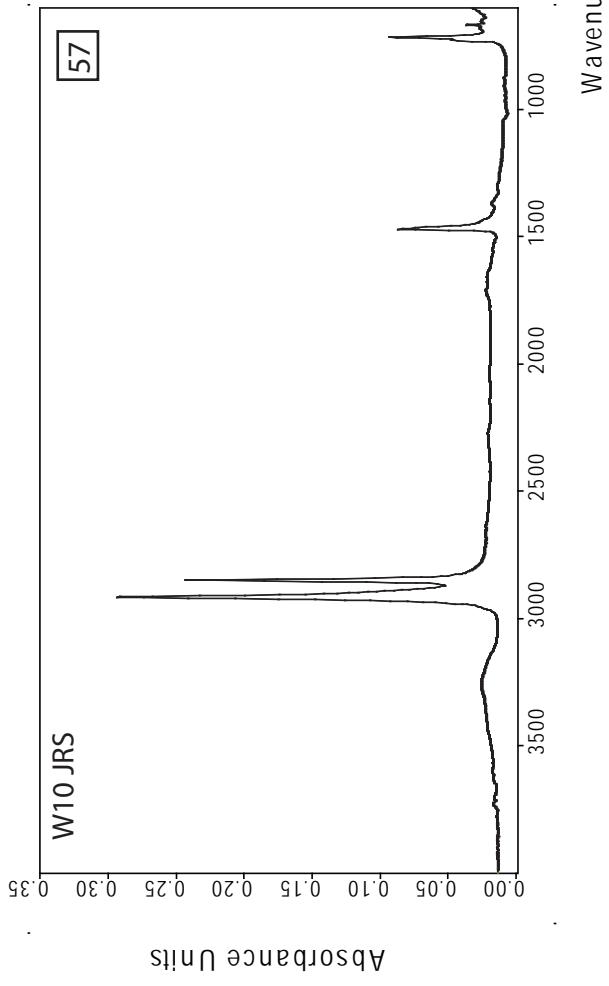
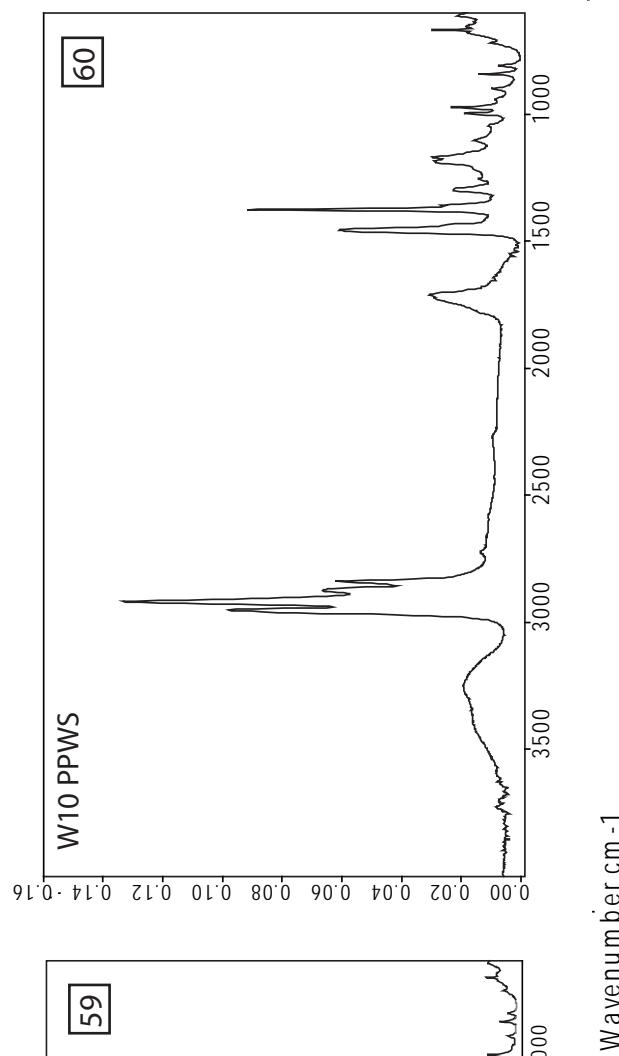
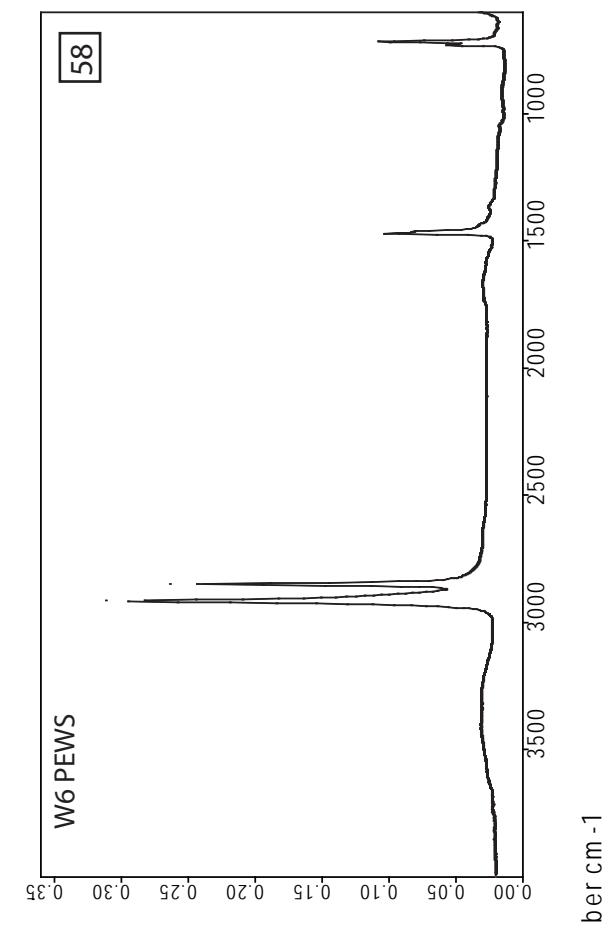
Wavenumber cm^{-1} Wavenumber cm^{-1}

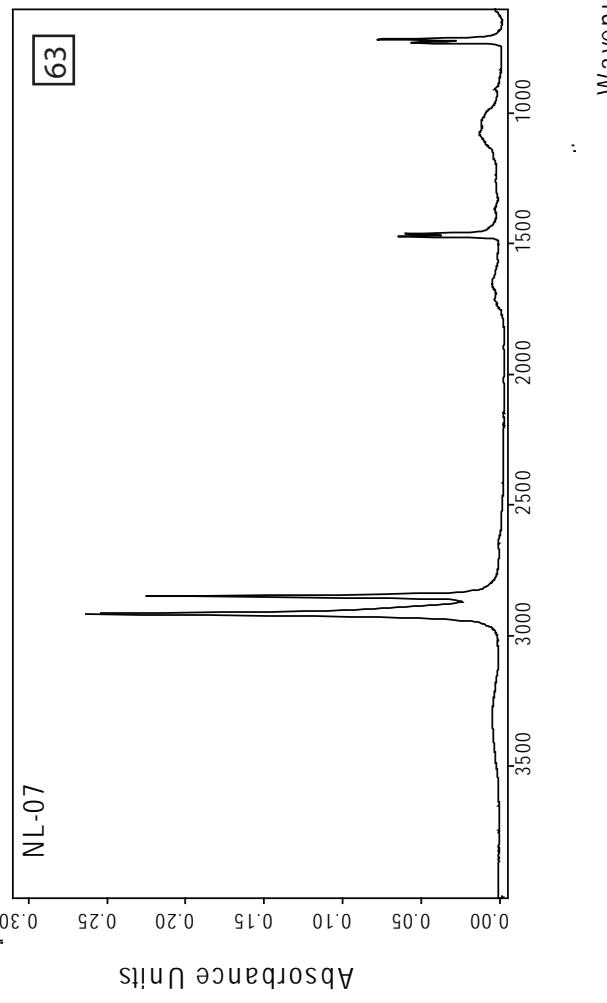
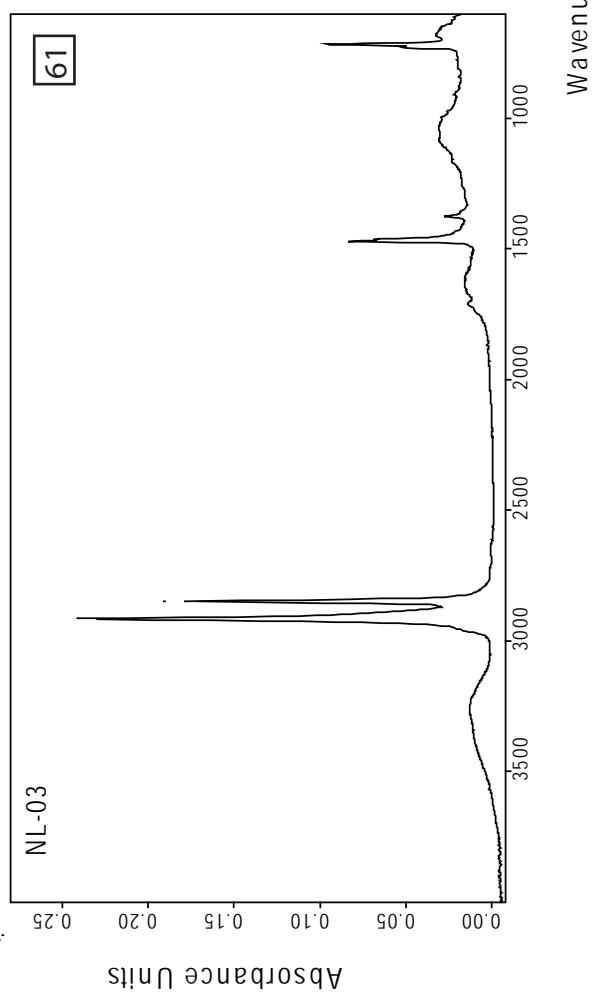
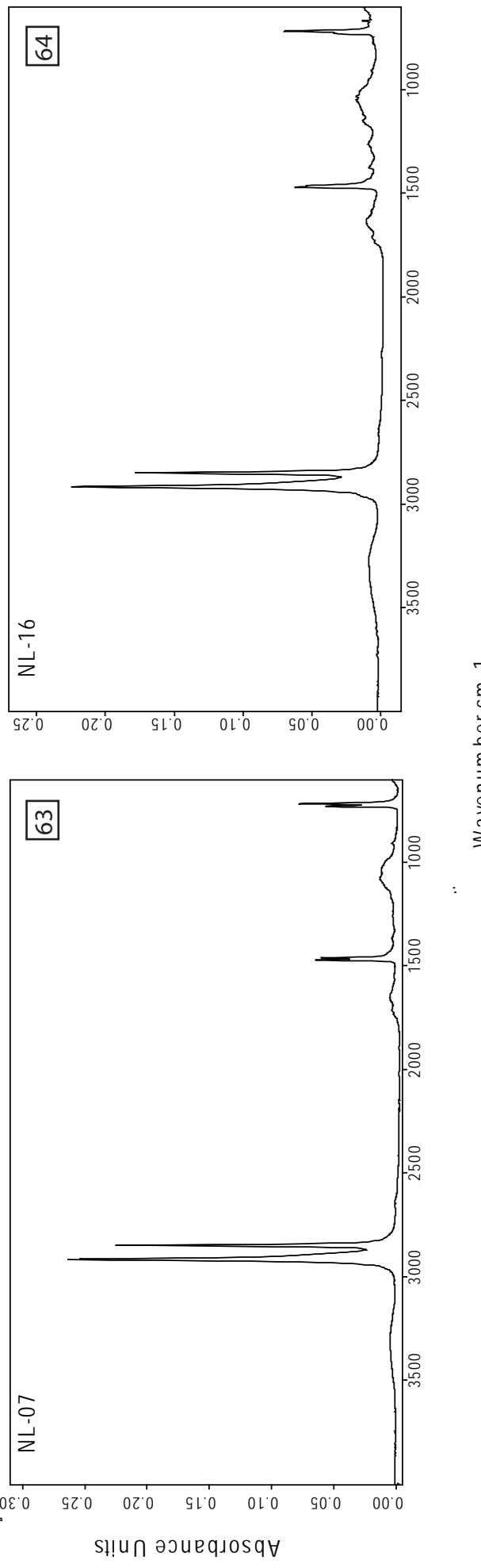
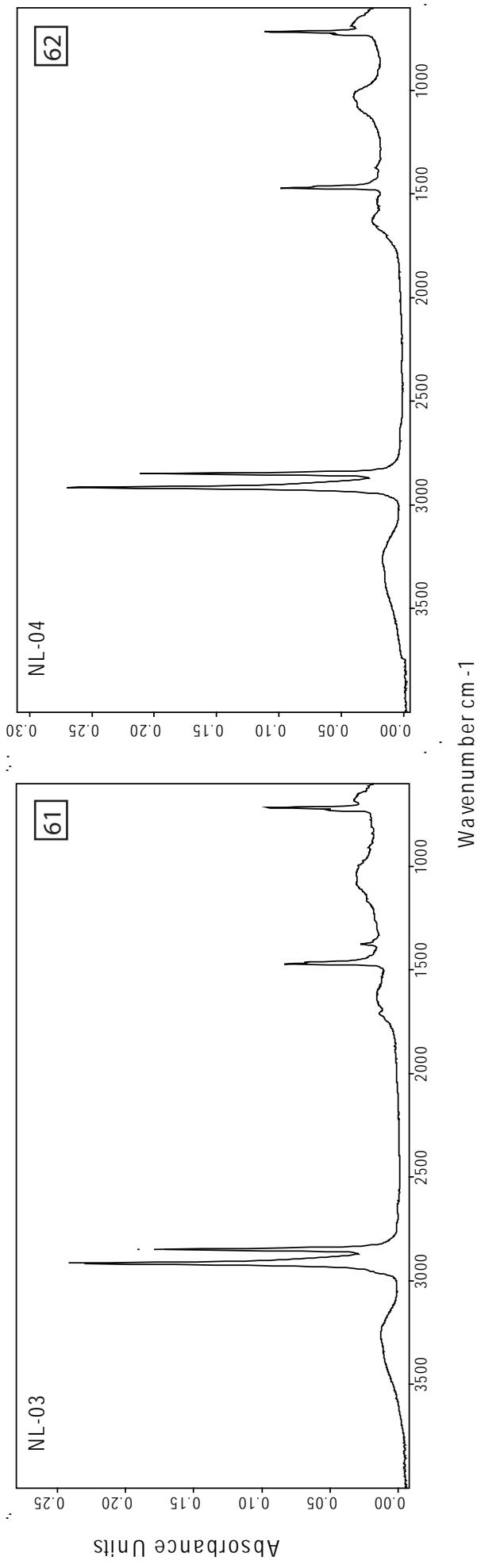


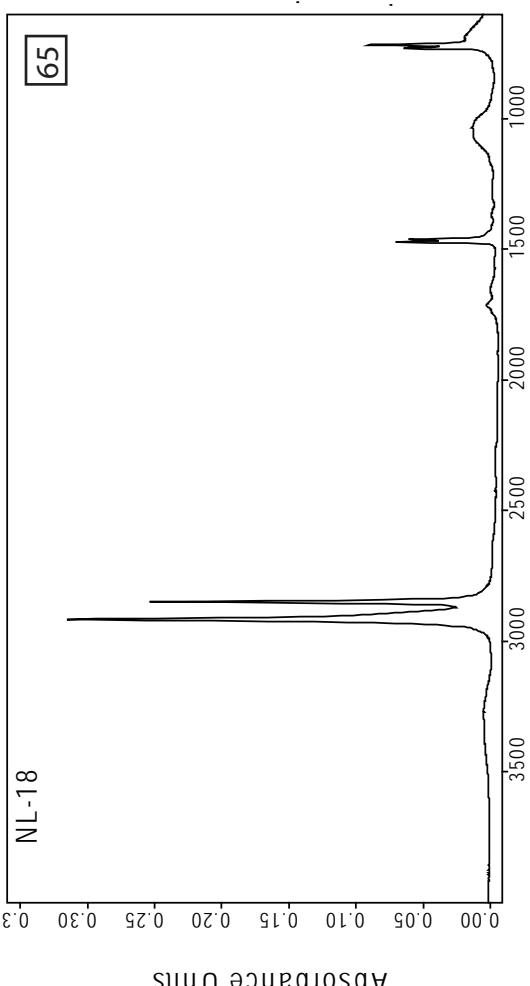
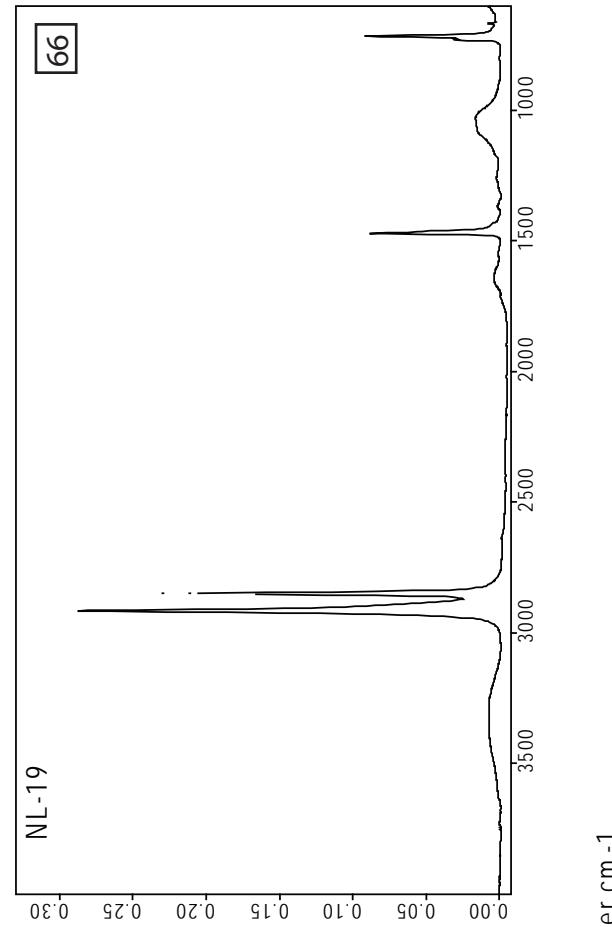
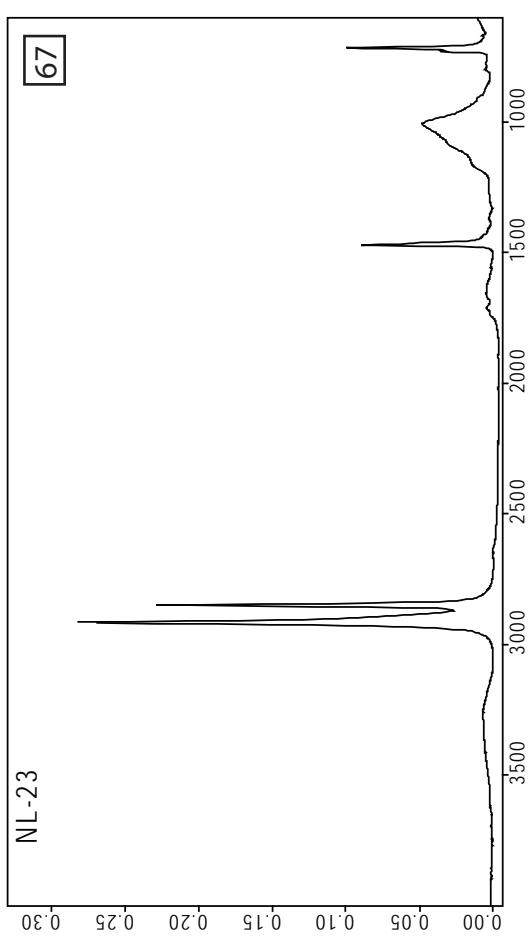






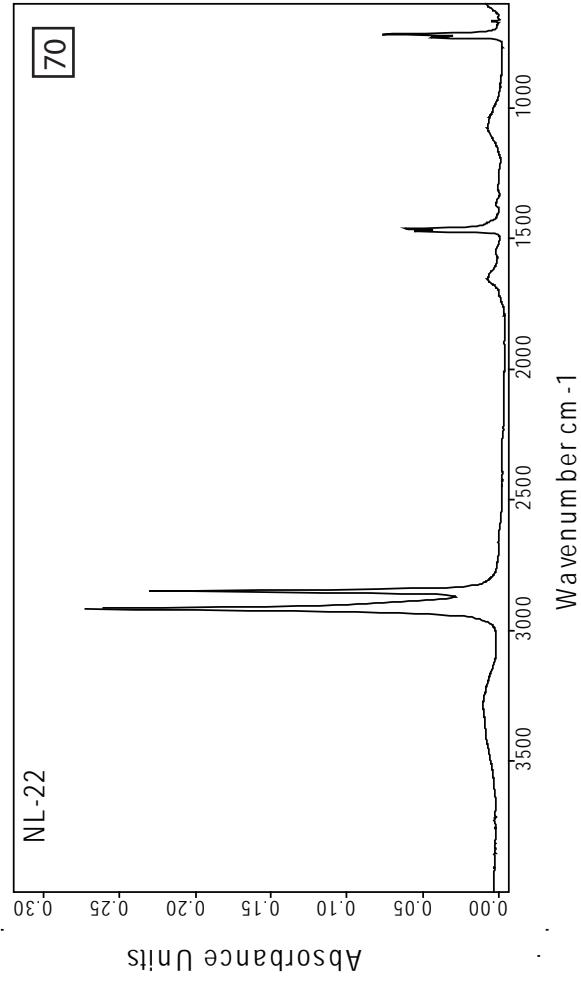
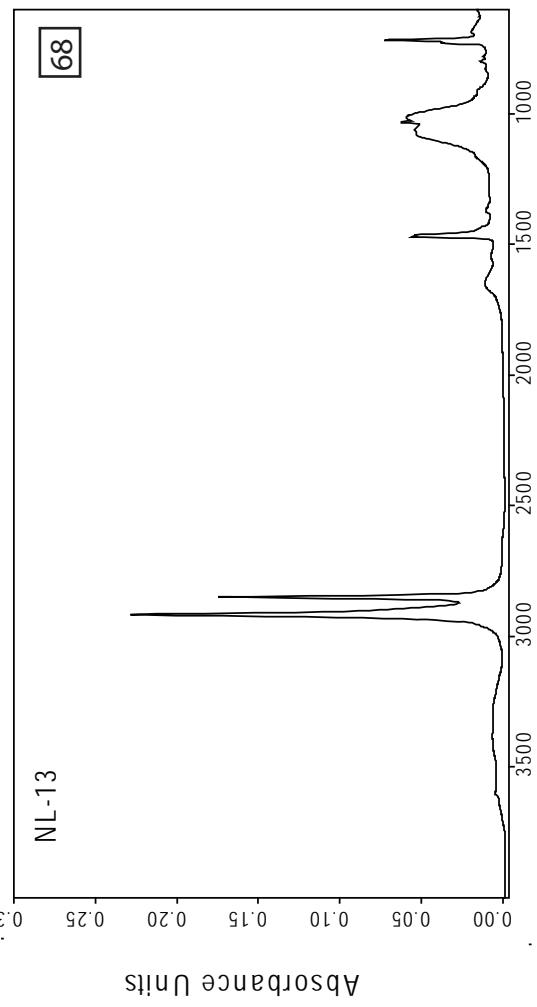
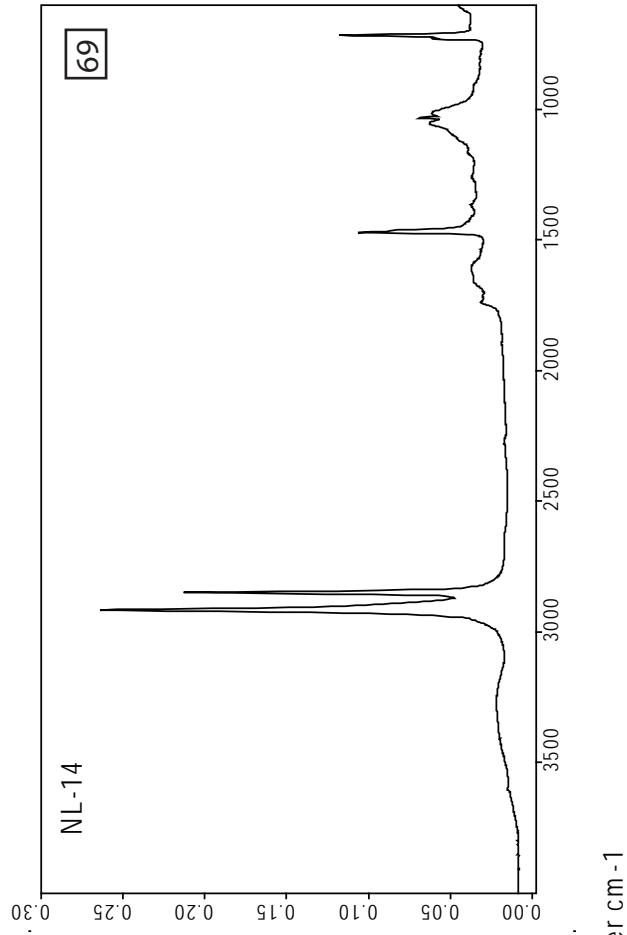


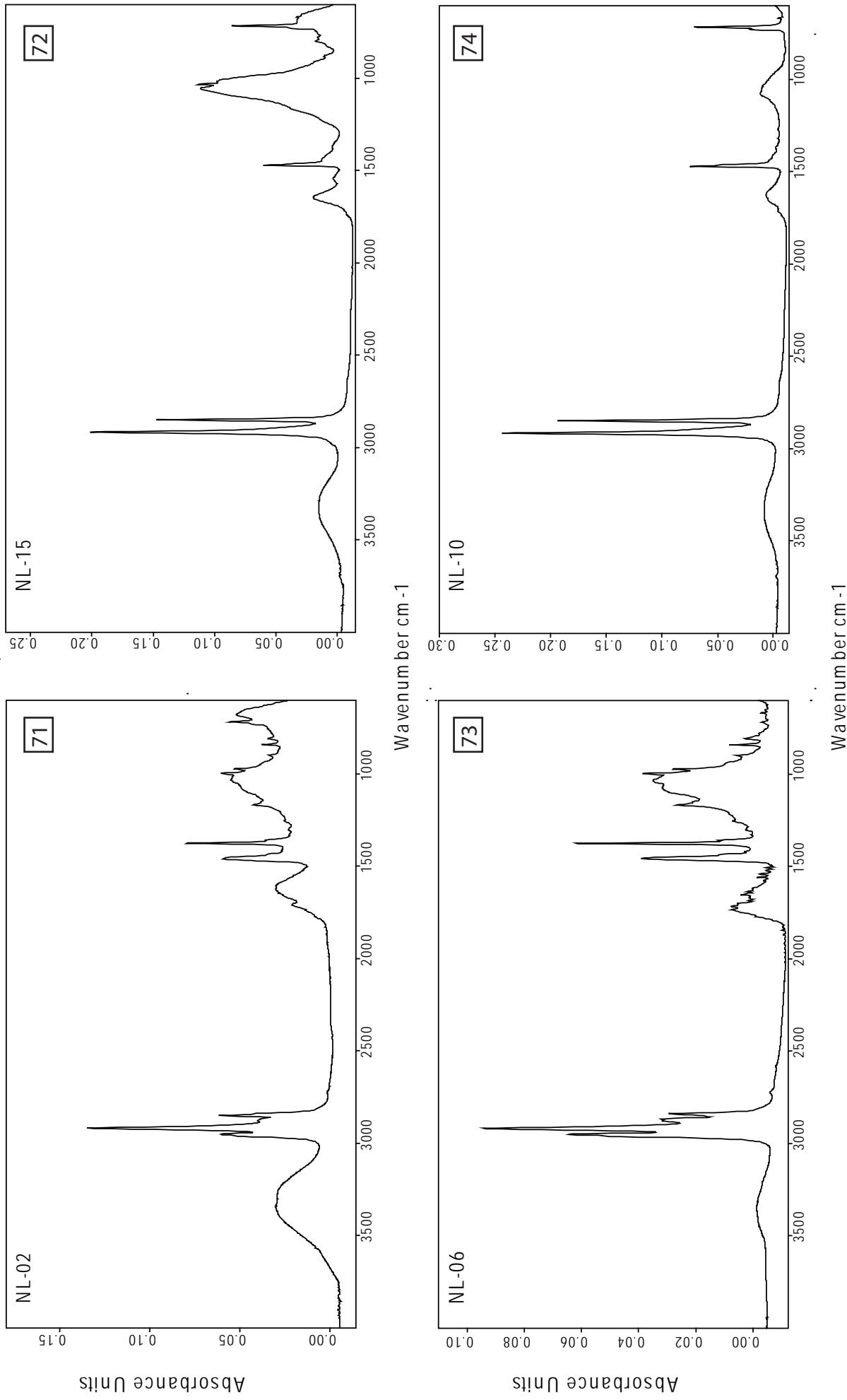


Wavenumber cm^{-1} 

Absorbance Units

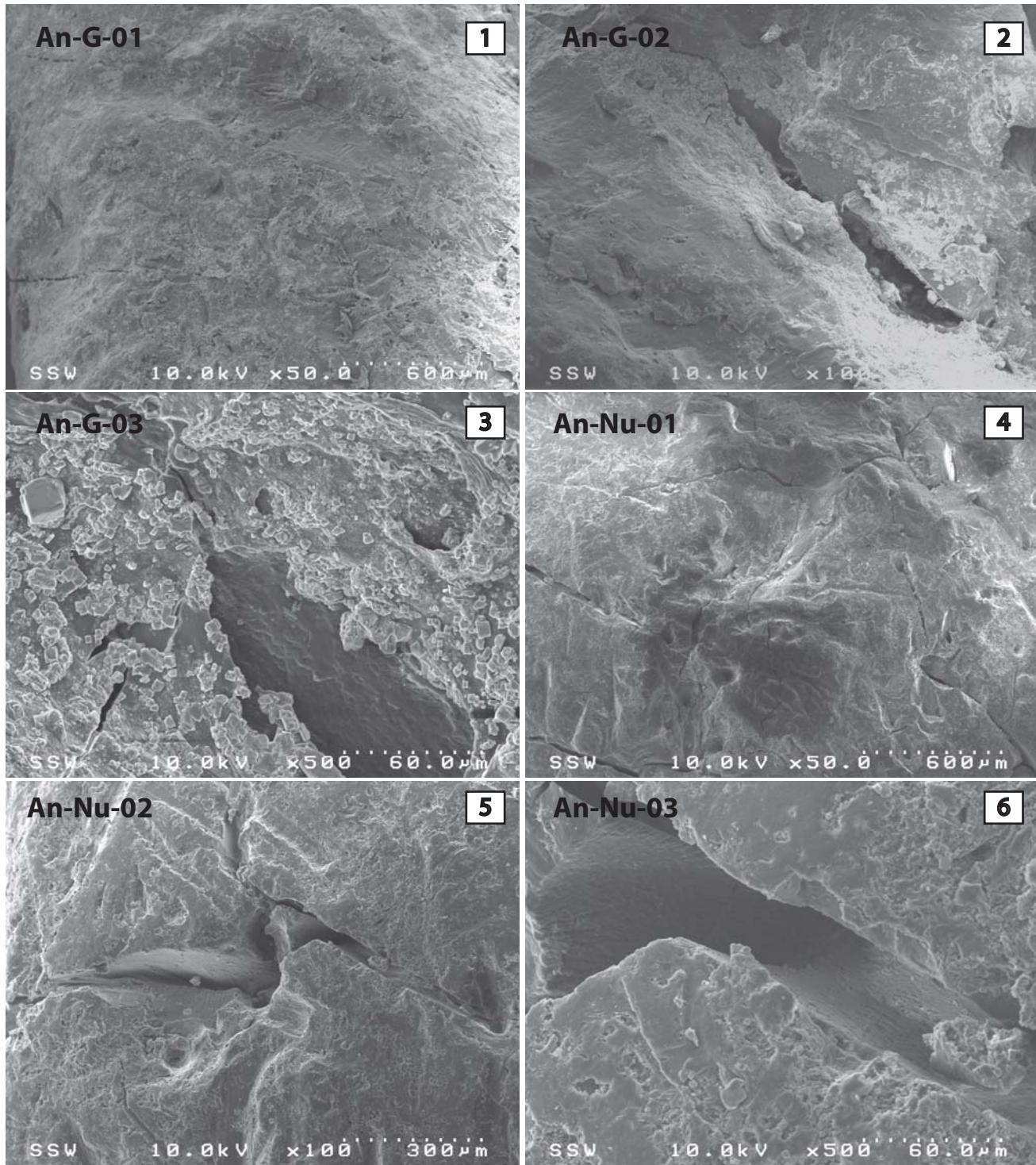
Wavenumber cm^{-1}

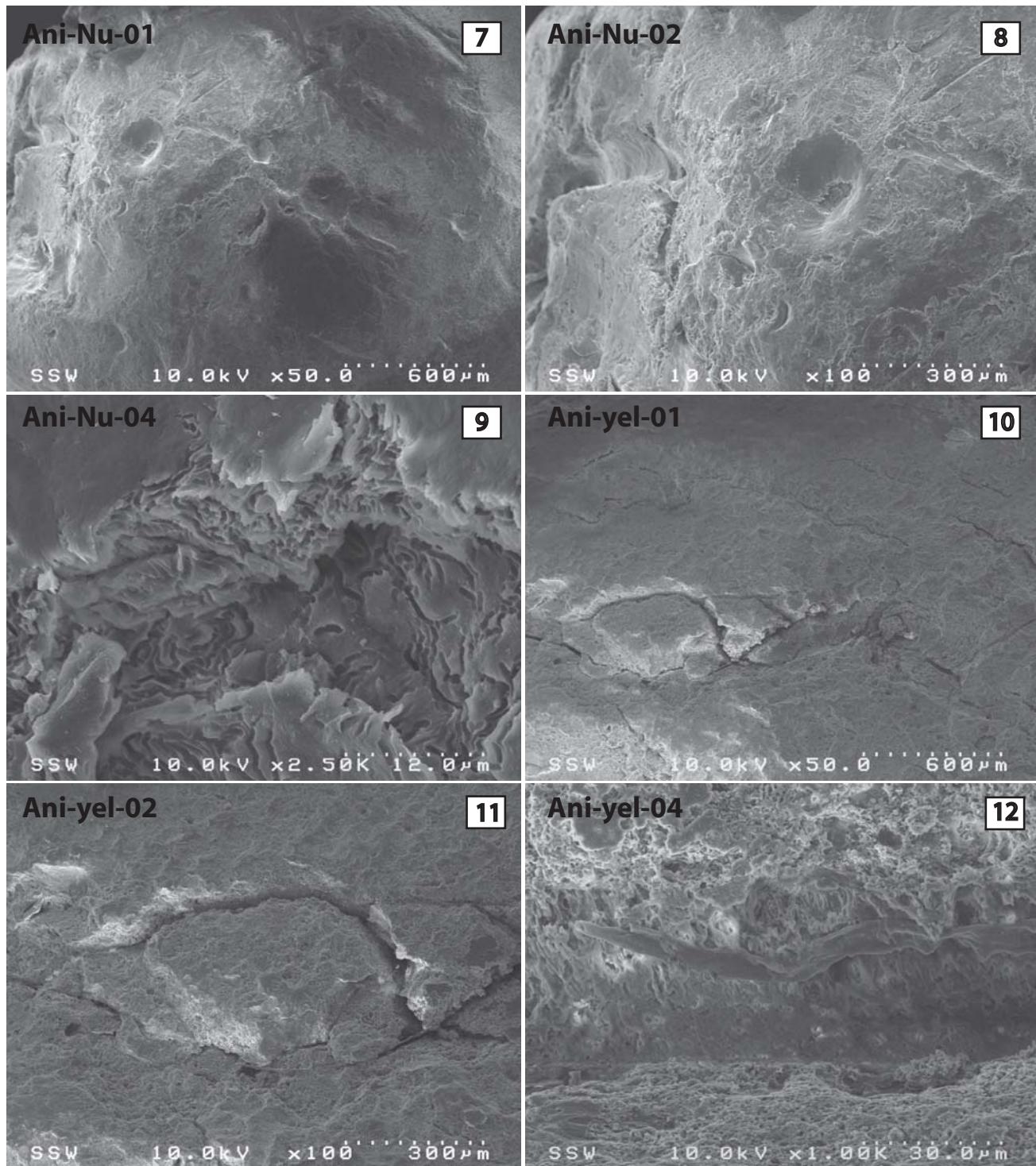


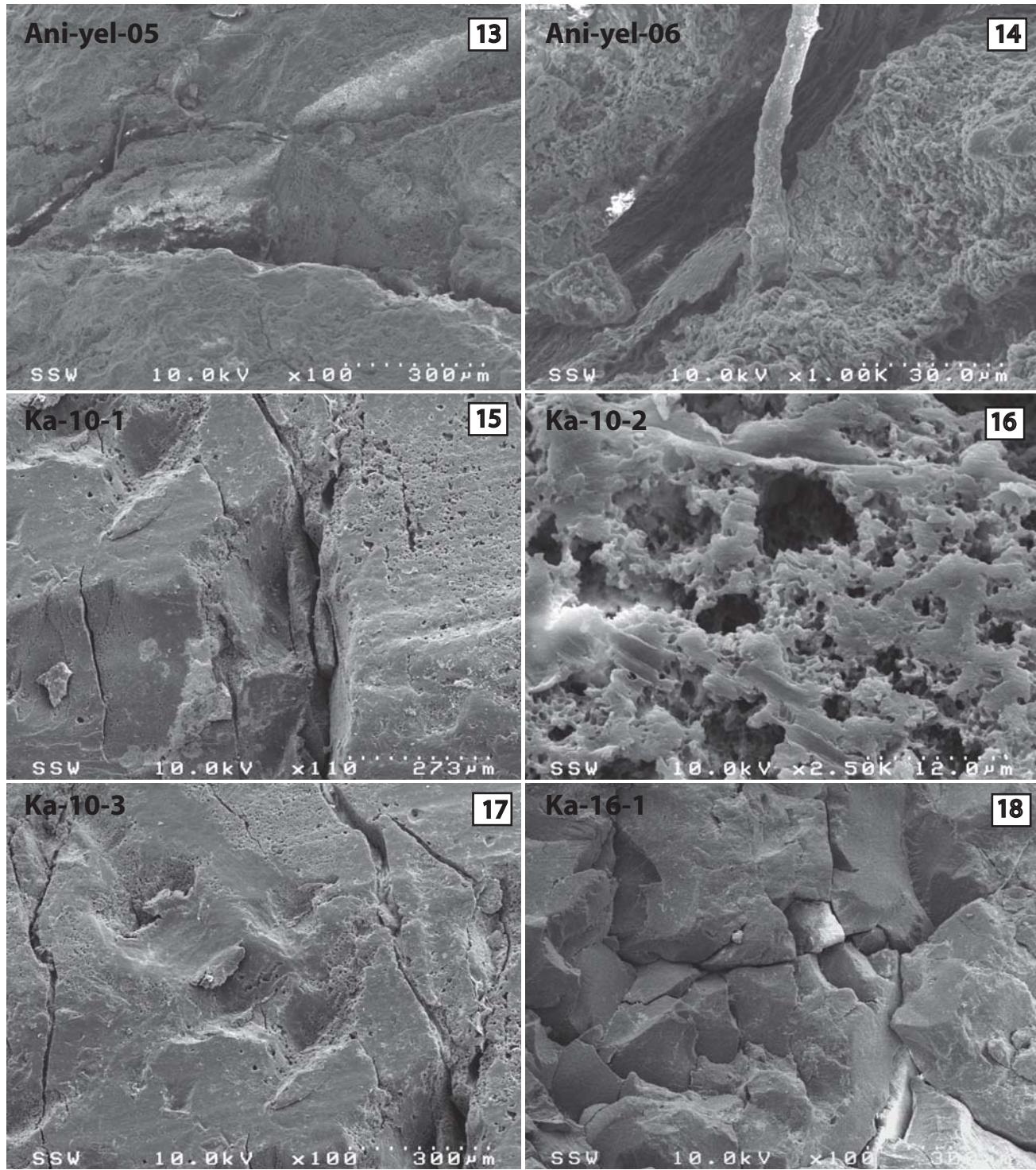


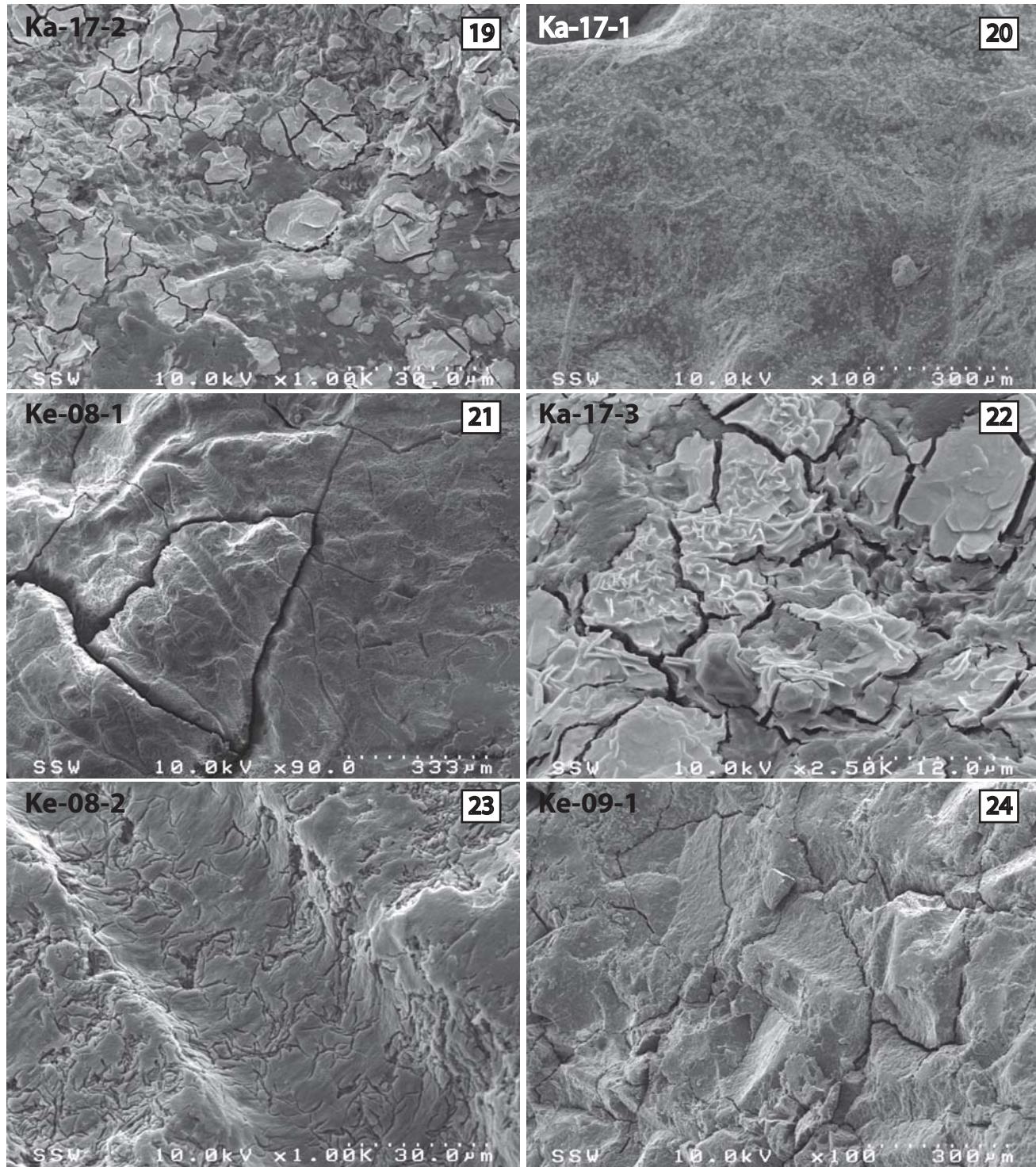
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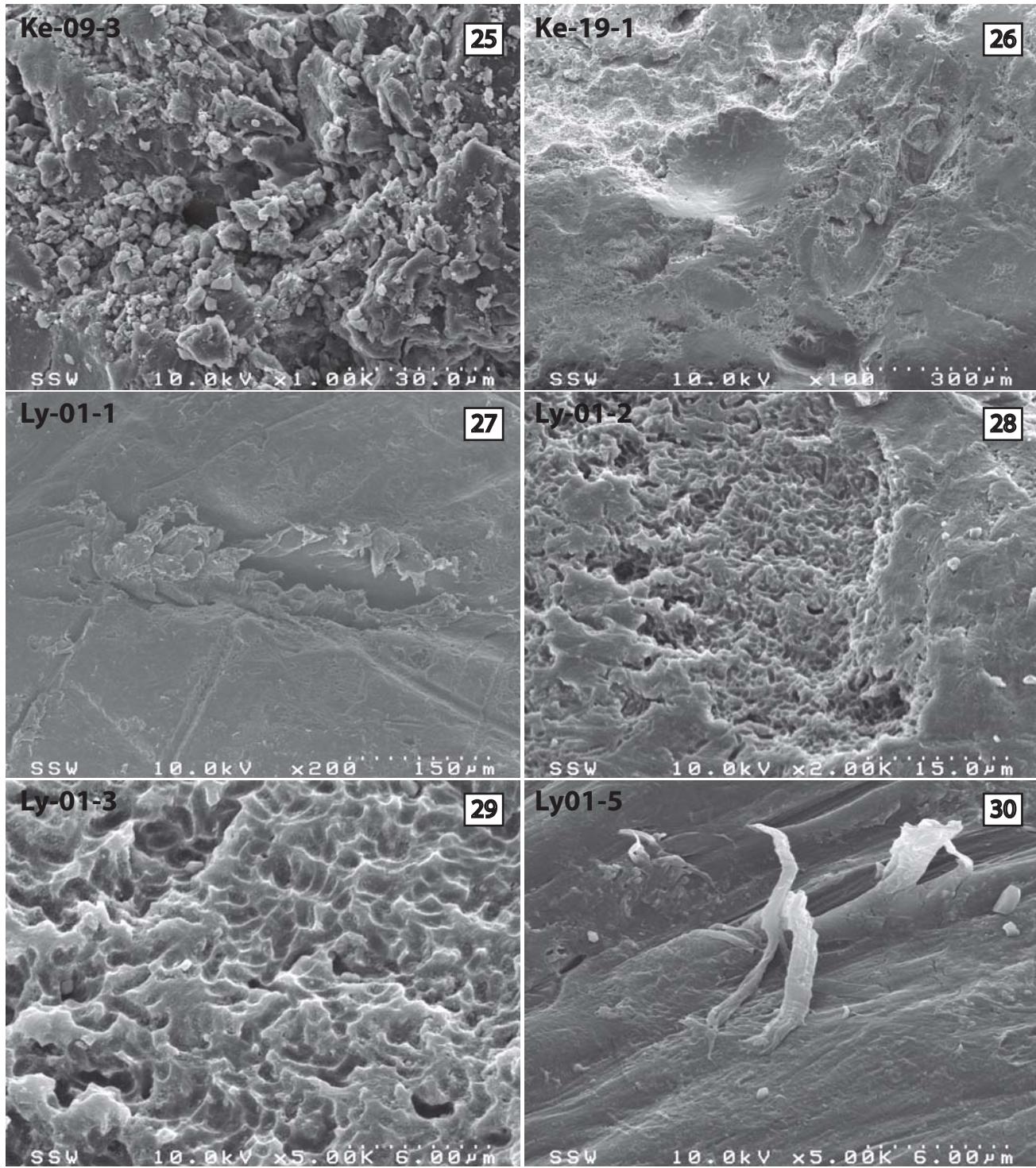
Scanning electron microscope images of plastic particles collected from beaches on the island of Kauai, and Newfoundland, as well as experimentally degraded samples. Images 1-64 are Kauaiian samples, images 65-139 are experimentally degraded samples, and images 140-157 are Newfoundland samples.

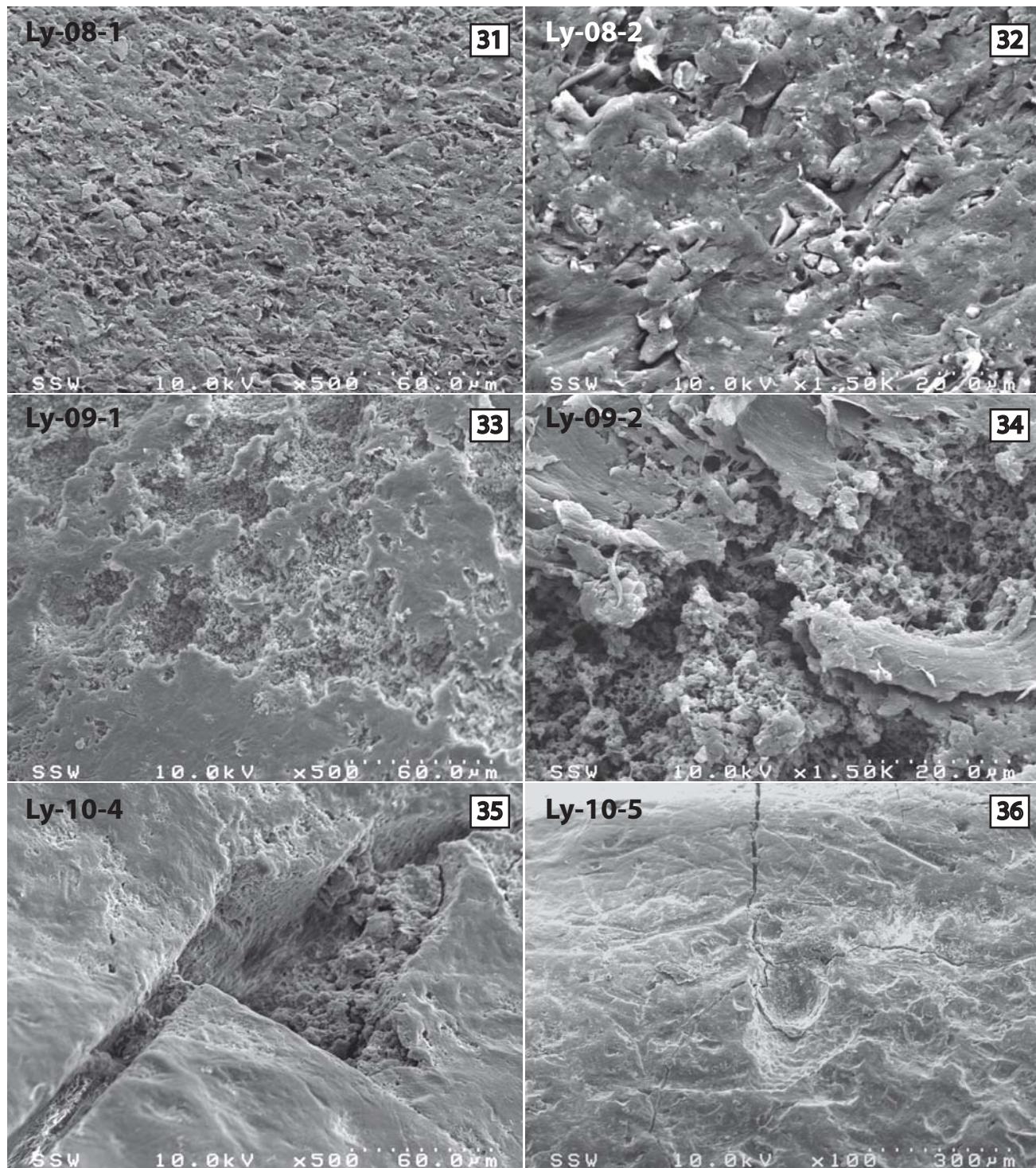


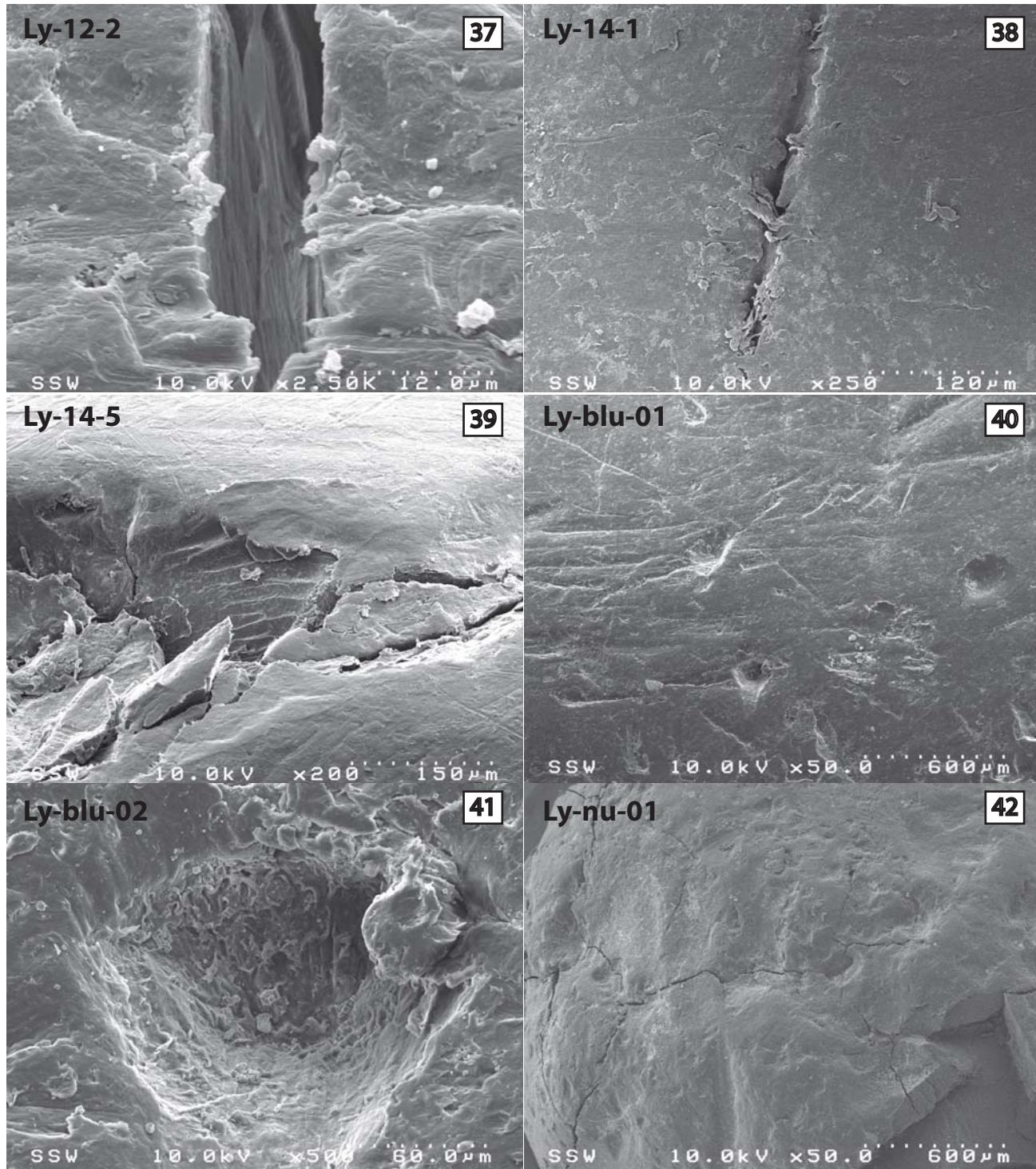


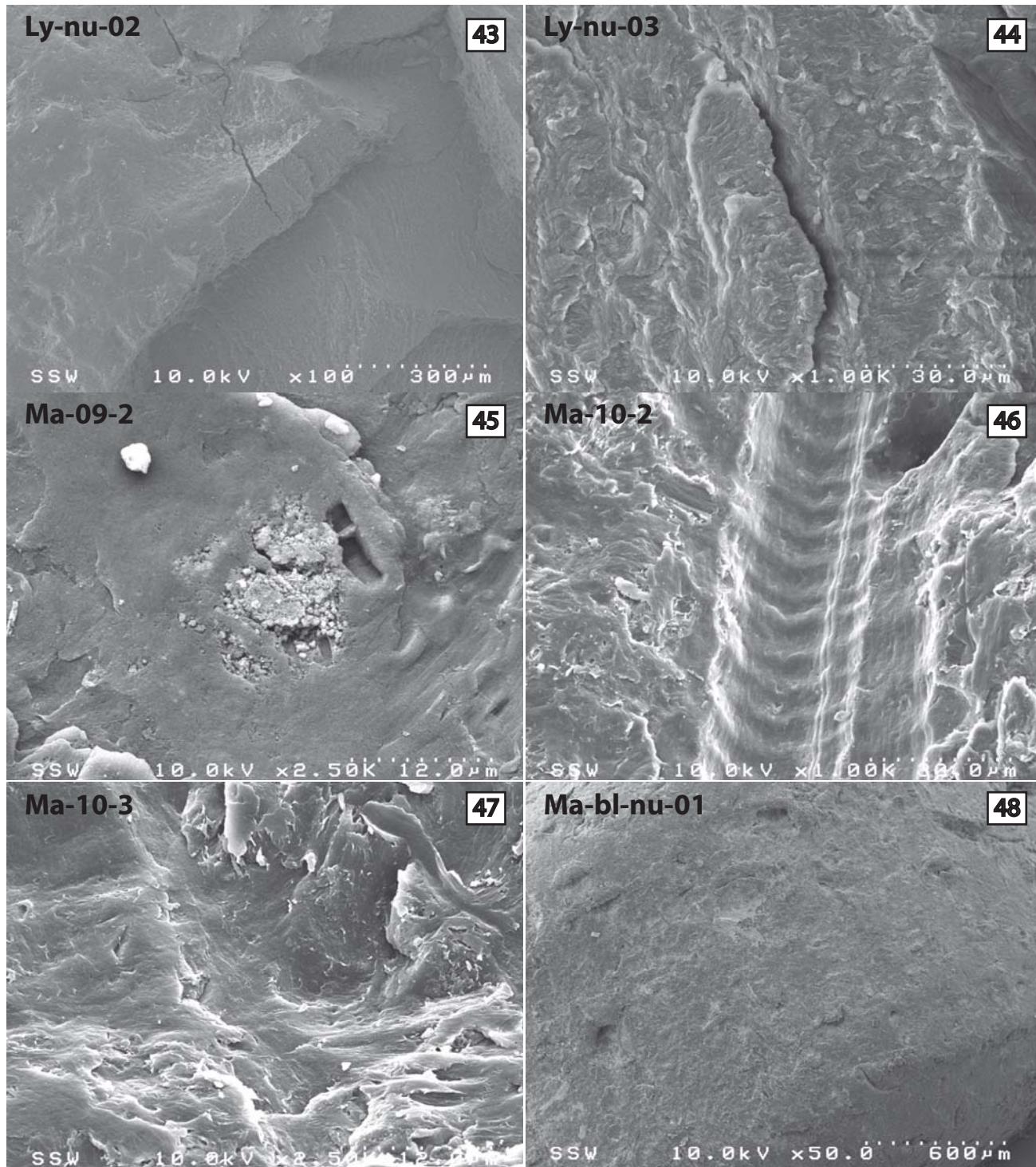


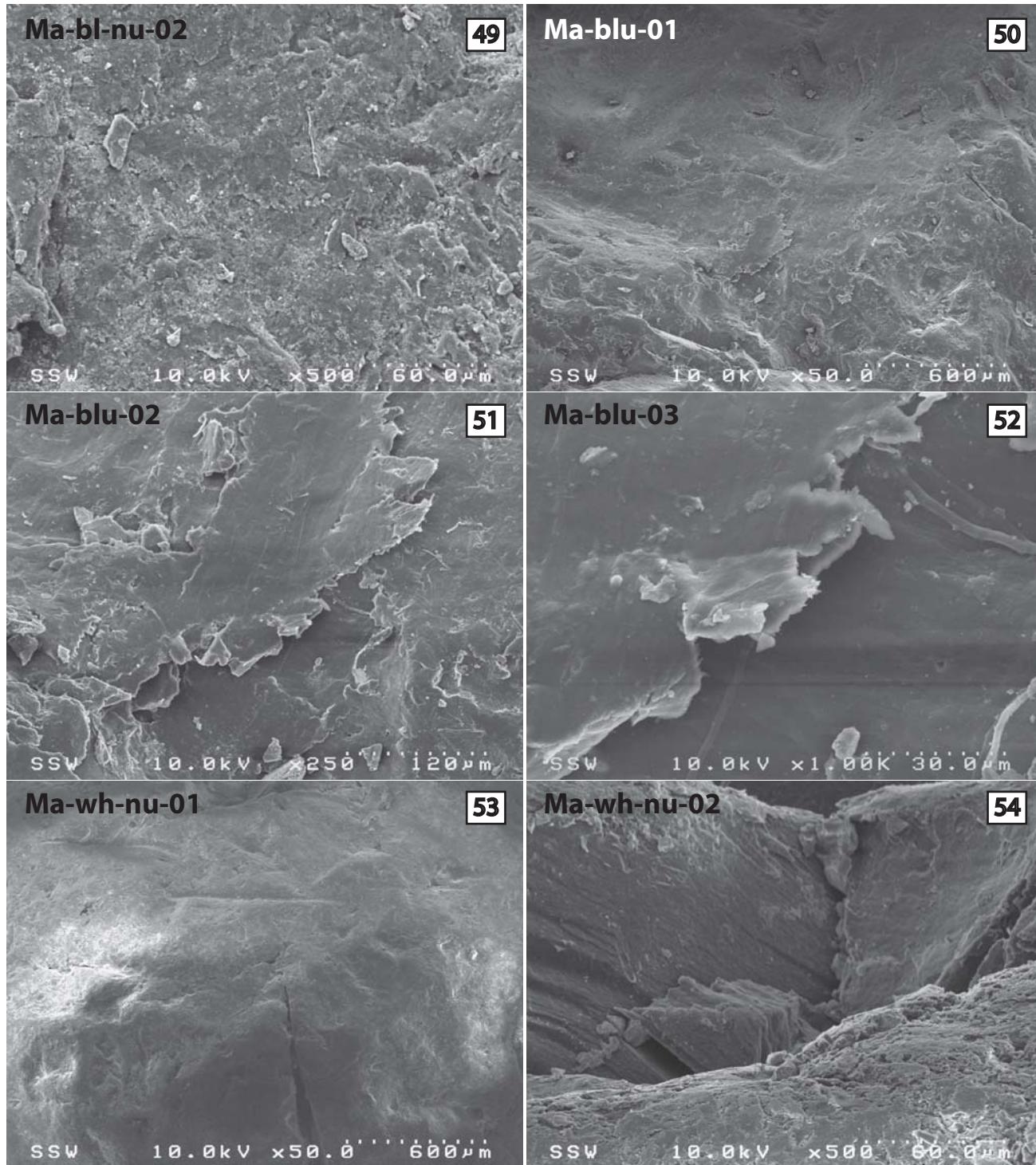


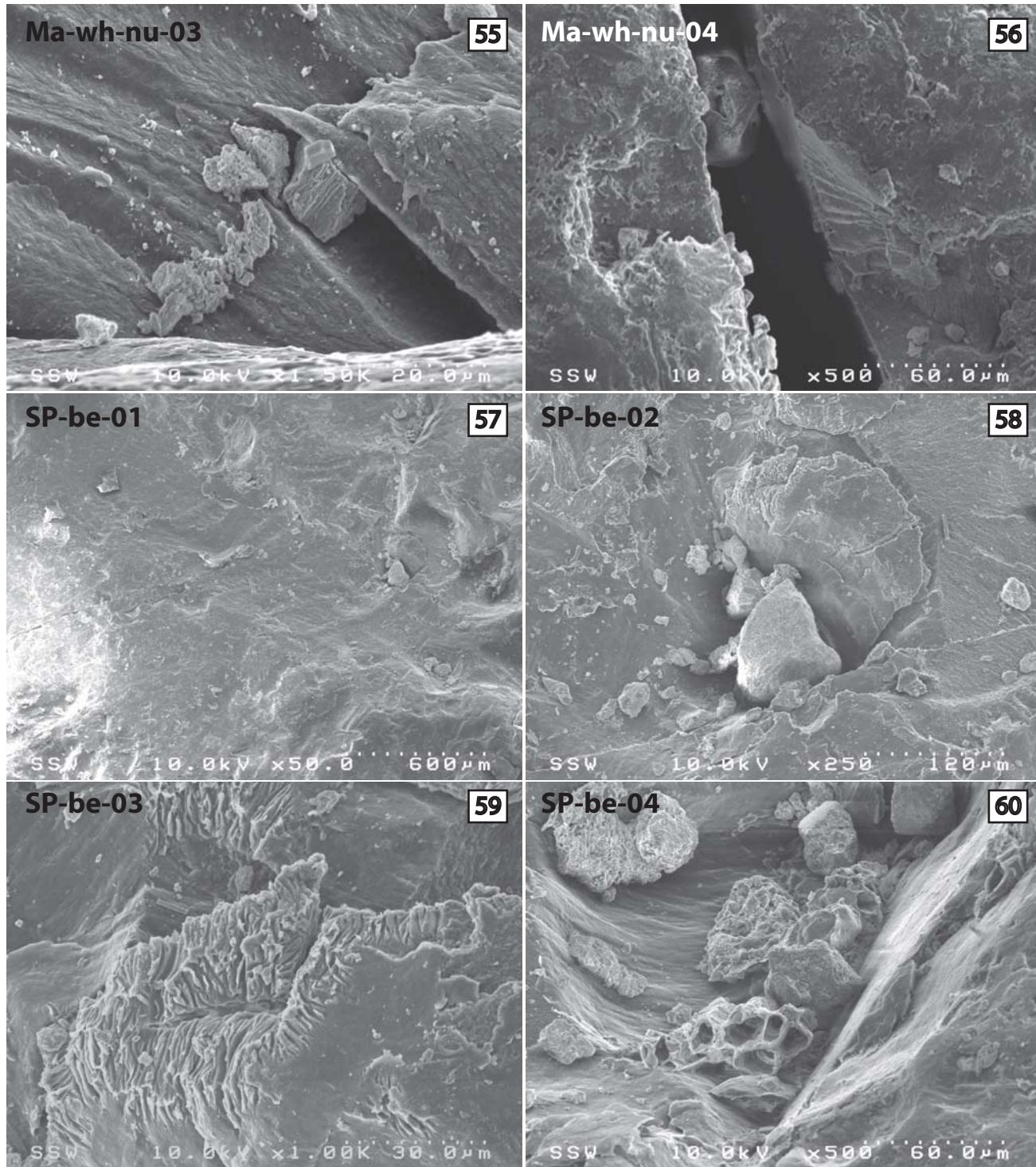


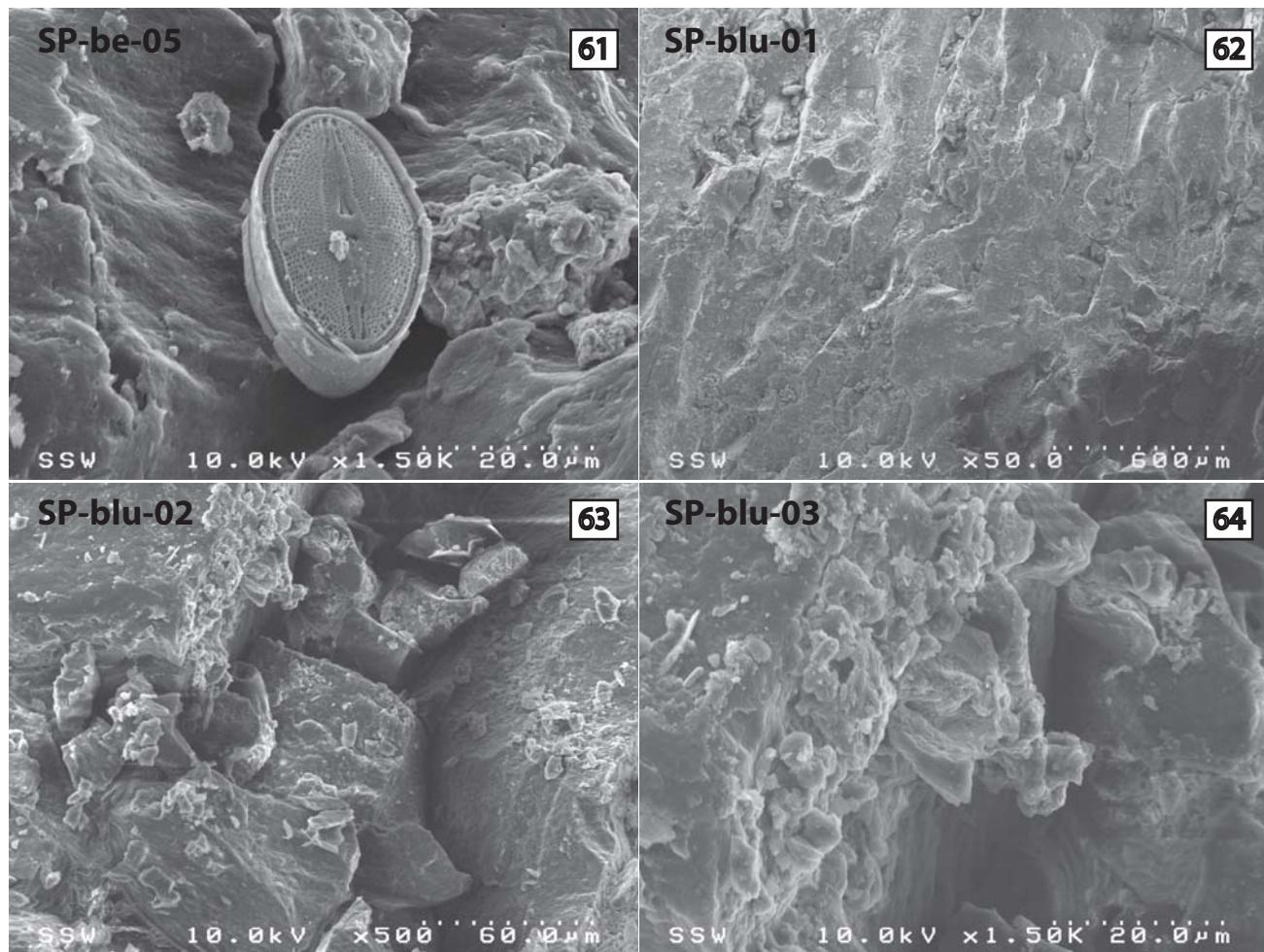


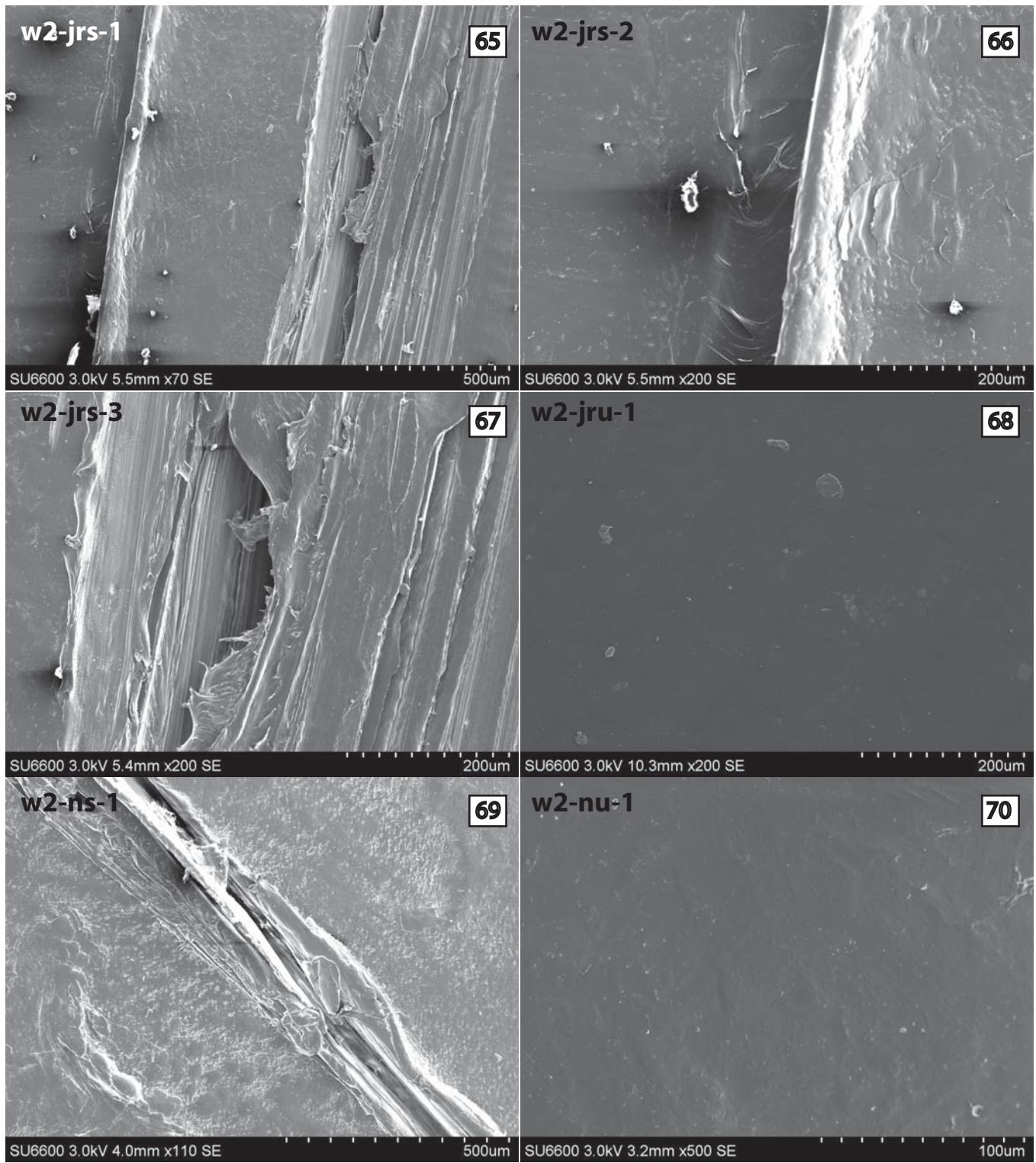


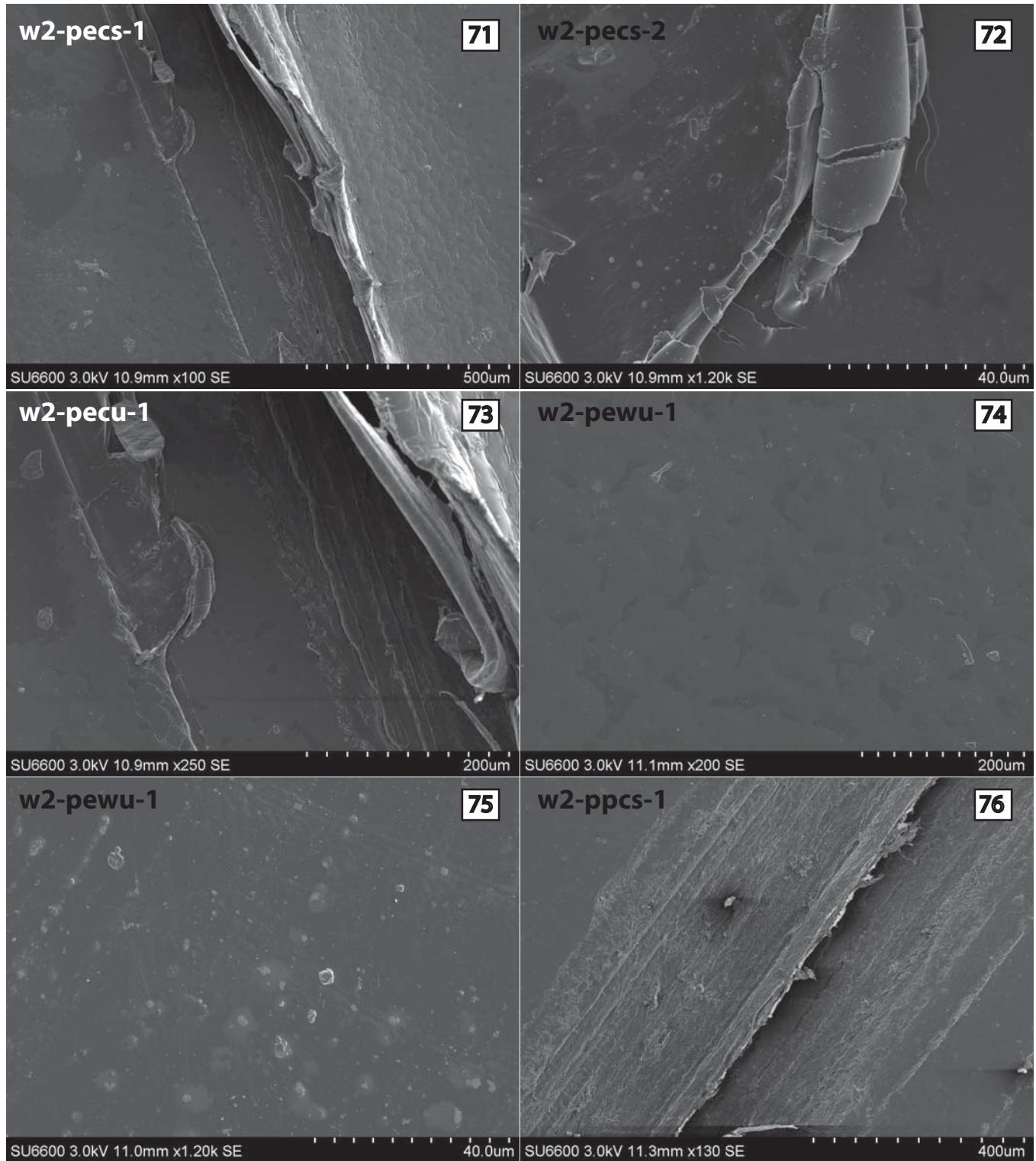


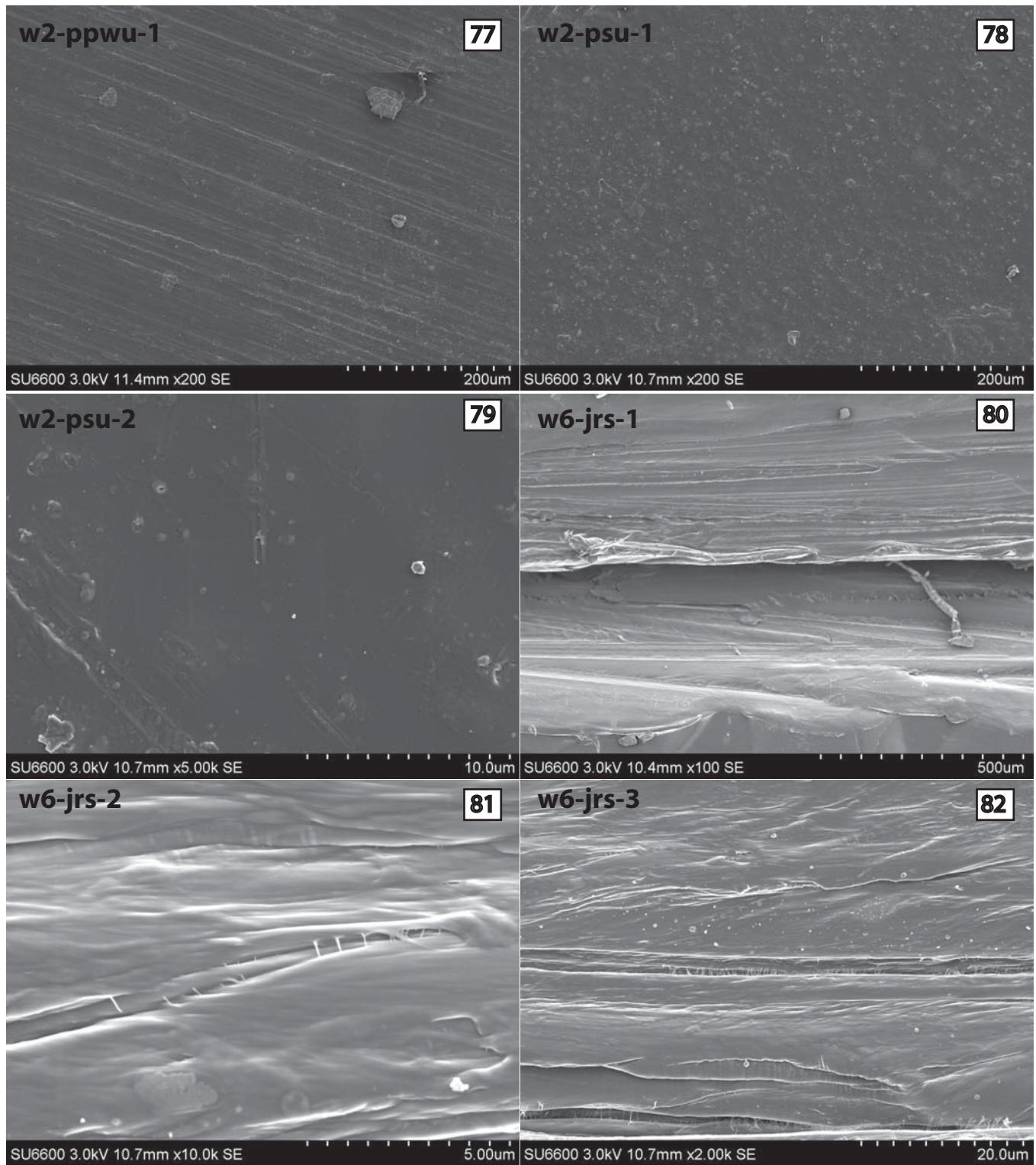


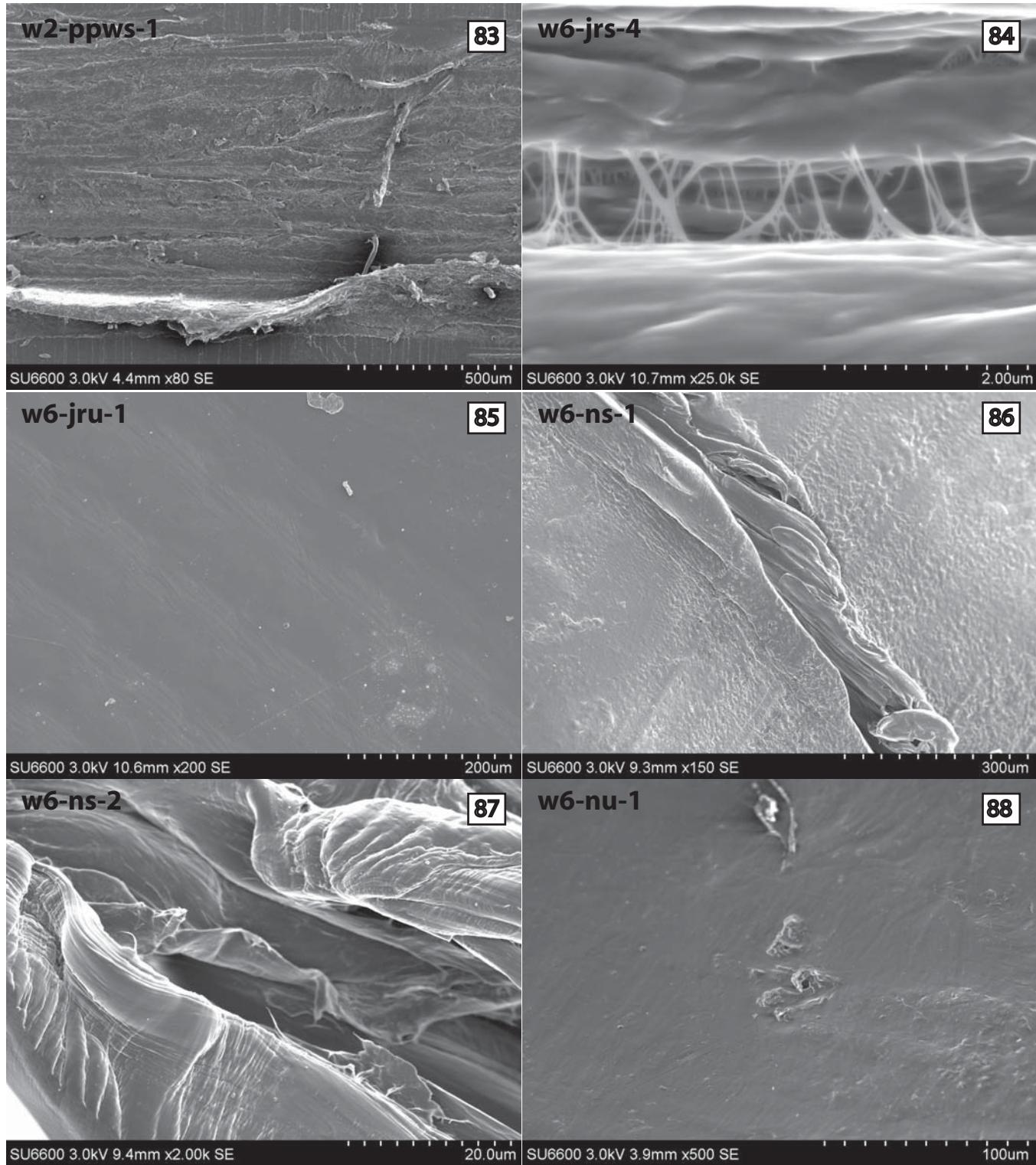


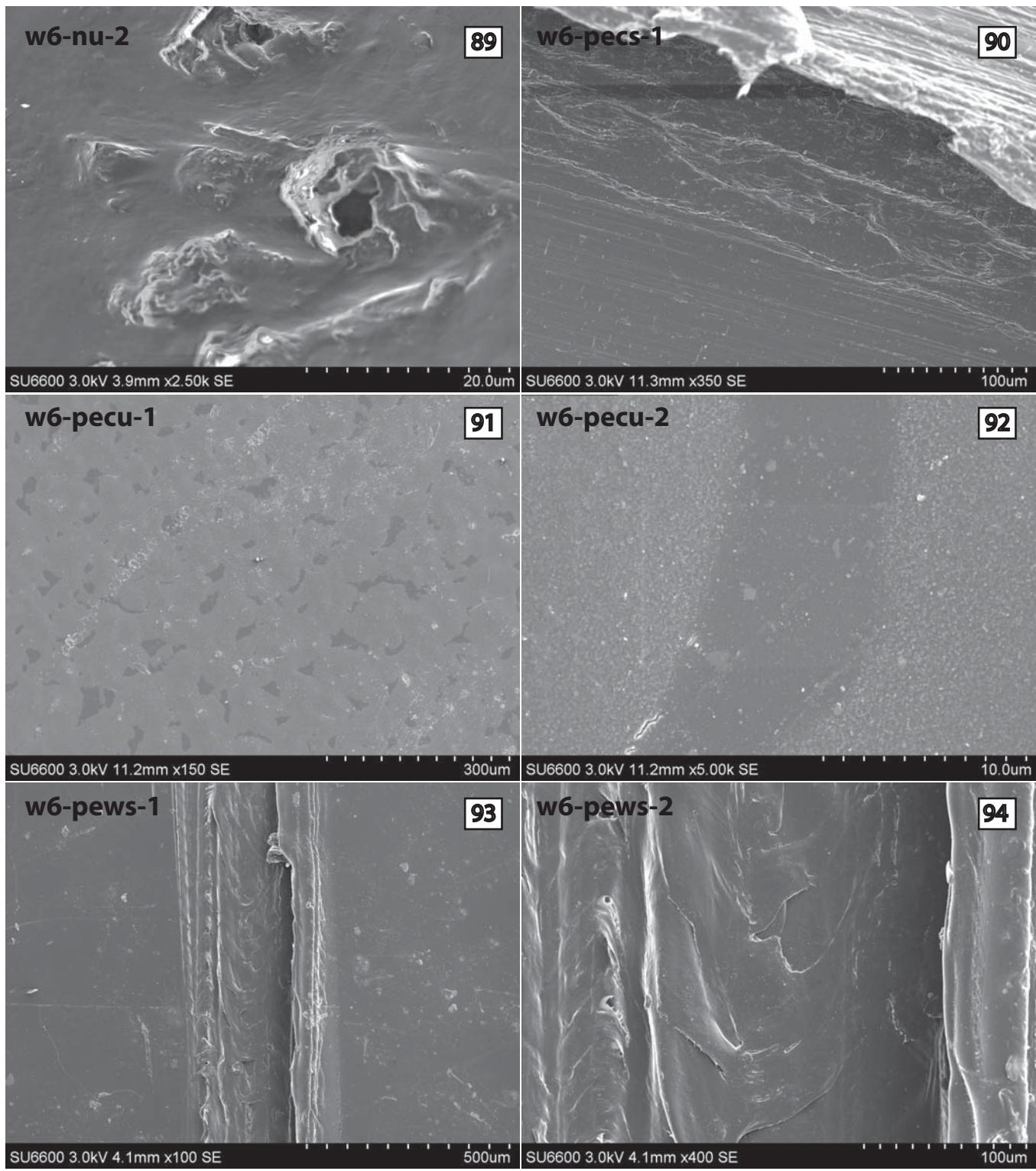


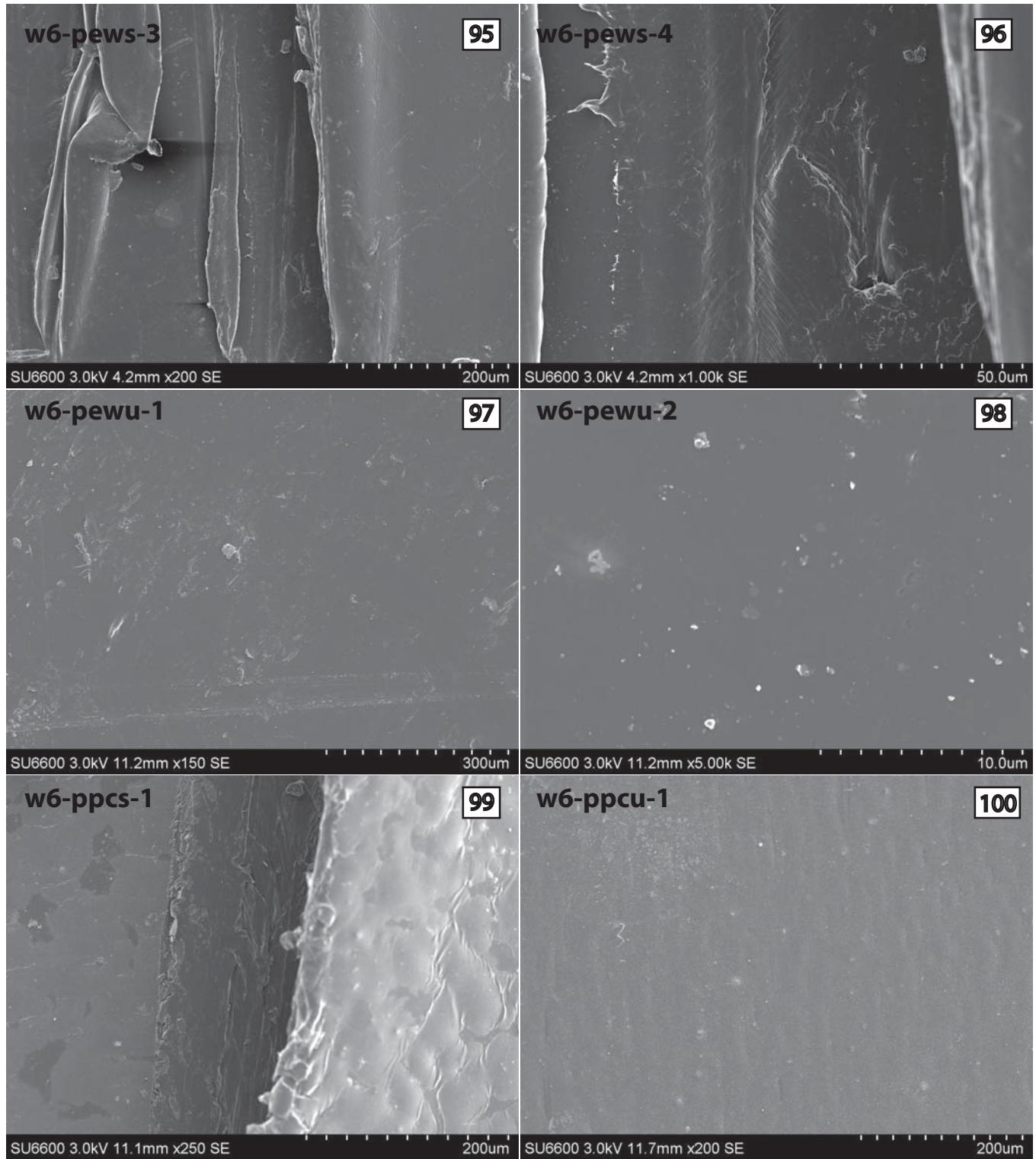


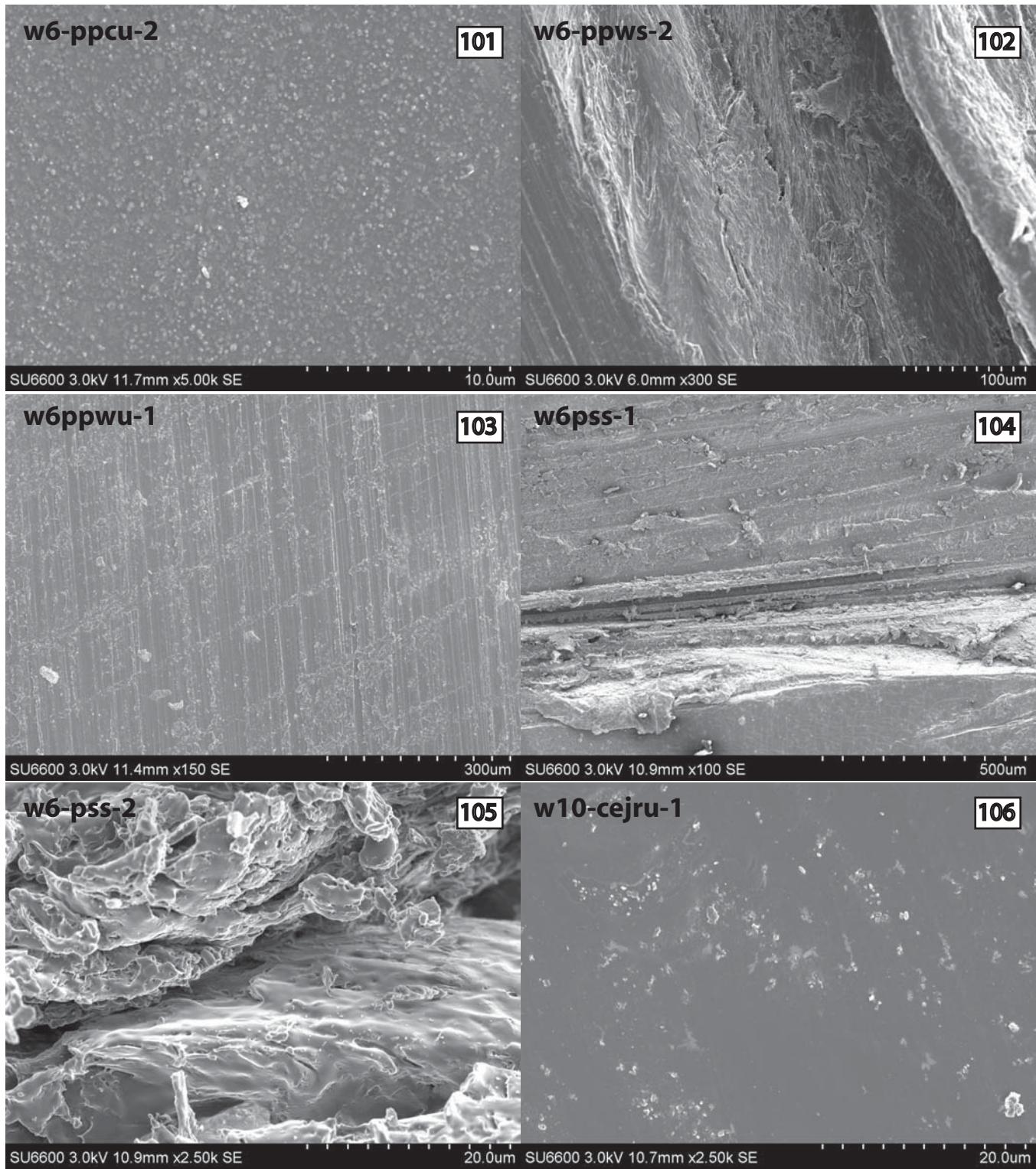


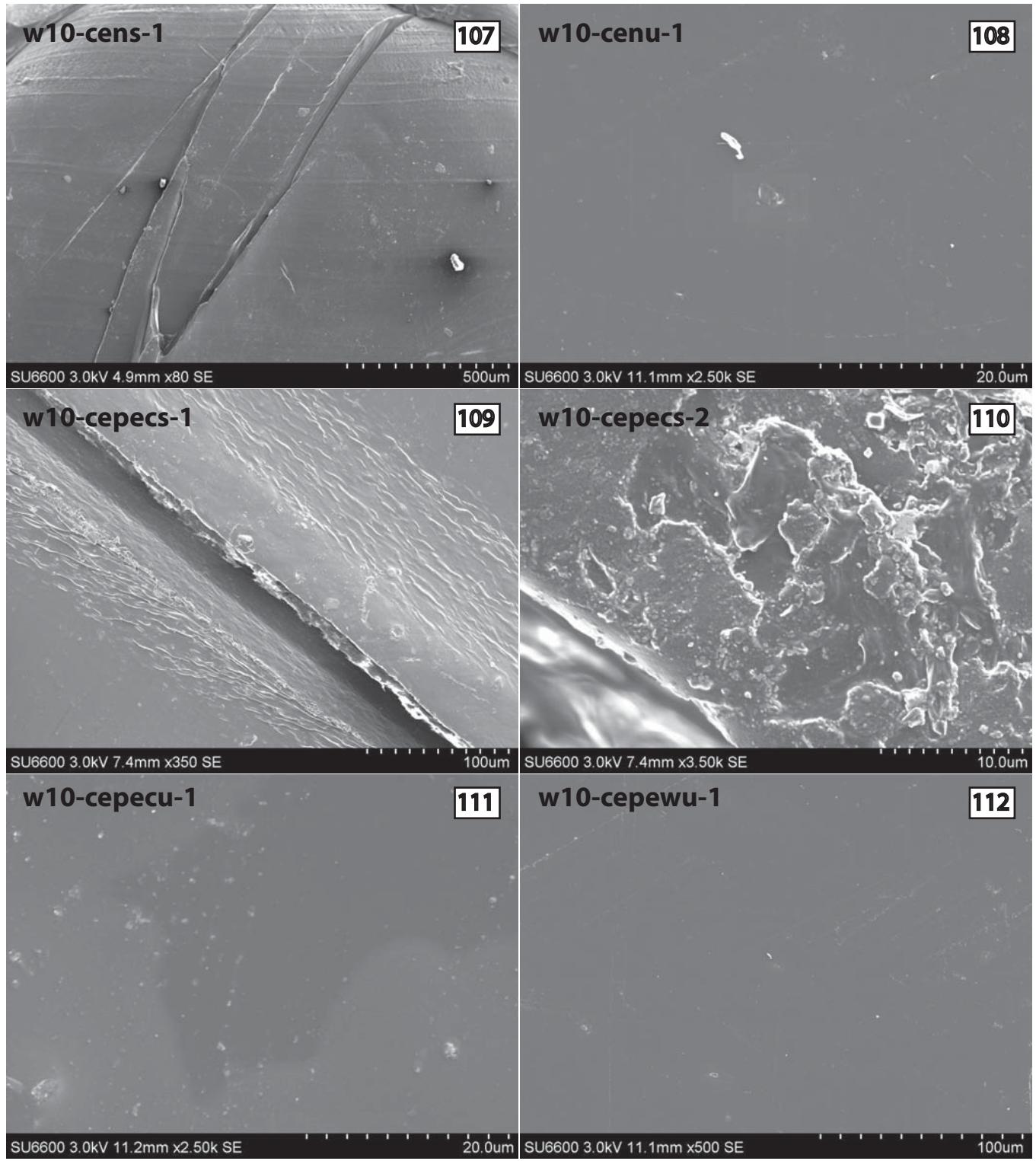


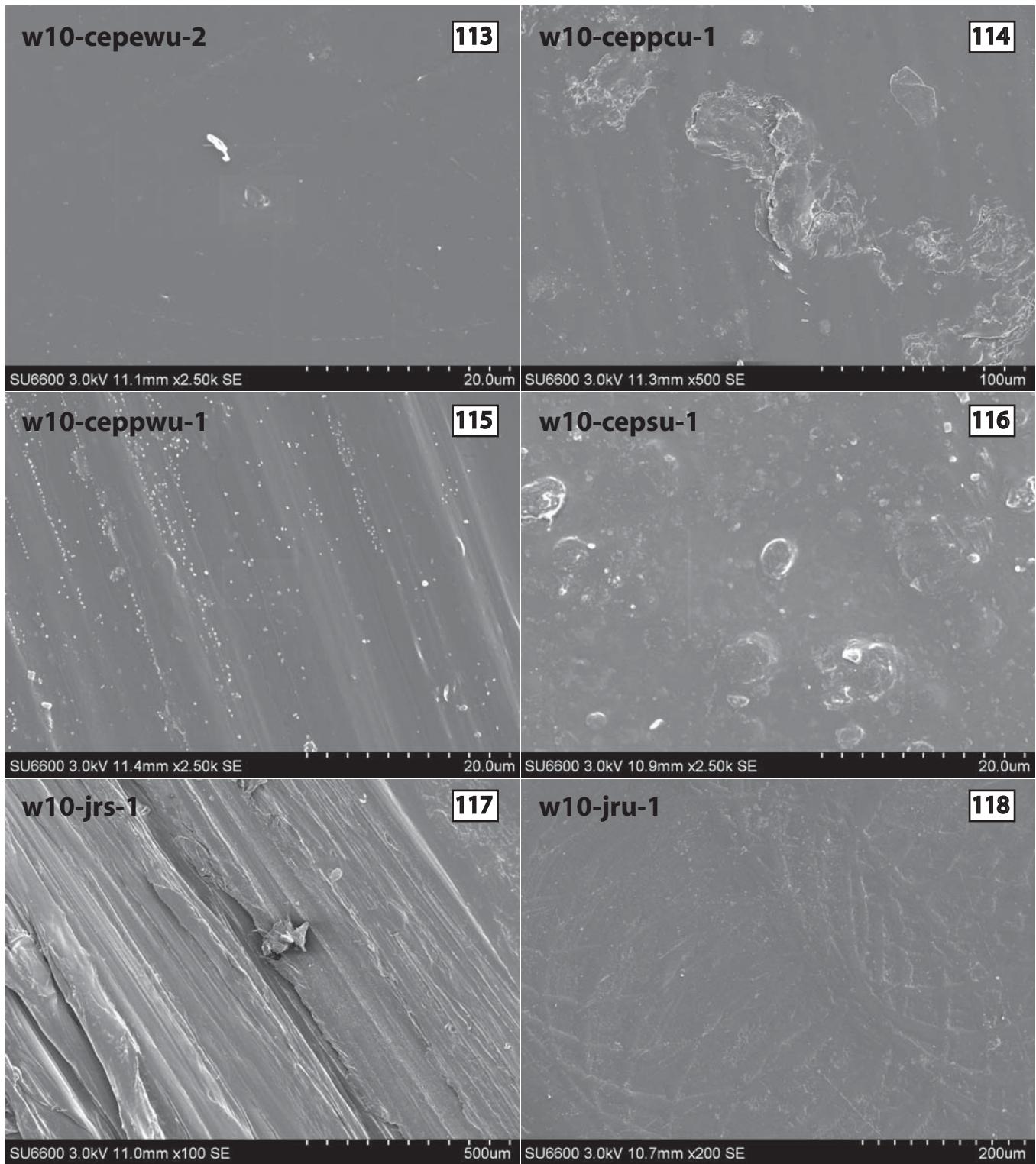


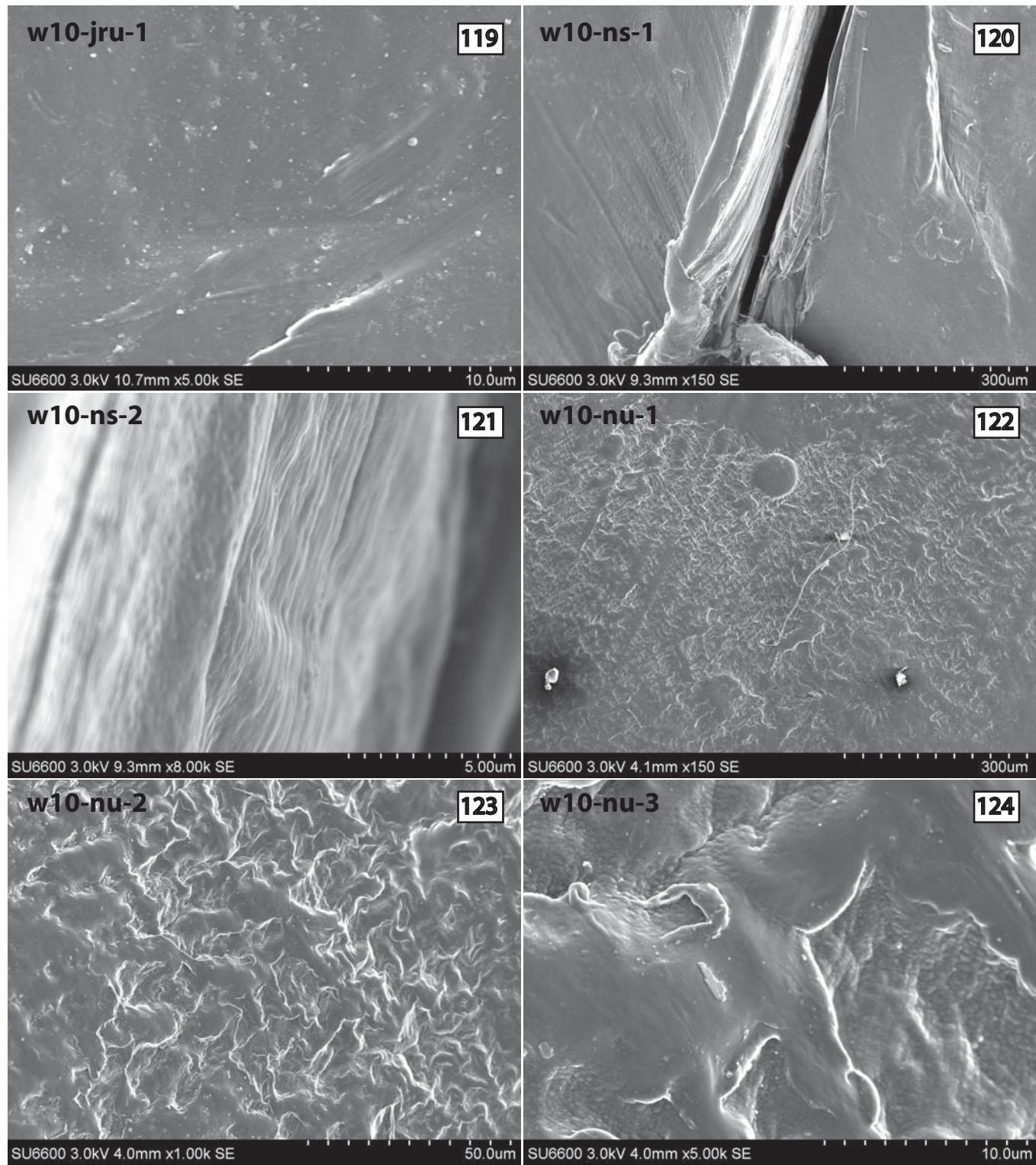


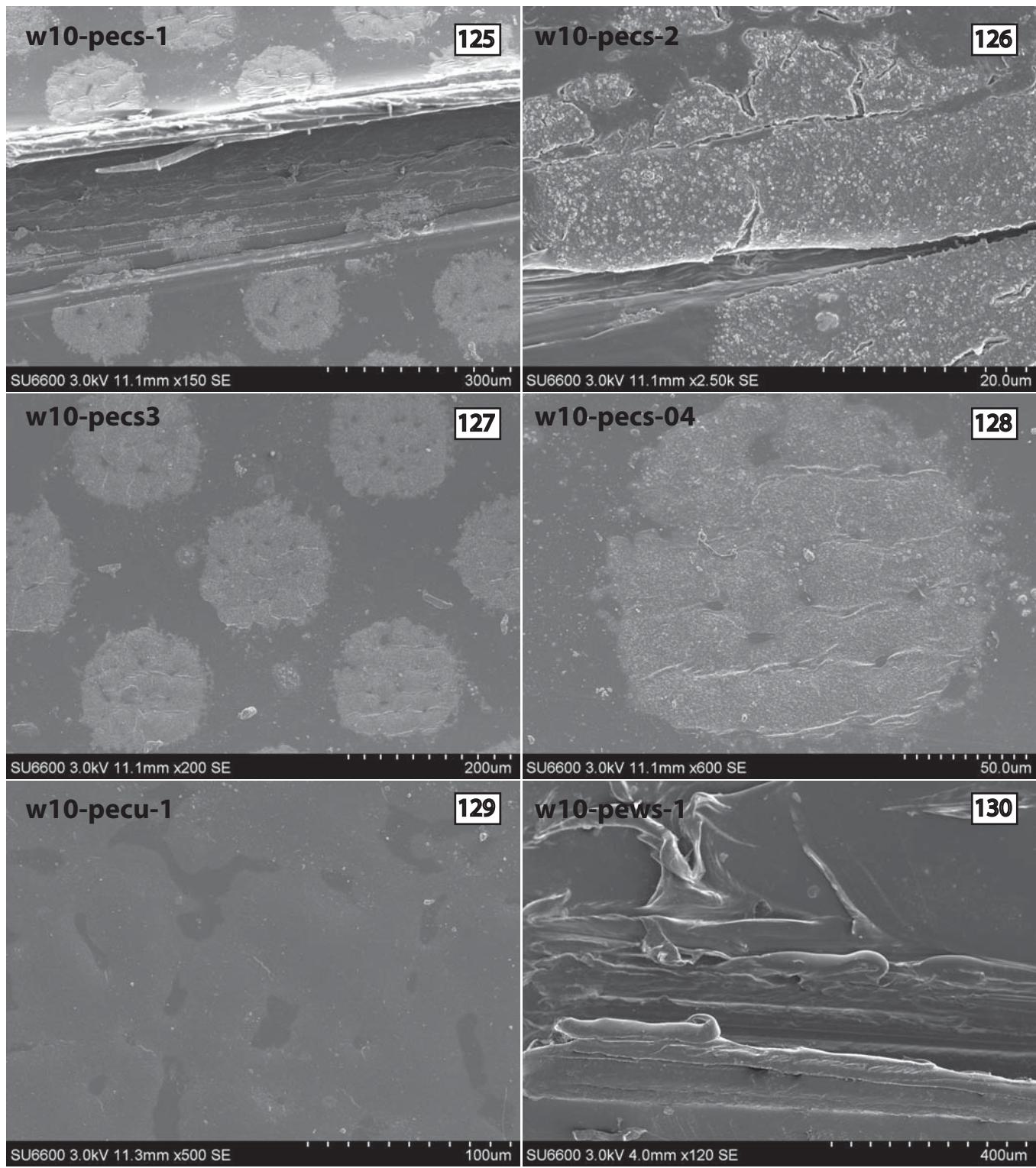


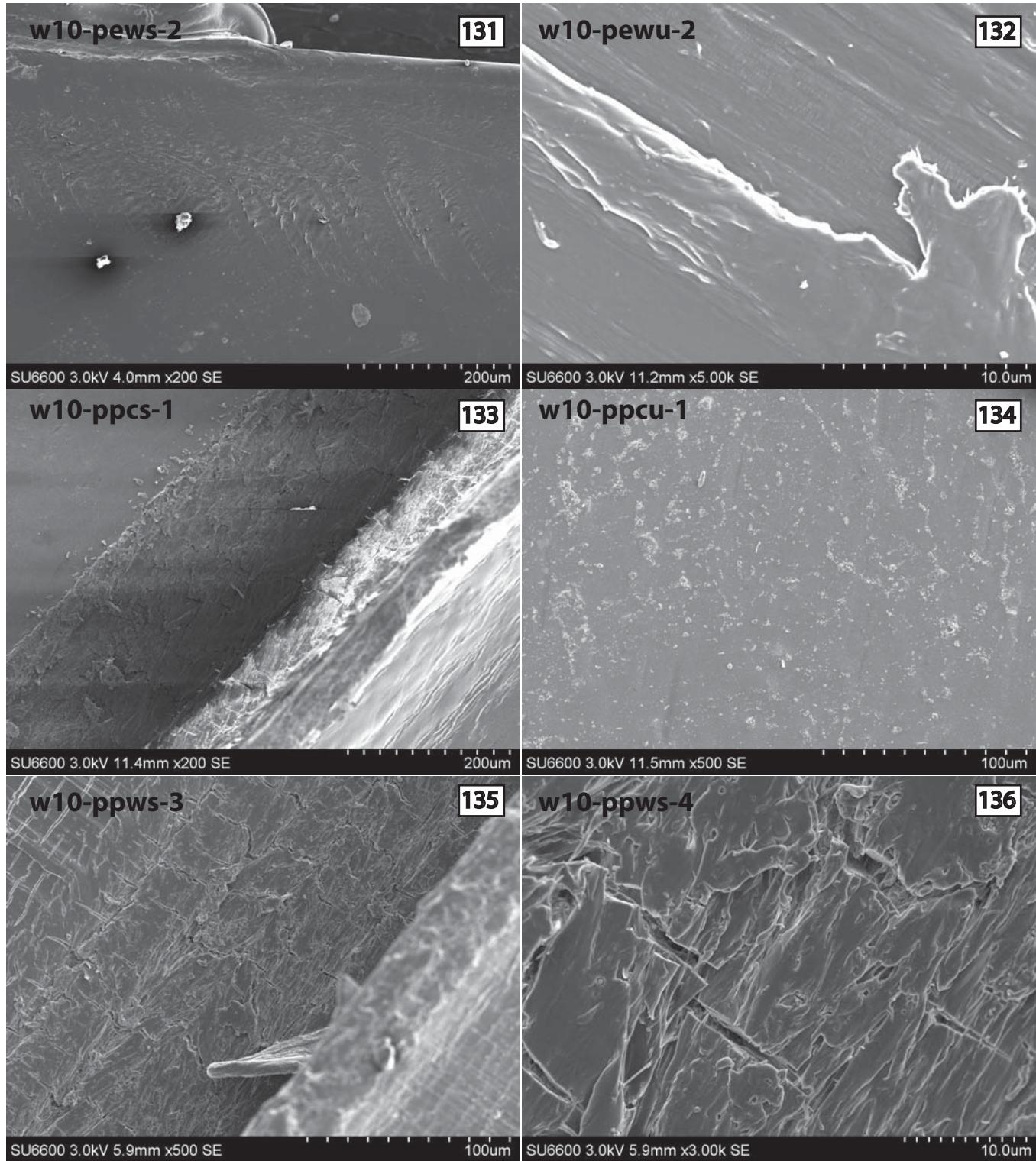


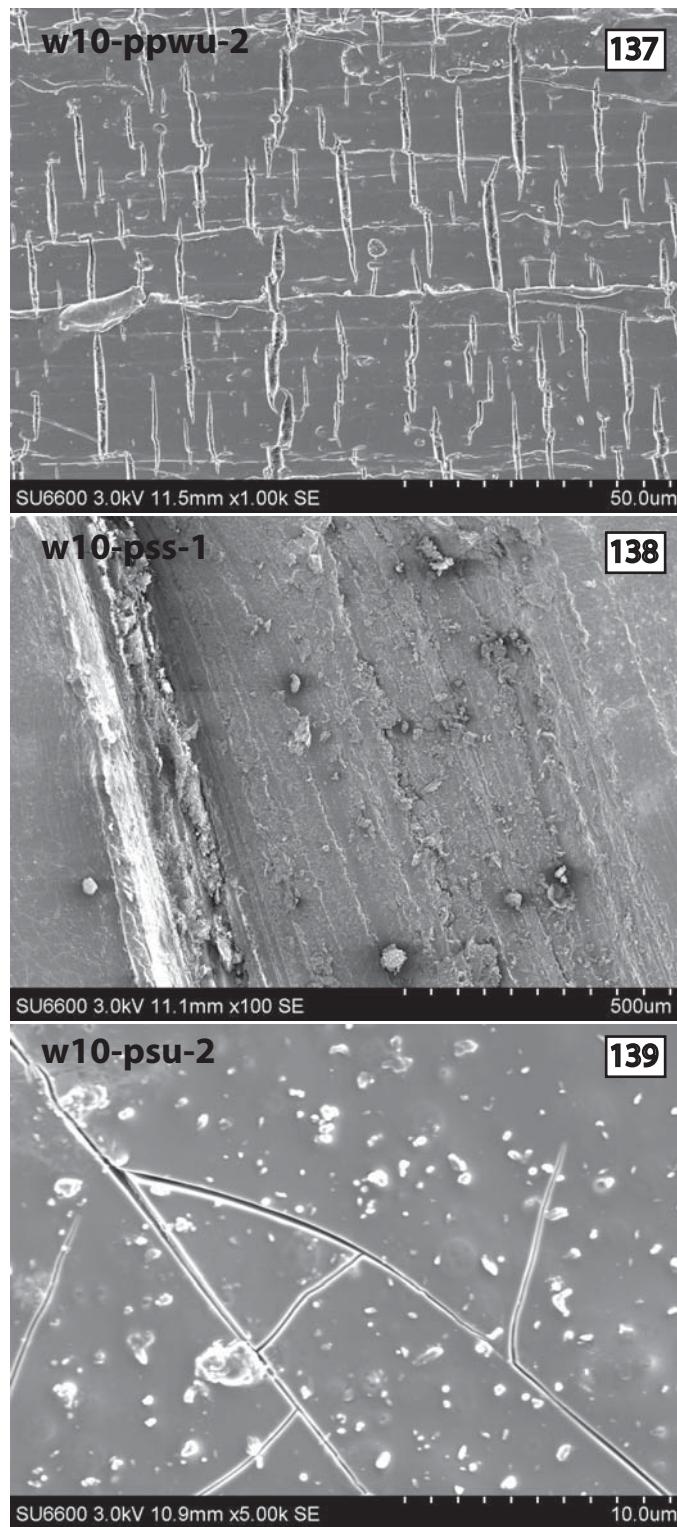


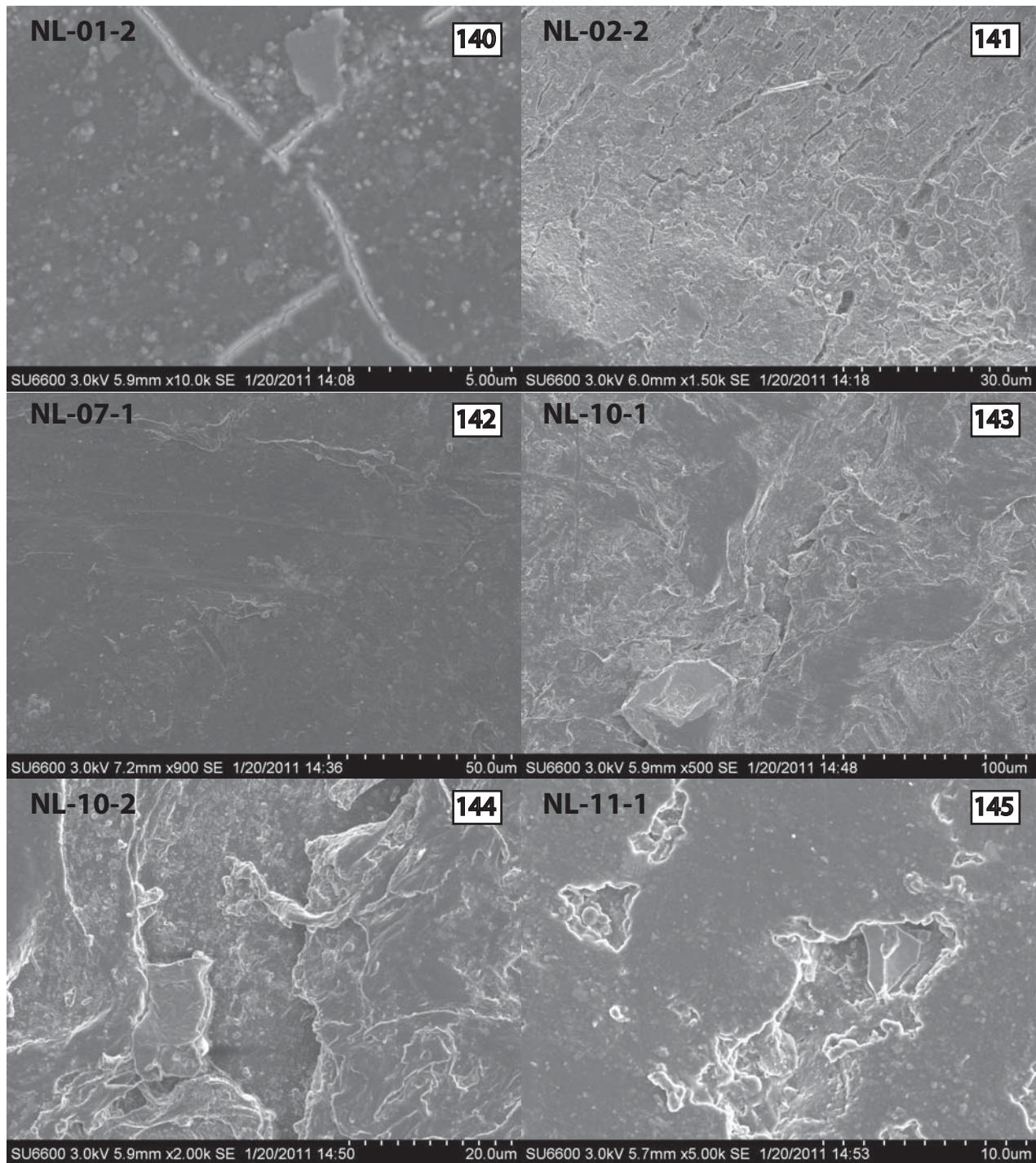


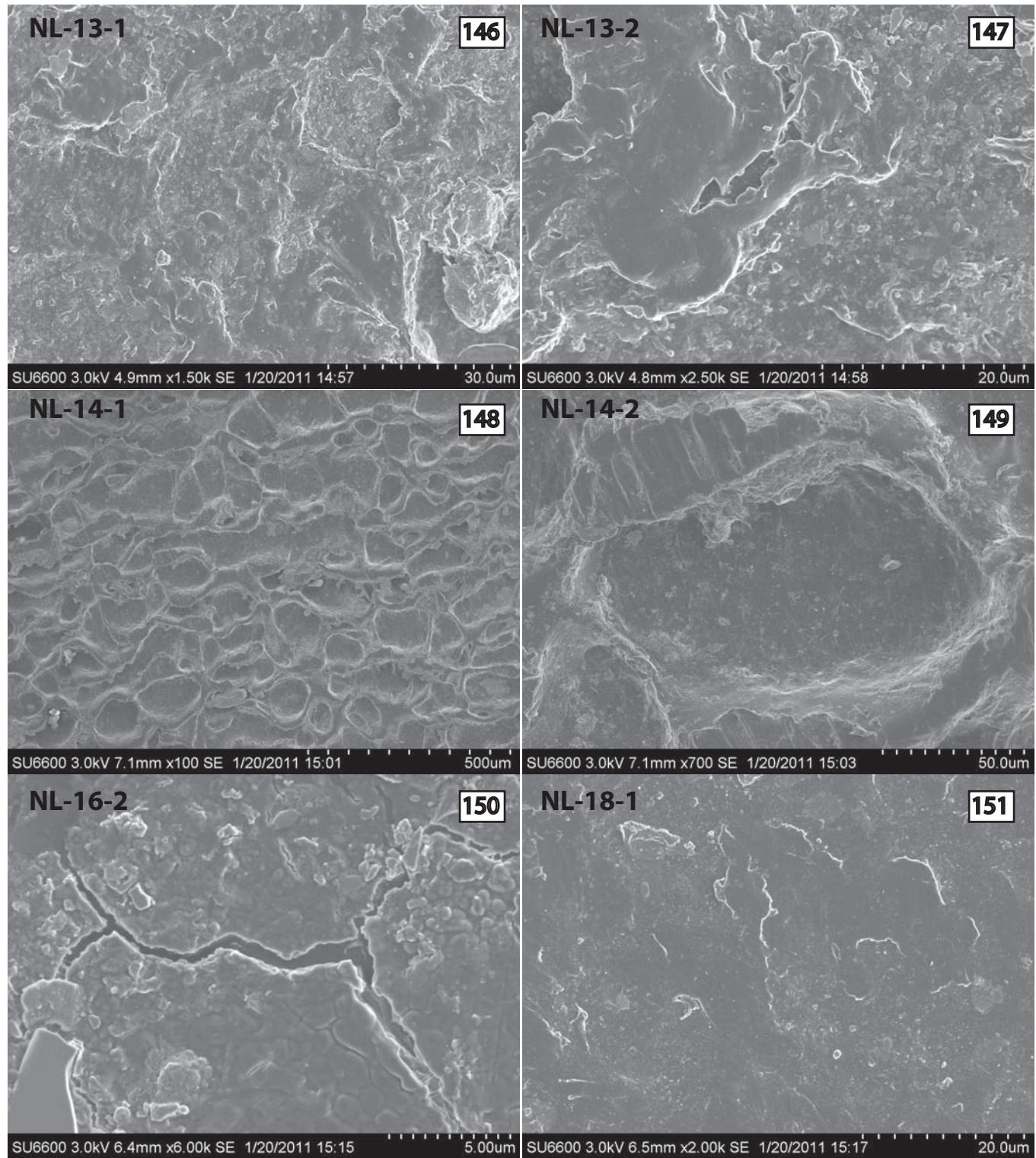


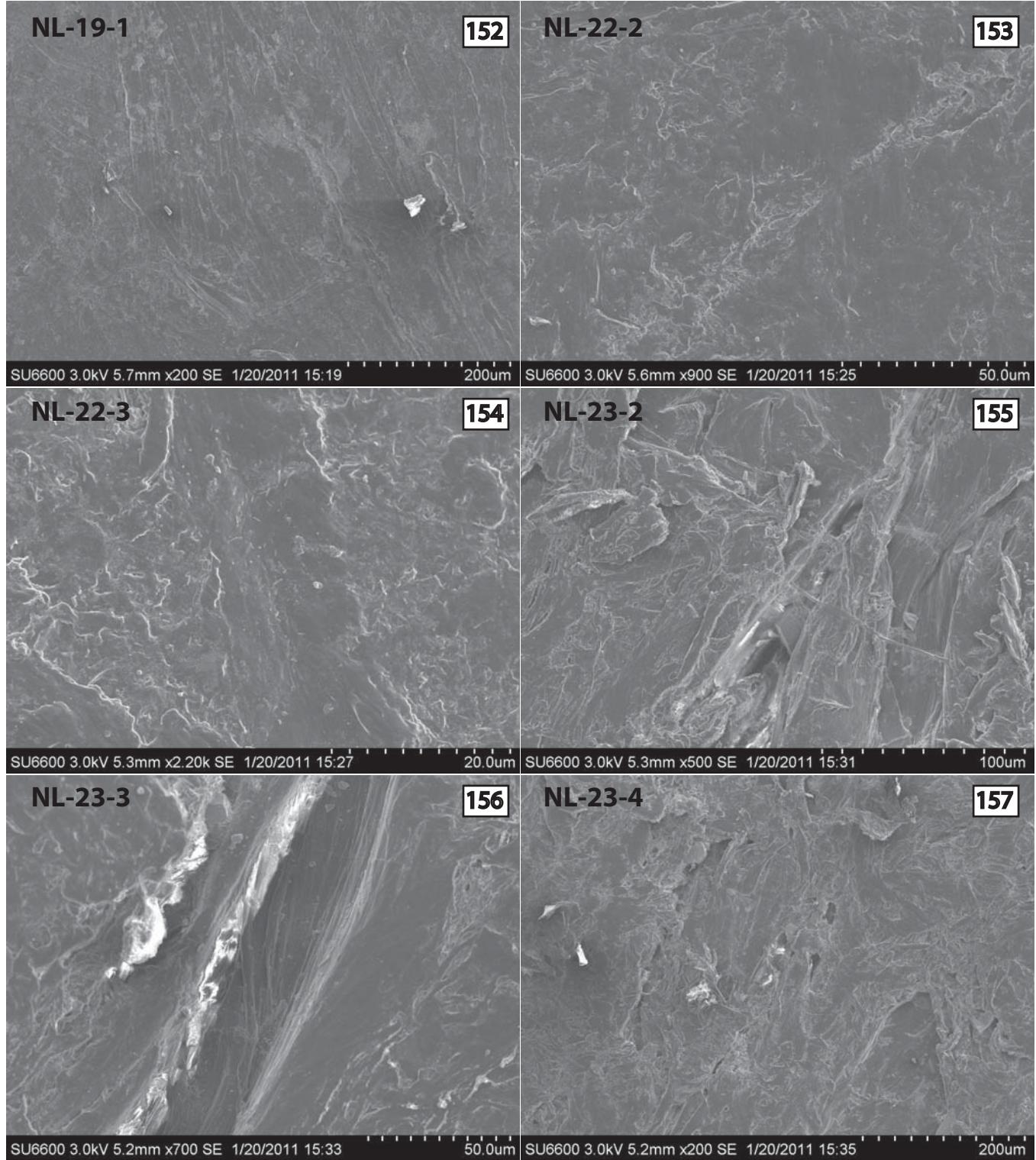






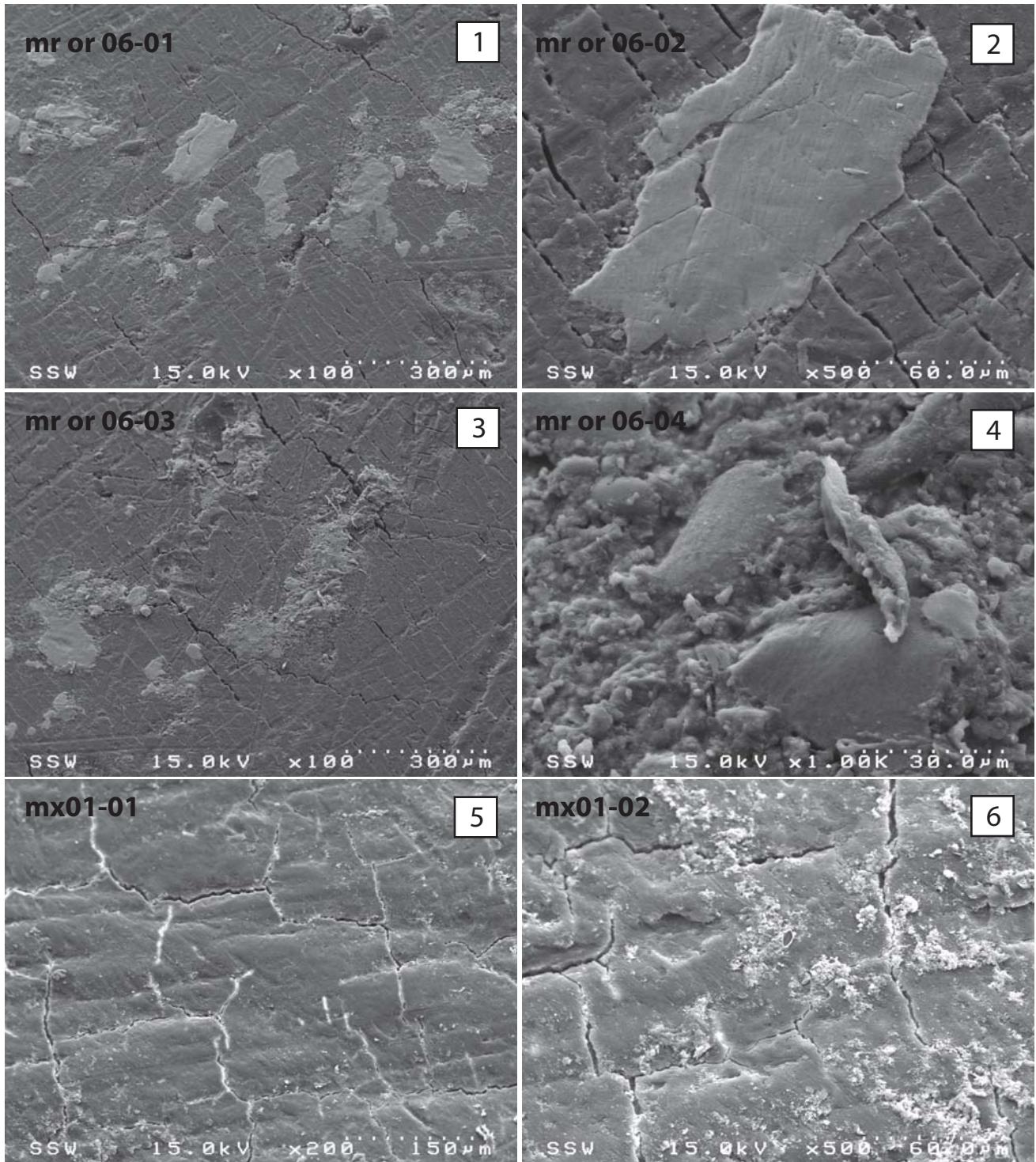


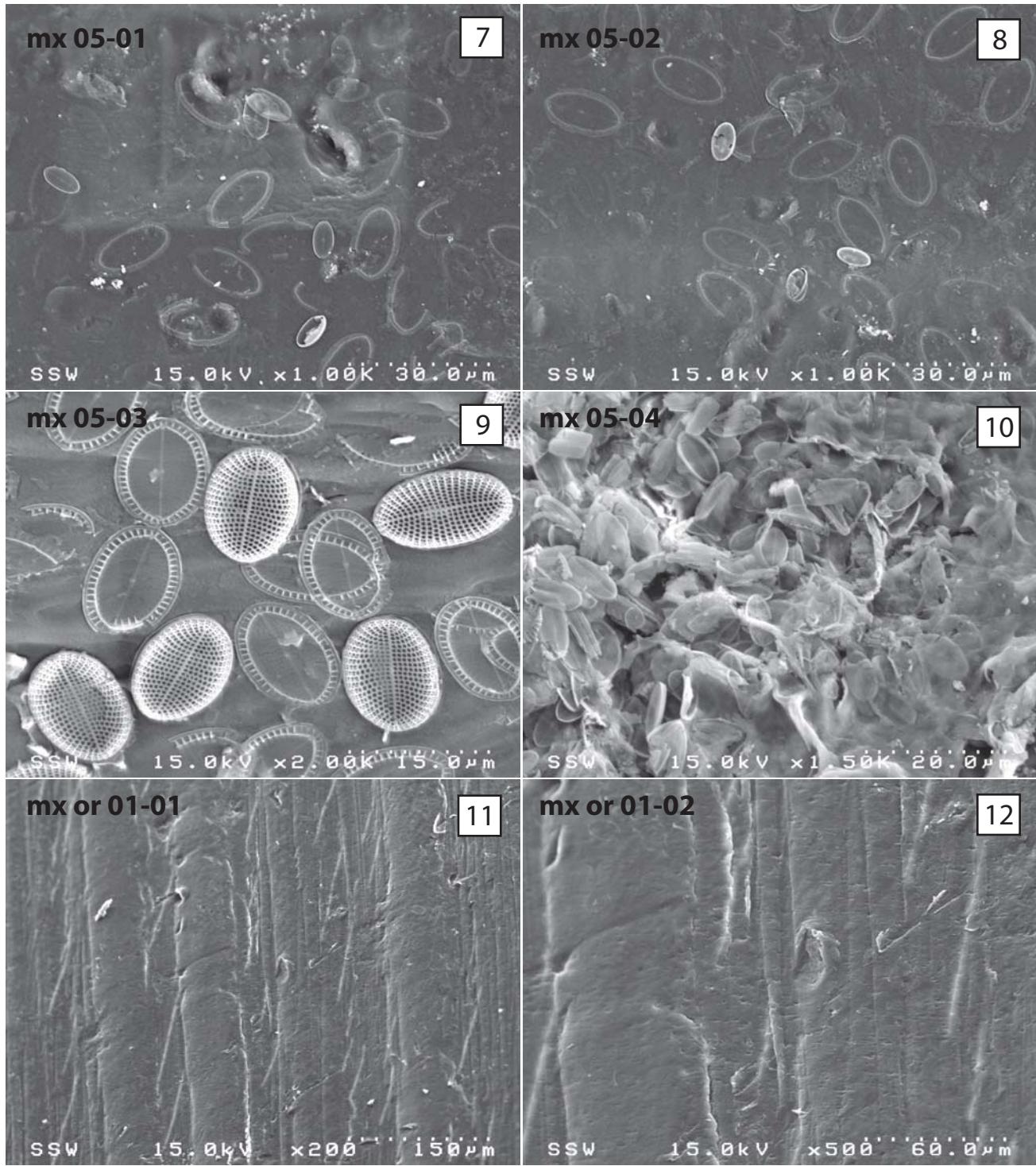


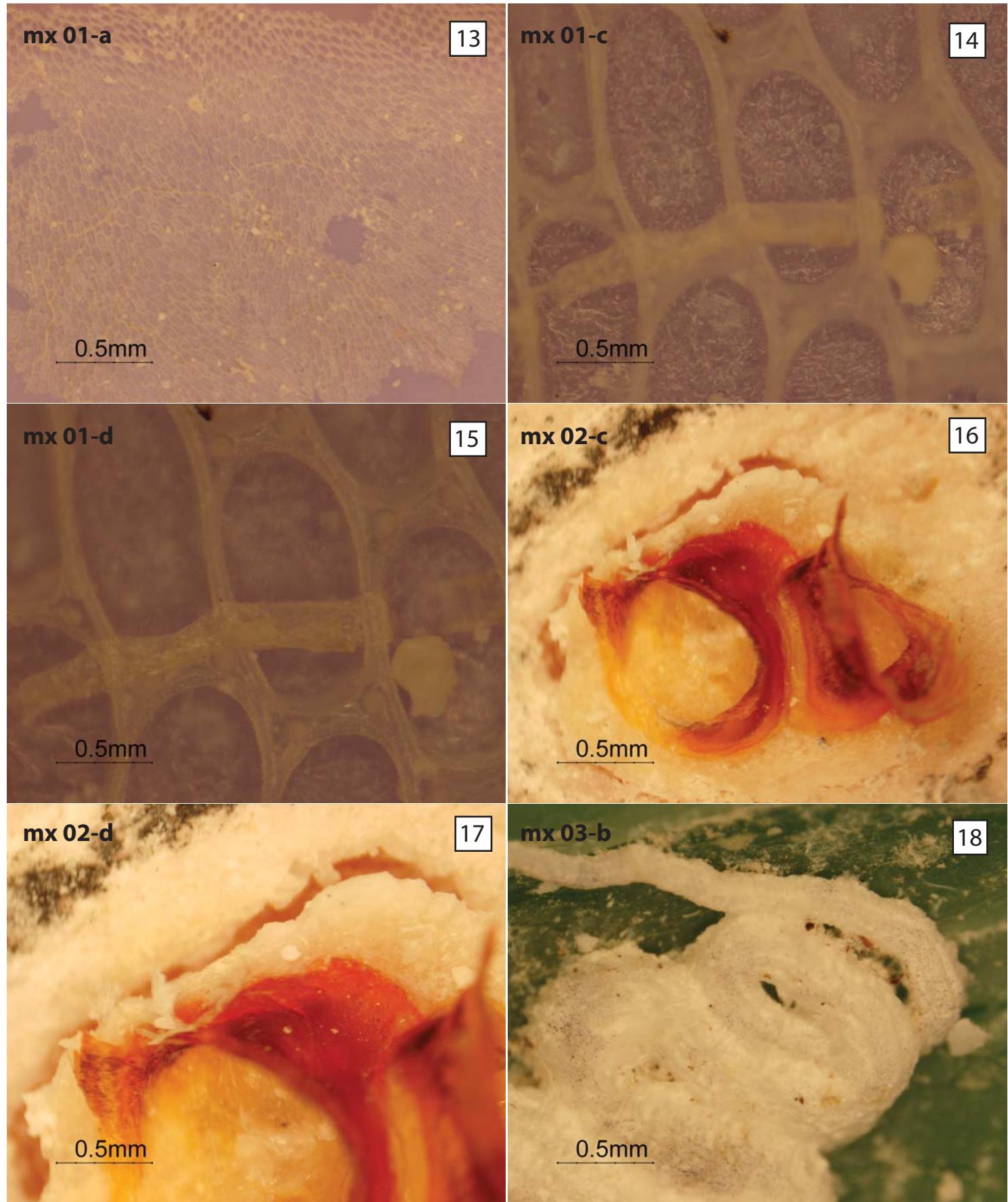


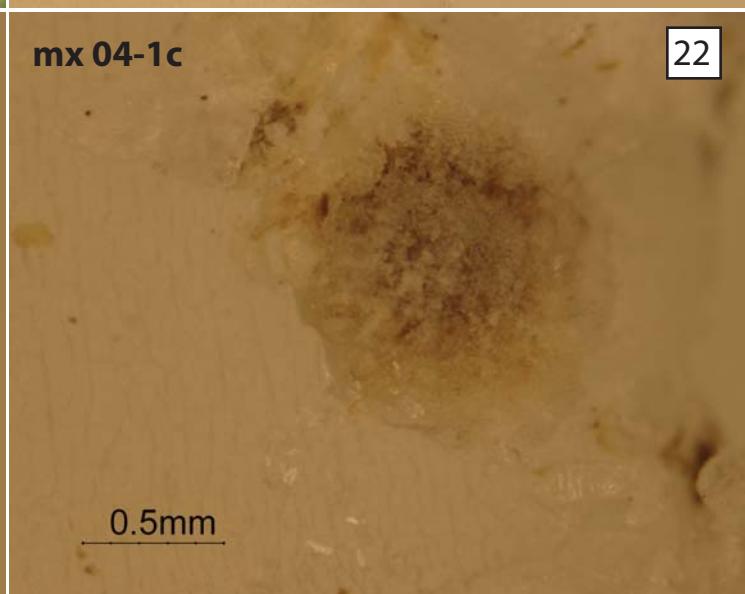
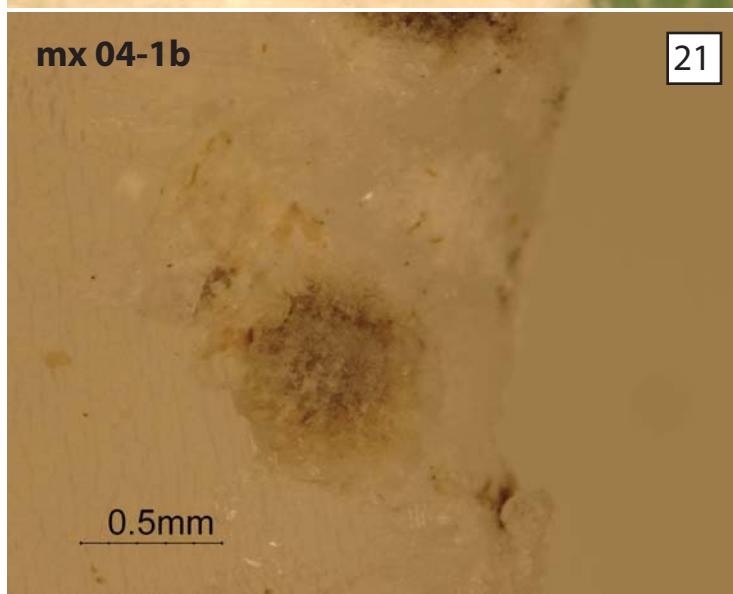
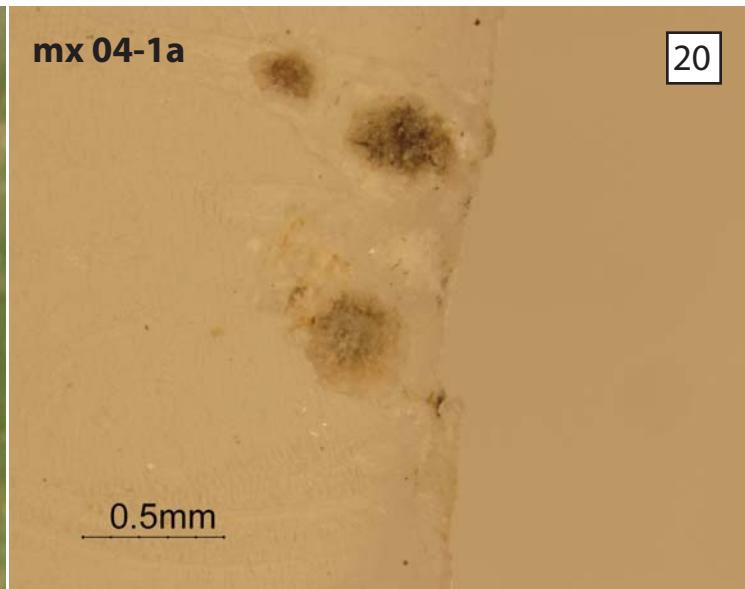
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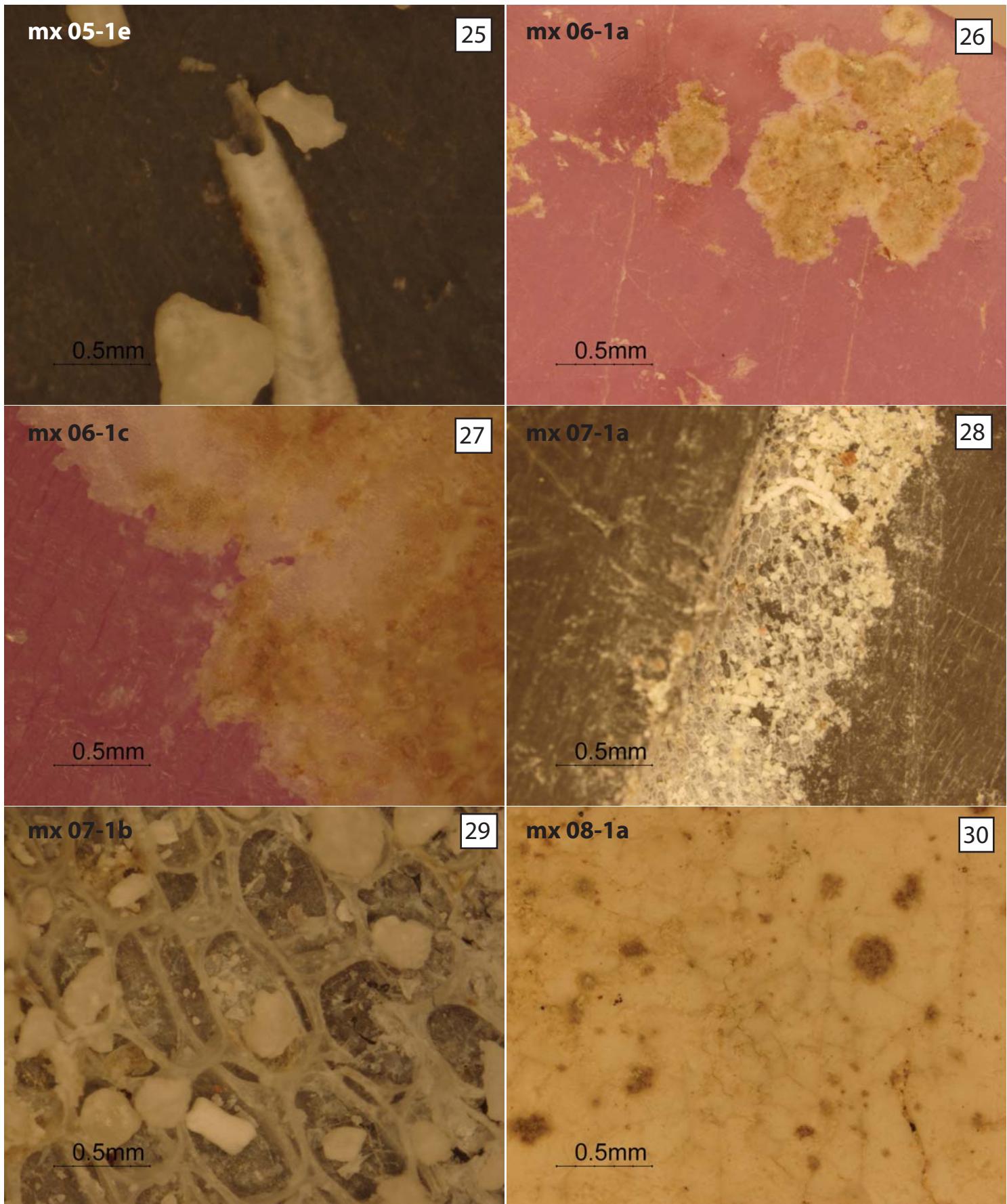
Scanning electron microscope images, digital photographs, and FTIR spectra of samples collected from beaches near Punta Maroma, Mexico. 1-12 SEM images, 13-32 are digital photographs of biological organisms on the surface of sampled plastic debris,33-43 are FTIR spectra indicating oxidation levels and polymer composition.

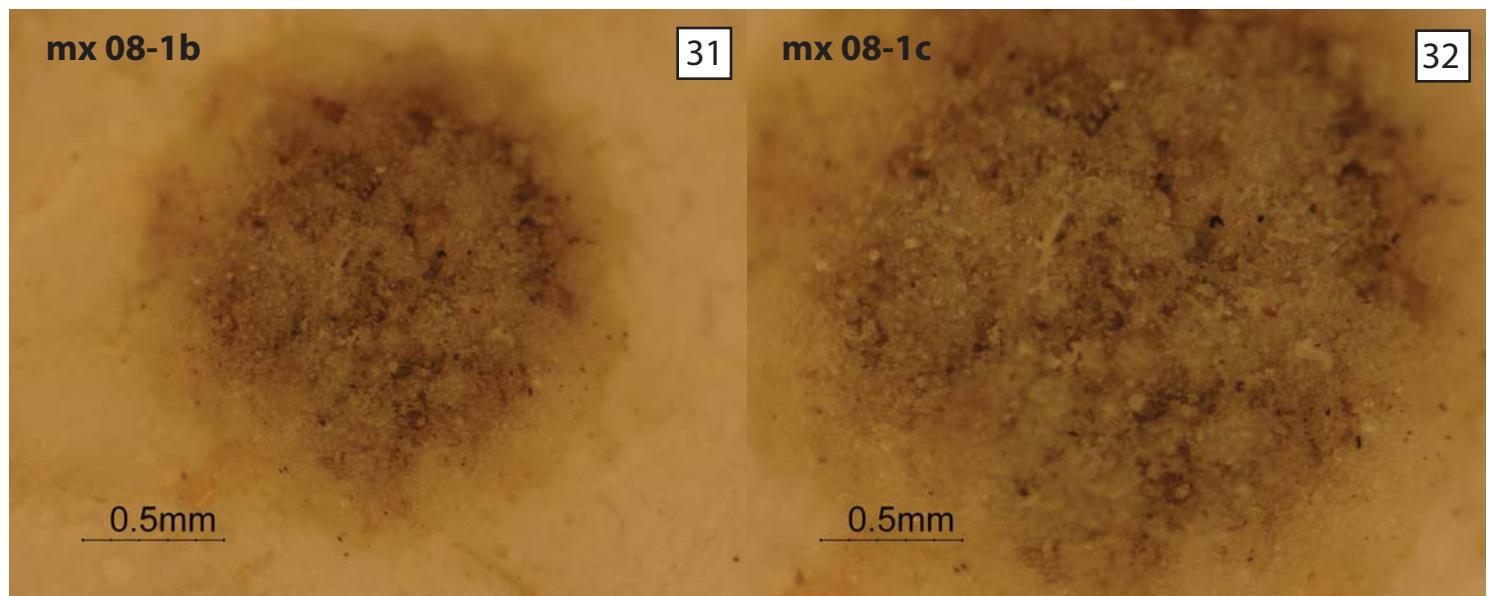


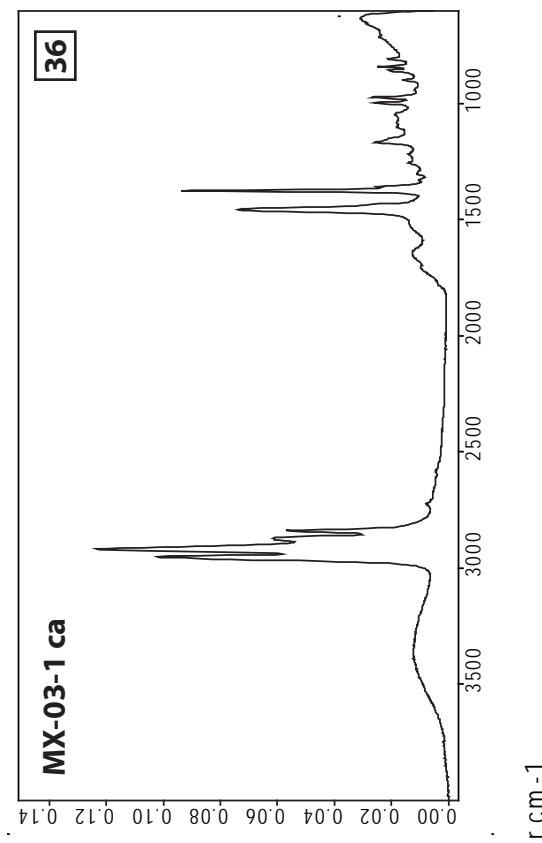
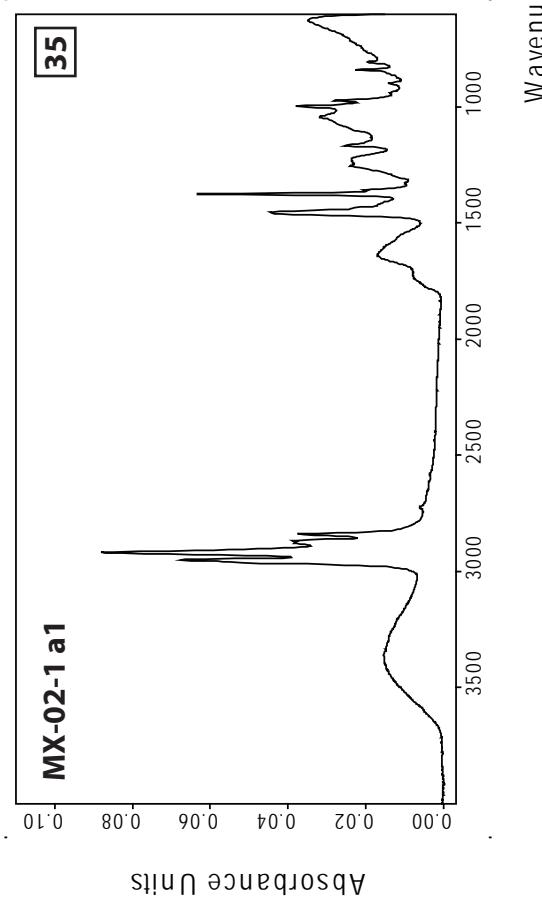
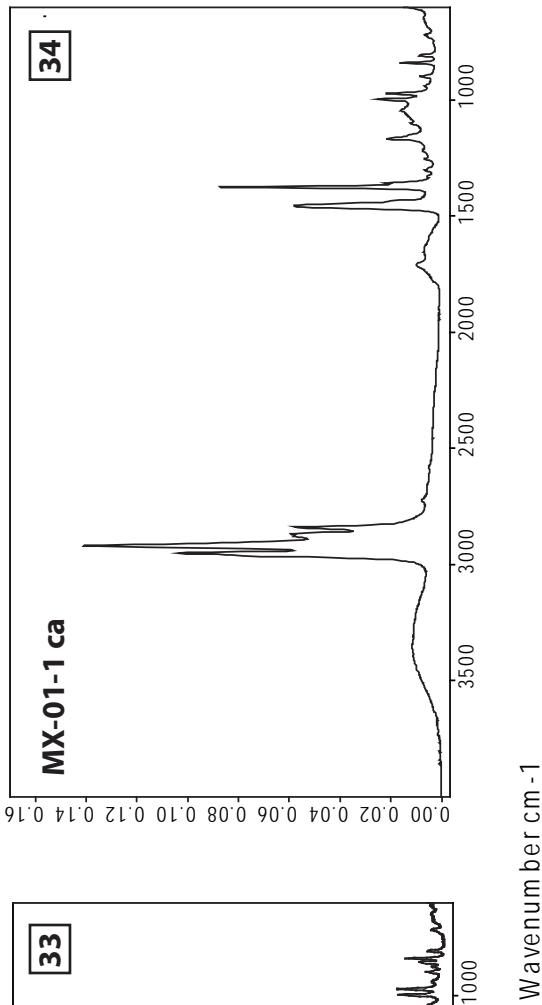
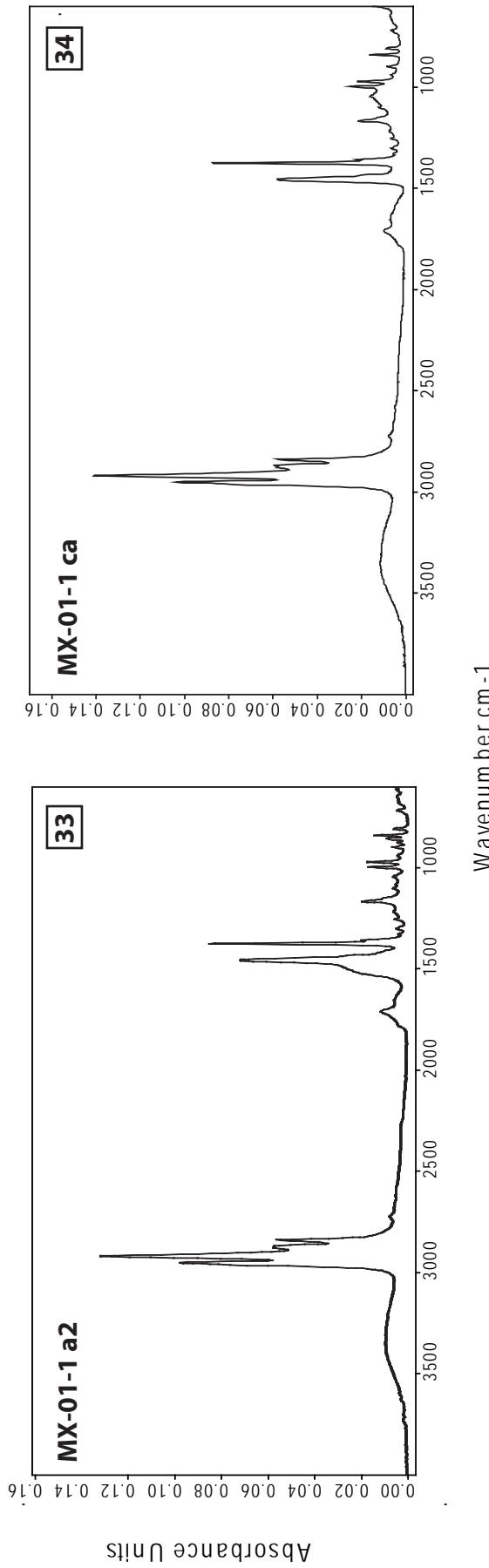


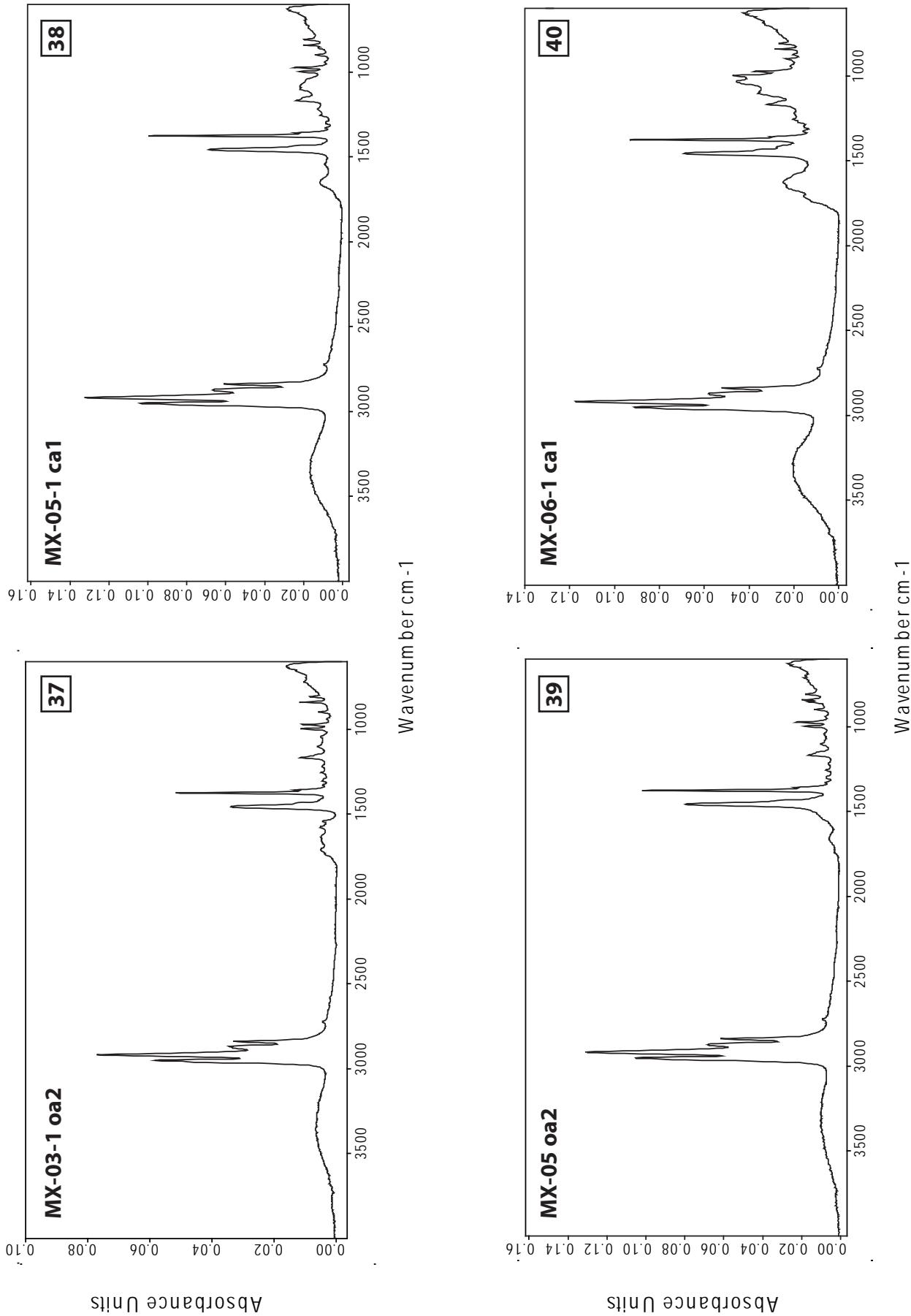


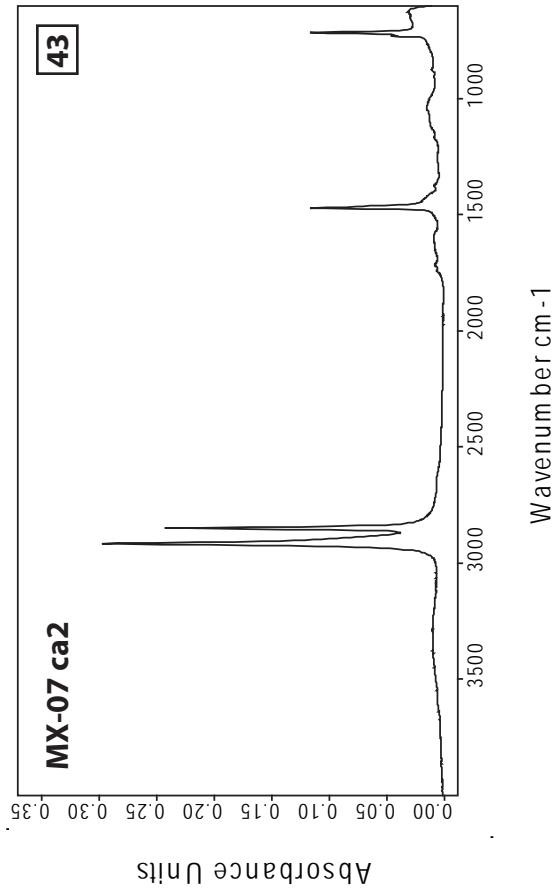
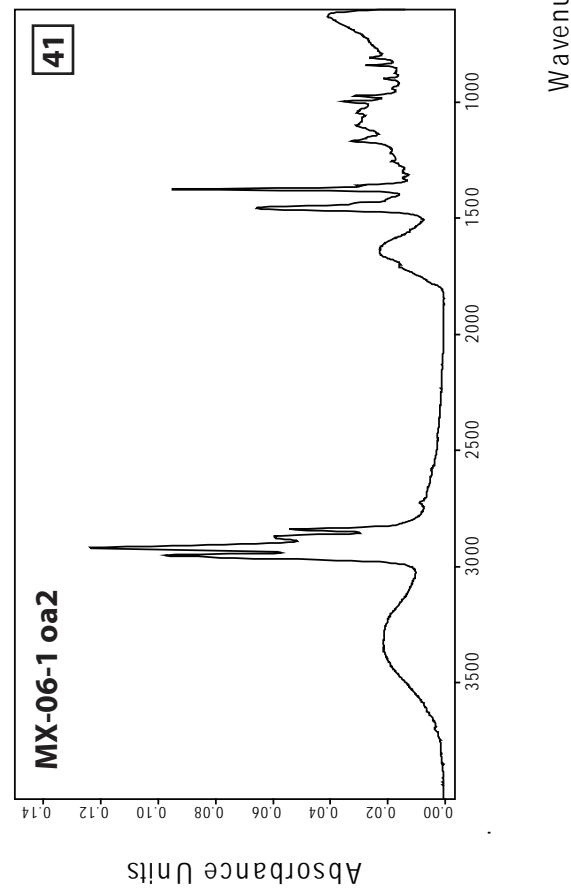
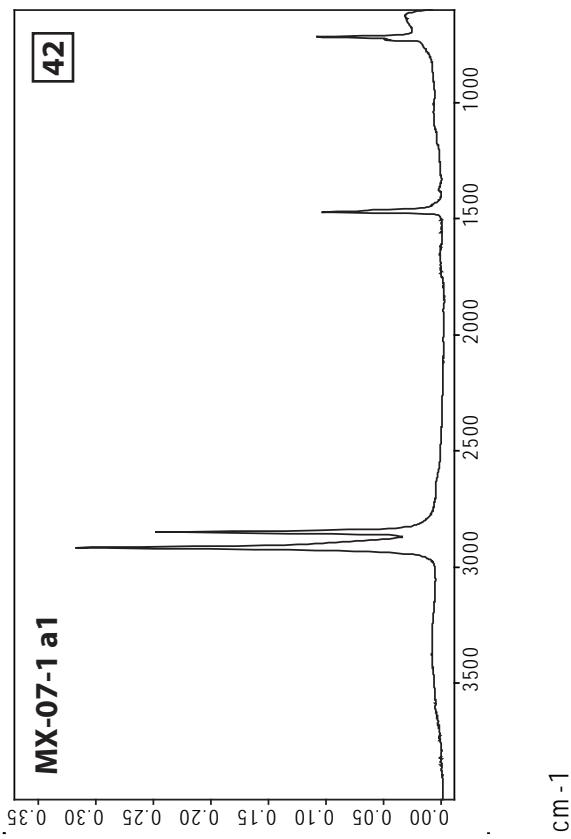












CURRICULUM VITAE

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Post Secondary Education and Degrees:	University of Western Ontario London, Ontario, Canada 2004-2008 Hons.B.Sc.
	University of Western Ontario London, Ontario, Canada 2008-2011 Ph.D.
Honours and Awards:	Western Graduate Research Scholarship 2008-2011
	Graduate Student Teaching Award (nominee) 2009-2010
	Graduate Thesis Research Award 2009-2010
	The Robert and Ruth Lumsden Award in Earth Sciences 2009-2010
	Ontario Graduate Scholarship in Science and Technology 2011-2012
Related Work Experience:	Graduate Student Teaching Assistant University of Western Ontario 2008-2011
	Graduate Fellow in Learning Development University of Western Ontario 2010

Publications:

- Cooper, D.A., and Corcoran, P.L. 2009. The Beaches of Kauai: A Plastic Paradise. 6th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2009 (Oral presentation).
- Cooper, D.A., and Corcoran, P.L. (2010). Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. *Marine Pollution Bulletin*, v. 60(5), pg. 650-654.
- Cooper, D.A., and Corcoran, P.L. 2011. Plastic Marine Debris: A New Type of Beach Sediment. 8th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2011 (Oral presentation).
- Cooper, D.A., and Corcoran, P.L. (2010) Effects of Chemical and Mechanical Weathering Processes on the Degradation of Plastic Beach Debris. Bridging Science with Communities SETAC North America 31st Annual Meeting, Abstract Volume , Portland, Oregon, November 2010: 9 (Poster Session).
- Cooper, D.A., and Corcoran, P.L. 2010. Effects of Chemical and Mechanical Processes on the Degradation of Plastic Beach Debris. 7th Annual Earth Day Colloquium. University of Western Ontario Centre for Environment and Sustainability, April, 2010 (Oral presentation).
- Cooper D.A., and Corcoran, P.L. (2011) Plastic Beach Debris on North America's Atlantic Coast: A New Type of Sediment? Water, Air, and Soil Pollution (Submitted).
- Cooper, D.A., and Corcoran, P.L. (2011) Distribution, deposition, and degradation of Plastic Beach Debris in and near Gros Morne National Park, Newfoundland, Canada. Gros Morne National Park visitor information centre park pollution awareness campaign (Poster).

Professional Development

September, 2008

- How to successfully negotiate a faculty contract
- Preparing for academic interviews

November, 2008

- Teaching Portfolios: Documenting your teaching
- Writing a Teaching Philosophy Statement
- Advanced Strategies for Teaching with PowerPoint
- What's the difference between an A and B? Strategies for marking essays

June, 2009

-Advanced Teaching Program for Graduate Students

November, 2009

-Teaching Mentorship Program

January, 2010

-Communicating with Journal Editors

-Writing for Publication and Getting Published

-"Demo"Graphy: Demonstrations as Effective Teaching Tools in the Science & Engineering Classroom

February, 2010

-Teaching Master Classes for Graduate Students

May, 2010

-University of Western Ontario Certificate in University Teaching and Learning

2010-2011

- Manuscript Reviewer, Marine Pollution Bulletin