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CHARACTERIZATION OF A CARDBOARD RECYCLING FACILITY'S PLASTIC WASTE FOR BENEFICIAL USE

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Dissertation

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BENIFICIAL USE OF A CARDBOARD RECYLCING FACILITY'S PLASTIC WASTE FOR BENEFICIAL USE

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An issue with old cardboard container (OCC) recycling is the generation of a plastic waste that currently either gets land-filled or burned. A Wandel screen, a common process unit, generates 35% of overall rejects that contain 75% of the facility's total plastic output. Plastic-rich Wandel wastes have not been well characterized. This study evaluated the plastic waste stream for engineering new, second-life products. Wandel wastes were composed typically of hot melt adhesives (37%), polypropylene (32%), polyethylene (17%), and polystyrene (9%). Proportions varied 10% or less in each polymer category. The plastic waste was compounded, milled and injection molded into test specimens. Differential scanning calorimetry (DSC) analysis showed that the polymers exist generally in separate phases. Thermal gravimetric analysis (TGA) determined that the onset degradation (405°C) of the mixed stream is an average of its components. In tensile tests, the mixed plastic waste stream performed comparably to its starting materials (tape, hot melt glue, thin film, etc.) with a modulus of 9.6 MPa, ultimate strength of 8.7 MPa, and toughness of 52.6 J. After initial material characterization, the material was compounded with wood flour (WF), cement, ash and maleated polyethylene (MAPE). WF and MAPE increased the tensile modulus by 65%, ash and cement increased moduli by 49% and 39%. All additives decreased error in breakage indicating an increase in internal compatibilization. MAPE decreased crystallinity and compatibilized both mixed polymers and additives. Samples were characterized by DSC and TGA. Additives decreased phase separation. TGA analysis showed wood flour, ash, cement and MAPE thermally stabilized the plastics. These improvements make this mixed plastic waste more attractive for reuse.

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CHAPTER 1

Introduction and Statement of Problem

Research Problem: Plastics are growing exponentially in production and as waste in the world. Few plastics are recycled and mixed plastics are considered ‘not recyclable’. This thesis seeks to utilize a substantial mixed plastic waste stream from an industrial source as a new, usable starting material.

This thesis explores mixed plastic waste from the Smurfit-Stone Container’s kraft pulp mill in Missoula. Old Corrugated Container (OCC) recycling facilities at pulp mills generate plastic waste as well as usable fiber. A typical OCC facility repulps about 500 tons/day of used corrugated packaging. Repulping results in an average 9-10 tons/day of OCC rejects – about 75% mixed plastics and 25% low tear-strength fiber with small amounts of other contaminants (foil, paper, staples, etc.). Currently, most of this plastic and fiber waste is burned for energy capture. If the amount of waste exceeds the permitted burn quantity, the remainder is land-filled. New regulations under consideration by EPA may make the practice of combustion of OCC plastic rejects for energy capture more problematic.

At today’s rates, it would cost the mill an estimated $380,000 per year to dispose of the all the OCC rejects in the local Allied Waste landfill. Not included is the cost of replacing the fuel value of the OCC rejects. Obviously, financial drawbacks come into play, but also local environmental impacts should be considered (air emissions and disposal burden). Plastics by nature have the valuable property of mutability, which means they can be recycled into a plethora of new materials and products. The plastic material in the OCC reject waste brings the possibility of reincarnation into something more useable at the very least, and, with proper application, may venture into the realm of being profitable.

Environmental Impact of Emissions from Plastic Burning

Plastics combust easily but incompletely. They produce copious amounts of black smoke plus decomposition and volatilization products [Simoneit, 2005]. These emissions enter the ambient air space and create human exposures. U.S. EPA regulates emissions at industrial sources but does not compel measurements of emission components in ambient air [EPA, 1990]. Plastic types occur in the municipal waste at 21% low-density polyethylene (LDPE), 19% polypropylene (PP), 17% high-density polyethylene (HDPE), 12% polyethylene terephthalate (PET), 8% polystyrene (PS), and 4% polyvinyl chloride (PVC) [EPA, 2010] PVC reassembles into dioxins upon burning and has historically been the plastic of most concern with regard to incineration. This may be misguided, however, since recent research suggests most plastics when combusted release of toxic additives or generate toxic byproducts. A 2005 study on the tracers of trash burning revealed many alkanes, aldehydes, polycyclic aromatic hydrocarbons (PAHs), and antioxidants. Not surprisingly, the highest emissions were from plasticizers. PAHs like benzopyrenes, perlyene, and coronene were identified. Some of these have been shown to be powerfully carcinogenic [CDC, 2009]. Plasticizers are also of concern because they, too, are classified as suspected carcinogens by EPA and endocrine disruptors by other researchers [Rhodes, 1995; Streufert, 1980; Gray, 1999]. Release has implications for bioaccumulation in animals, people and the environment as well as ecotoxic effects [Helmroth, 2002].

Environmental Impact of Disposed Plastic Waste

The vast majority of plastics ever produced still exists today either buried in land-fills or strewn on land and sea. Generation of plastic waste continues to grow almost exponentially while recovery struggles to gain a few percent per year (Figure 1.1). While some plastics are biodegradable under proper conditions, the land-fill environment is perfect for preservation. Land-filled debris is not exposed to oxygen, nitrogen and UV radiation, rendering all buried plastics practically immortal. Due to the increasing use of plastics in products and subsequent neglect of plastic wastes, another problem is the accumulation of litter in the environment. Furthermore, studies are emerging reporting that these 'disposed' plastics release chemicals such as plasticizers and other toxic additives into waterways [Tullo, 2003]. As plastic reuse becomes more recognized as a sustainable economic strategy, litter problems may be increasingly mitigated *on land*. In the oceans there is an escalating serious problem with plastic litter. The full impact of plastic litter in the ocean is unknown at this time. The mass of plastics in the ocean has been estimated as high as 100 million metric tons. Discarded plastic bags and other debris end up in the ocean, accumulate in extensive rafts at five main gyres. They pose direct dangers to wildlife and the ocean environment that sustains them [Moore, 2008]. Clearly, this is not an intentional consequence of disposal that creates an important global impact.

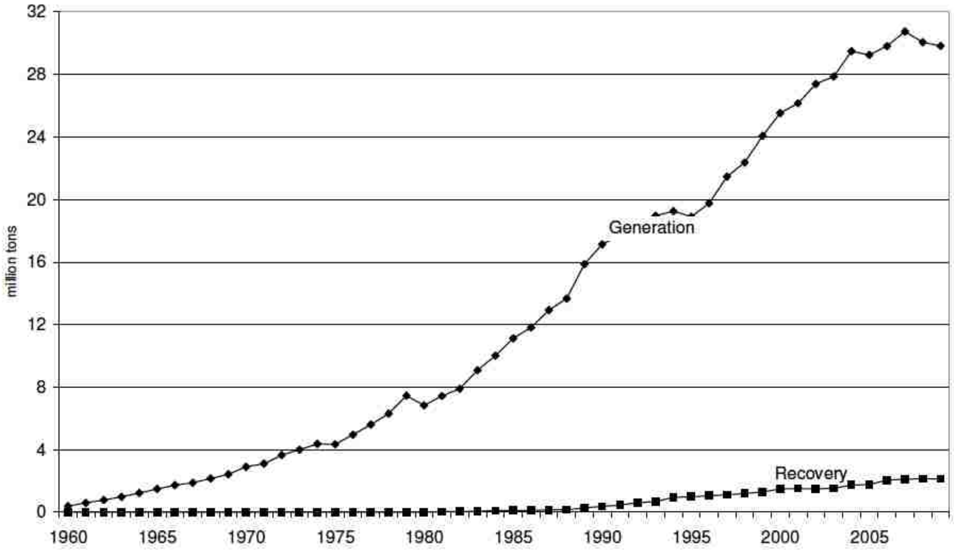


Figure 1.1 Plastic generation and recovery between 1960 and 2009. [EPA, 2009]

Rather than regarding plastics as disposable, we should evaluate them as a reusable resource. Plastics have unusual properties inasmuch as they are not only very durable, but they are also mutable, which allows them to be reformed into a wide variety of applications.

In 2005, about 12% of the solid wastes deposited in landfills in the United States were attributed to plastics, equaling about 28.9 million tons [EPA, 2006]. These statistics are measured by weight, not volume, which means that relatively light plastics take up far more room in landfills than is indicated by their percentage. Additionally, these figures only include municipal waste and do not include other sources of wastes from construction demolition and industry areas.

Only 200 thousand of the 28.9 million tons plastic waste was recovered in 2005 [EPA, 2006]. Thus, only about 7% of the plastic produced each year is being recovered and recycled. Out of the seven different plastic resin codes, #1 and #2, that corresponds to PET (polyethylene terephthalate) and HDPE (high density polyethylene), comprise the bulk of the recovered plastics. A little more than half of the plastic that is recovered and reused is HDPE (50-60%). Another quarter (20-30%) is PET.

Plastics with codes 3-7 comprise only 10-15 % of recycled plastic materials. A few recycling facilities in the US accept plastics with codes 3-7, but these resins are not recycled domestically. These plastics are shipped to China where they are chipped then melted. There are two primary problems with outsourcing our plastic waste for recycling. First, many countries such as China, lack the labor and environmental laws to accomplish recycling in a safe and energy effective way [Gurnon, 2003]. Second, the energy costs and emissions in transporting these wastes are immense. Since previous studies have revealed that the majority of plastic in the OCC rejects at the Missoula Mill are PP (polypropylene, code #5), new markets must be developed if this material is to provide a value-added product. Mixed plastics are considered even more difficult to recycle and are usually assigned the number seven code, if any code at all. New technologies are needed both to handle plastic recycling for all codes and to handle mixed plastics safely and responsibly in the US.

Since previous studies of plastics in OCC rejects at the Missoula Mill indicate that the most prevalent resin is polypropylene and that it is co-entrained in a mixed plastic and fiber process, new techniques and applications need be explored. This research seeks to address these issues as a means to help the Missoula Mill in particular, and other industrial facilities in general, produce a value-added product from plastic waste stream.

Thesis Organization

Chapter 2: Provides a review of literature and background information pertinent to this research.

Chapter 3: Discusses how the Wandel waste stream (WWS) material was processed and the analytical instrumentation used to test this waste stream.

Chapter 4: Concentrates on basic characterization of the raw Wandel waste stream (WWS).

Chapter 5: Investigates miscibility of the mixed plastic in the WWS.

Chapter 6: Explores the WWS as a starting material for wood, cement, and ash composites.

Chapter 7: Concludes findings from chapters 4-6.

CHAPTER 2

Literature Review

Chapter 2 contains the background and foundational material with which this dissertation is concerned. First, a short history of thermoplastics is provided that includes relevant information on how chemical structure can be correlated with the material properties of different polymers. Next is a discussion of why mixed plastics are usually considered not recyclable. Then the use of wood fibers and plastics to produce composite materials is introduced, including the importance of using maleated polymers to obtain better adhesion. Finally, the existing literature regarding use of cement and ash in polymer composites is summarized.

Thermoplastics

The first plastic developed in the US was in 1868. John Wesley Hyatt discovered celluloid by mixing pyroxylin, nitric acid and camphor. This material was used as the first photographic film. The next widely used polymer Bakelite was discovered in 1909 by Dr. Lee Hendrik Baekeland. Bakelite was the first polymer to be liquefied and molded into shapes under heat and pressure. Every decade after this discovery saw an exponential increase in discovery of new plastics. Their production led to ever increasing displacement of other materials. Then in the 1920s cellulose acetate and nylon were developed. In the 1930s, acrylic glazing resins were invented, and polystyrene (PS) was commercialized. In the 1940s, polyethylene (PE) was developed as radar cable sheath for WWII and acrylonitrile buyadiene styrene (ABS) was created out of research geared towards finding a synthetic rubber. The 1950s saw the discovery of polypropylene (PP) and acetal/polycarbonates.

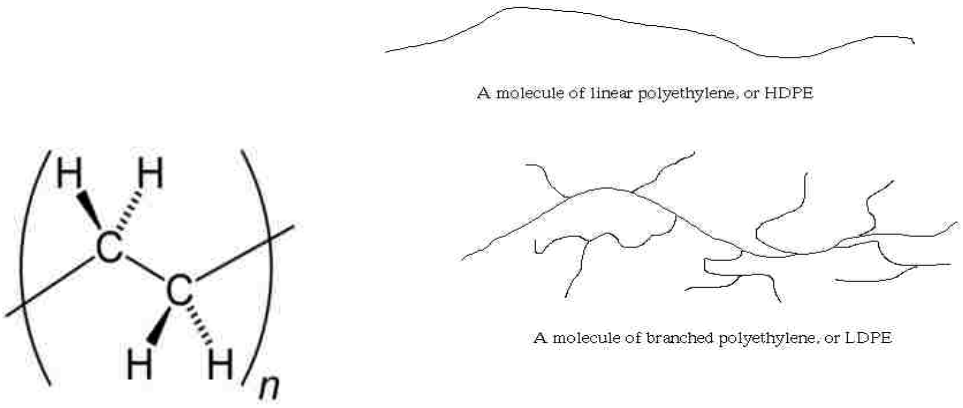
Since their inception, plastics have continually replaced other materials. Plastics are a cost effective, lighter alternative to metal and more fragile materials like glass. In fact, they are so inexpensive that product development and generation has become more and more tailored towards disposable products creating more waste issues. Plastics have some significantly different chemical behaviors in comparison to metals - they polymerize in chains with the possibility of cross-links and they are generally electrical insulators instead of conductors. These differences lead to significantly lower stiffness, recoverable strains, and time dependent viscoelastic deformations [Robeson, 2007].

Thermoplastics are a class of polymers that soften when heated and become glassy when cooled. They have long chains of carbons that weakly interact with each other through London dispersion forces. Differences in the extent of the weak interactions and branching account for many of the varying properties of unlike polymers. Morphology of thermoplastics can be divided into crystalline, semi-crystalline and amorphous. These distinctions describe the ordering of the internal structure; crystalline is highly ordered and amorphous has no order.

Olefins are the most commonly produced plastics and are derived from alkenes (e.g., PE and PP). Both PE and PP are most usually manufactured from petrochemical starting materials, ethylene and propene, respectively. PP, for example, is polymerized via a vinyl addition synthesis. Polyethylene occurs in several different ordered structures, referred to as ‘grades’ by industry. High density polyethylene (HDPE) has linear carbon chains without branching while low density polyethylene (LDPE) is much less ordered with side chains of PE off the backbone structure (Figure 2.1a). There are other grades in between those of HDPE and LDPE that have intermediate characteristics. PP (Figure 2.1b) can be highly ordered but the common grade produced is an isotactic semi-crystalline polymer with a crystallinity between HDPE and LDPE.

are more cost-effective to manufacture. Tacticity describes the ordering of the substituent groups off the polymer backbone. In an isotactic polymer substituent groups are highly ordered occurring at regular intervals and atactic describes a configuration with no long range repeating pattern. Polystyrene (PS) has many possible starting materials ranging from the original synthetic route via decarboxylation of cinnamic acid to the catalytic dehydrogenation of ethylbenzene. Once the styrene monomer has been obtained, its vinyl group allows polymerization through anionic chain growth. Most PS is atactic which renders it amorphous (Figure 2.1c).

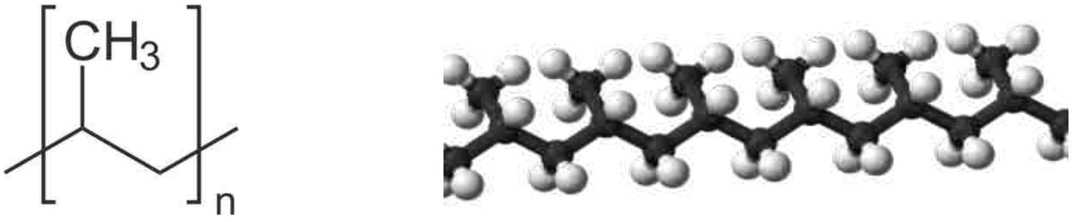
a.



General PE structure

Differences between the molecular structure of HDPE and LDPE

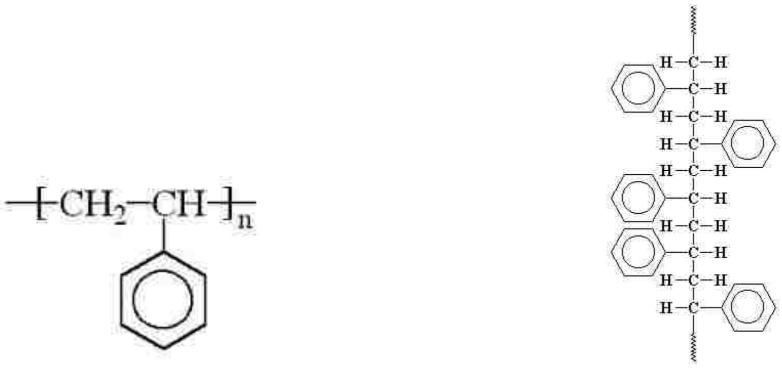
b.



General PP structure

Isotactic PP molecular structure

c.



General PS structure

Atactic PS structure

Figure 2.1 Structures of common polymers: a. HDPE & LDPE, b. PP, c. PS

Recycling Mixed Plastics

Large-scale plastic recycling technology is antiquated at best. Most wide-spread recycling utilizes only PET and HDPE as previously mentioned [Amos, 2003]. These compose only 30% of plastics that get land-filled, with another 48% of land-filled plastics being PP and LDPE [EPA, 2009]. The current process requires PET and HDPE to be manually separated, chopped into flakes, dried, melted, then extruded into pellets. These are then sold to industry manufactures of products like carpet and fleece, which are considered "downgraded" applications. This recycling technology is not the most efficient, just the most widespread. One of the problems with recycling in this manner is that manual sorting is time consuming, costly and inaccurate. In comparison to paper processing, virgin plastic material takes five times less energy to produce and 50 times less energy to recycle [Shutov, 2000]. New technologies will hopefully continue to improve this gap for plastics and add resins beyond PET and HDPE.

Why are mixed plastics not recycled? Recycling mixed plastic is not a common practice for three main reasons: 1) plastic containers have impurities due to product use (e.g., remnant food in packaging, detergent left in bottles); 2) mixed plastic has inconsistent polymer composition in day-to-day collections (e.g., one day more PE, the next day more PP); and 3) many polymers are considered 'incompatible' with one another. To solve these issues cleaning and separation steps are necessary.

The strength of a polymer comes from the ability of its molecules to "stack up" closely creating extensive contact zones for stronger intermolecular interactions. The difference between the tensile strengths of LDPE and HDPE is due to stacking ability (Fig 2.1a). While both are obviously based on the same polyethylene backbone, HDPE has no branching and the long polymer chains can pack tightly giving it its well-known strength. LDPE has branching off the polymer backbone resulting in both a lower density and a more ductile behavior. Despite sharing the same structural backbones, HDPE and LDPE have poor phase interaction when mixed together. If you add in PP and PS, with different backbones, the packing and intermolecular interactions become even poorer. Because of diminished strengths, mixed plastics have not been pursued for recycling in the past. It was initially believed by polymer scientists that few polymers were compatible (miscible) with one another and miscibility was necessary for mixed plastic recycling. More recently, many different levels of phase compatibility between unlike polymers have been identified and emerging mechanical/chemical techniques that increase mixing have been developed. Plastics with partial compatibility can now be considered usable in new product applications.

Miscibility in Polymer-Polymer Alloys

Miscibility in polymer blends is governed by thermodynamics [Chanda, 2007]. A negative change in the free energy (ΔG) is needed to obtain miscibility. True miscibility is defined as homogeneous down to the molecular level. Since the change in entropy (ΔS) is very small, it is the change in enthalpy (ΔH) that must be zero or negative according to Equation 2.2:

$$\Delta G = \Delta H - T\Delta S \qquad 2.1$$

T in this equation is the absolute temperature. A negative enthalpy value can be obtained through intermolecular forces between polymer phases. The greater the attraction between two phases, the greater is their miscibility.

Completely miscible polymer blends will combine to produce transparent materials; varying levels of immiscible mixtures will be opaque. Ultracki et al., 2003 discusses polymers that are slightly immiscible being somewhere between a solid emulsion and a solid solution of a minor polymer in a major polymer, and can be considered a polymer alloy. These phases will occur in separate submicroscopic domains with the major polymer forming the continuous matrix phase and will contribute most to overall properties. When components are less miscible, the phase separation will form larger domains and weaker interfacial bonding. These interfaces, therefore, will contribute to poorer properties and strengths than either of its components. Some polymer alloys exhibit a synergistic effect in which mixing yields an improvement in properties. This phenomenon may result from favorable dipole-dipole interactions between the polymers of the alloy. Different polymers may be miscible at specific concentrations. The biggest problem with immiscible blends is the poor physical attraction between phase boundaries leading to greater phase separations. Compatibilizers can be employed to improve adhesion of the differing polymer domains on the microscopic level. Other ways to promote phase overlap is shear mixing and processing at higher temperatures.

Interfacial Tension

Interfacial tension coefficients can be determined via experiment or calculation and have been considered in the past to be most reliable way to determine polymer compatibility. Methods that just use solubility parameters to predict compatibility of polymers are unsuccessful, as they do not consider dipole-dipole interactions. Furthermore, predictions of properties for immiscible blends are more complicated due to varying morphologies during processing. One phase will form a continuous matrix and the second polymer will be dispersed into microstructures such as spheres, lamellae, or fibrils. Whichever polymer is dispersed in the continuous phase will be responsible for most of the bulk properties.

Attempts have been made to provide a theoretical basis for binary system miscibility. While they may shed some insights into why selected polymers are partially miscible, they are not typically relied on in practical recycling applications with mixed plastics where there are many comingled polymer types. They are included here for completeness. Interfacial tension calculations can be performed for binary mixtures following the procedure of Ultracki, 2002. The tension between polymer phases is based on partial solubilities due to dispersion, intermolecular and hydrogen bonding forces. Equation 2.3 shows the mathematical relationship between the group and bond contributions to the calculation of the interaction parameter, δ_i.

$$\delta_i^2 = \delta_{id}^2 + \delta_{ip}^2 + \delta_{ih}^2 \qquad 2.3$$

where δ_i is the overall interaction parameter for a polymer,

δ_{id} is the contribution from London dispersion forces,

δ_{ip} is the contribution from dipole-dipole attractions, and

δ_{ih} is the contribution from hydrogen bonding, respectively.

Once δ_i is known for all the polymers of the blend, the Huggins-Flory binary thermodynamic interaction parameters, χ_{12}, can be calculated from equation 2.4.

$$\chi_{12} = (V/RT)\ [\delta_1 - \delta_2] \qquad 2.4$$

where V is the volume, R is the universal gas constant and T is temperature in Kelvin.

Finally, the interfacial coefficients can be written as:

$$V_{12} = KRT\ \chi_{12}^{n} = K_1\ (\rho RT)^{n-1}\{(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2 \qquad 2.5$$

where K and K_1 are coefficients, ρ is density, V_{12} is the interphasial tension coefficient resulting from an immiscible binary blend.

Miscibility of Plastic Combinations

The polymer technical literature contains many studies on miscibility of binary plastic mixtures. These have been determined via laboratory procedures as opposed to theoretical modeling methods. A selection of results germane to this thesis project is summarized as Table 2.1. Ternary and more complicated polymer blends have limited resource in current literature.

Polymer Combination	Miscibility	Note	Reference
PP/LDPE	Limited-Immiscible	Small portions of PP dissolved in LDPE phases	Dong et al., 1998
PP/LLDPE	Partial	Similar chain lengths leads to compatibility	Dong et al., 1998 Shanks et al., 2000
PP/EVA	Immiscible	Phase separation, 10% PP/90% PP with a second extrusion step improved morphology	Maciel et al., 1996
LDPE/LLDPE	Partial-Immiscible	[1]Miscible to the 50/50 percent composition range. Then LDPE is expected to be in the LLDPE phase.	Casellas et al., 1999 [1]Ibnelwaleed et al., 2001
LDPE/EVA	Partial-Limited	[1]Partial miscibility in the amorphous regions	Faker et al., 2008
LLDPE/EVA	Partial-Limited	Partial miscibility in the amorphous regions	Li et al., 2004
LDPE/Wax	Miscible-Partial	Low concentrations of wax are miscible	Rassiah et al., 2010
LLDPE/Wax	Mostly Miscible	Good co-crystallization	Hlangothi et al., 2002
PP/Wax	Miscible –Partial	Low concentrations of wax are miscible	Krupa et al., 2001
LDPE/EVA	Partial	Amorphous fractions of both polymers form a continuous phase.	Dabin et al., 2005

Table 2.1 Collection of binary polymer miscibilities pertinent to this research

Olefin polymer miscibility has been studied extensively but the literature reports conflicting results and actual miscibility of a specific polymer combinations vary significantly under differing processing conditions and actual percent compositions of each polymer. In a paper by Li et al., 2001, authors suggest an updated definition of miscibility that they defined as the degree of dispersion and detection of separate phases. This can depend heavily on the method used. One issue in comparing literature findings on miscibility between polymers is the technique and resolution used to arrive at a conclusion. Optical microscopy can resolve phase boundaries down to 1μm and TEM (transmission electron microscopy) down to 1ηm. Furthermore, polymer combinations in different ratios can exhibit incredibly different morphologies. For example Blom et al., 1998, reported that at concentrations below 20% HDPE could adequately penetrate the PP phase reducing the number and size of the regions, which in effect delayed nucleation and crystallization of the PP phase. For every older paper defining a polymer pair as immiscible, it seems there is a more current finding that describes the contrary.

PP has been found to have limited miscibility with LDPE [Dong, 1998]. Phase separations were identified through TEM. Although, there was evidence of small portions of PP dissolved in the LDPE phase. Additions of only 10% LDPE have been shown to depress spherulite growth in PP and has been inferred to mean partial miscibility of the couple. PP and LLDPE have similar miscibility at low LLDPE concentrations due to similar branching lengths [Dumoulin et al., 1984; Dumoulin et al., 1987; Dumoulin et al. 1991]. Another study by Hill et al., 1994 showed more specifically using hot stage optical microscopy (HSOM), during structure development crystallization bridging occurred between droplets. Next in 1998 Dong et al., investigated PP-LLDPE blends by TEM and discovered PP lamellae in the LLDPE phase. This finding suggests that fractions of PP can become dissolved in the LLDPE phase even though their phase was separate.

The addition of wax to polymers has been previously investigated [Krupa, 2001; Rassiah, 2010; Hlangothi et al., 2002]. Wax can be added to mixed formulations to increase processablity and lower melting temperatures of mixed plastic systems. Wax has been found to be miscible at lower concentrations (~10%) with PP [Krupa, 2001]. At 10% wax content in LDPE, blends has been shown to be synergistic, improving properties over that of the virgin LDPE [Rassiah, 2010]. Wax and LLDPE have been shown to co-cystallize and exhibits good miscibility [Hlangothi et al., 2002]. This is thought to happen because the short wax chains incorporate easily into the LLDPE structure during crystallization.

Example Mixed Plastic Products

There will always be a need for new materials and it is clear that mixed plastic waste, with some effort, can take the burden off having to manufacture products from virgin materials. While mixed plastic recycling can have drawbacks (miscibility, inconsistent composition and residual product contaminants), it is still possible to produce useful products from these materials. Industry has taken a proactive and creative approach to finding innovative ways around these problems by developing compatibilizers/additives that increase interaction of dissimilar polymers. This practice encourages mixed polymer recycling.

2K Manufacturing in England has developed a process that turns mixed post consumer waste (PCW) into a plywood panel called Ecosheet [Economist, 2009]. This product performs much like plywood without rotting or splintering. Remnants and demolition materials can be continuously recycled into more Ecosheet, minimizing waste. To make the product, they grind the mixed waste into a powder and sinter layers of polymers to form the sheet. Creative applications and processing can overcome some of the downfalls of mixed polymer recycling.

Mixed plastic waste has also found other applications around the world. In Germany, post consumer waste (PCW) is being used as the material in railway sleepers [Woidasky et al., 2008]. Railway sleepers are conventionally made from wood or cement. Making them from plastic offers a lower weight alternative. Furthermore, making railway sleepers from plastic offers advantages of vibration absorption to dampen noise and a longer life span. Plastic does not crack and does not require a biocide treatment as wooden ones do.

The UK company, TPR Outbuildings, has developed a process that converts mixed thermoplastic waste into a moldable liquid compound. It can be poured like cement to produce housing structures and outbuildings. Other applications include: 1) using plastic wastes as a pyrolysis fuel to provide fuel for houses and cars [TPR, 2012]; and 2) using mixed plastic wastes as aggregates in cement [Zainab et al., 2008; Inhabit, 2012].

Plastic lumber is another well-known use of mixed plastic recycling. Its polymer content can come from waste streams that have already been high-graded for their HDPE and PET. Here, polymers that are usually considered ‘incompatible’ are mixed to produce high cross-section products that have adequate strength to function as construction materials [Lampo et al., 1997]. The wood plastic composites materials will be discussed in more detail in the next section.

Wood Plastic Composites (WPC)

More than any other application, WPC decking has helped generate consumer interest in recycled mixed plastic products and remains its most wide-spread application. Since the early 1990s, the use of wood flour in plastics to produce composite materials has grown substantially. Over 1.5 million tons of WPC products are produced worldwide each year [H`ng, 2011]. Furthermore, consumer demand for these products continues to grow.

The concept of WPCs is not a new one. The first major application of WPCs in the United States was in 1983 when American Woodstock began producing flat sheets of 50% wood and 50% PP for automotive applications [Clemons, 2002]. The first major consumer product to gain popularity as an over-the-counter sale item was composite decking. The Trex Company was the originator of first generation WPC lumber. Trex developed a formulation that utilized post-industrial/ consumer plastics. They used low-grade waste plastics, such as shrink-wrap and other thin film wastes (LDPE), in their products. Before this reuse, shrink-wrap had no possibility of being recycled and constituted a problematic waste stream. Not only did Trex divert the waste from landfills, they gave it value as a resource.

Subsequently, a few companies began using higher quality recycle plastics to produce solid WPCs (e.g., 50% wood and 50% HDPE) for home decking and landscaping applications [Clemons, 2002]. Since then the consumer demand has grown to a global market that generated $3.4 billion in 2011 [BCC Research, 2011]. Improved processing (die design, screw design, etc.), coupling agents, wood fiber properties and plastic resins have enhanced the WPCs into a second-generation material that markedly outperforms the original products [Markarian, 2002]. The composite decking market is currently growing at an annual rate of about 13%.

Fundamentals of WPC Materials

This section provides background information on the constituents that are blended with the WWS to create WPC materials. It first describes of the chemicals present in the wood fibers themselves and then discusses the nature and mechanism of the most frequently employed coupling agent, maleated polyethylene (MAPE).

Primary Structure of Wood. Whether hard or soft, wood is typically composed of three main chemical constituents - cellulose, hemicellulose and lignin (Figure 2.2). Cellulose is a crystalline polymer derived from β-linked glucose and comprises about 41-43% of the wood fiber by mass (Figure 2.2a). During polymerization, cellulose units add to one another to form extended chains [Smook, 1992]. This allows the chains of molecular cellulose to fit closely together over long distances, which makes for a high strength material. Hemicellulose content ranges from 20 – 30% and occurs as an irregular heteropolymer of 5- and 6-carbon sugars (Figure 2.2b). Lignin is the third main ingredient, comprising between 23 – 27% of wood (Figure 2.2c). Lignin is the intercellular cement that binds fibers together. Chemically complex, lignin is based on polyfunctional phenolic rings bound by three-carbon linker units. Lignin intertwines among the other two components and forms covalent bonds with the hemicellulose.

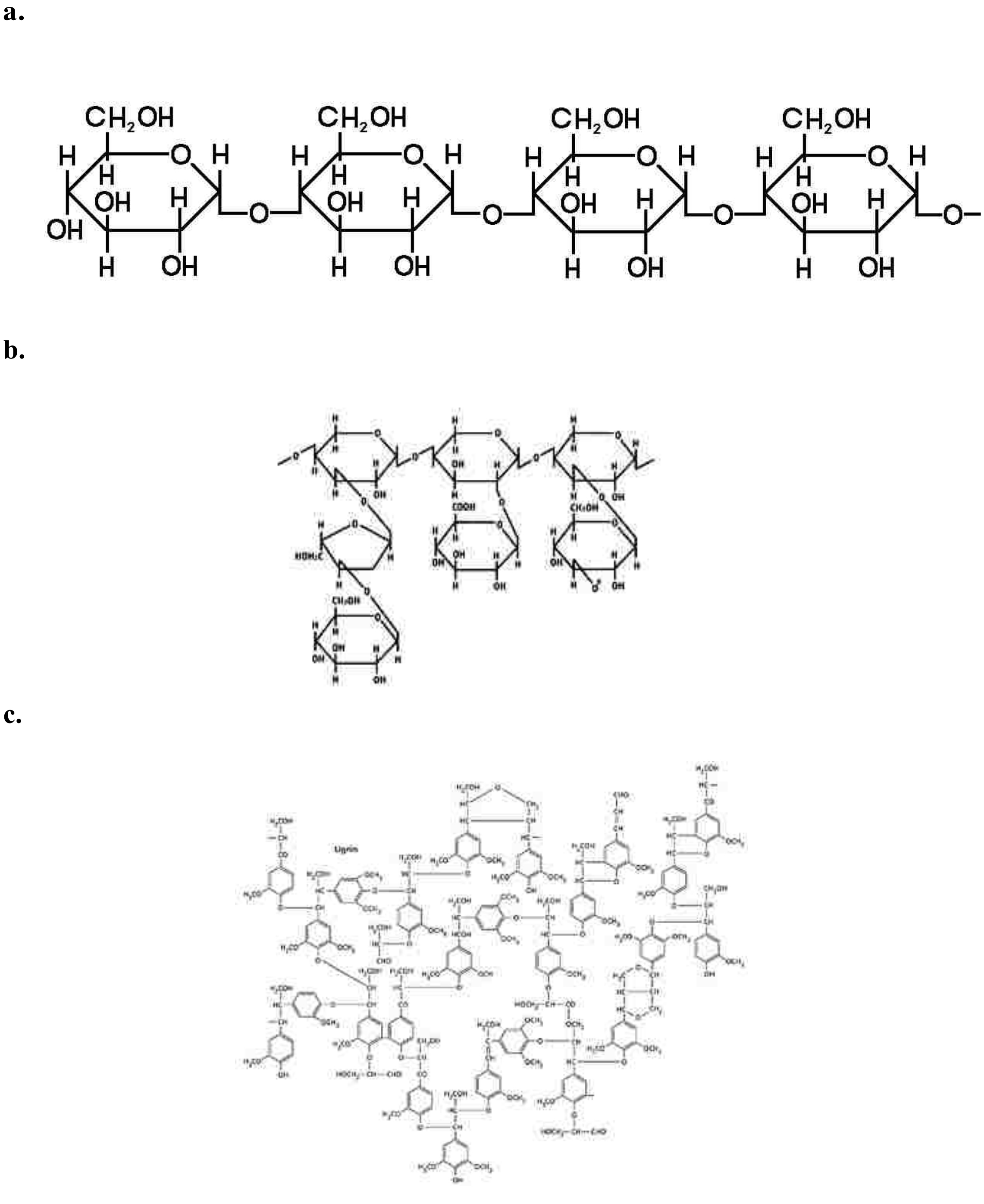


Figure 2.2 Main structural components of wood: a. cellulose (from http://de.ryerson.ca/ de_courses/index_uwi.aspx?course=BC10A&mod=01&id=73909&startdate=May%208, %202010), b. hemicelluloses (from http://www.drfishersmix.com/images/chemical-composition/arabinoxylan.gif) c. a typical lignin (from http://www.bioquicknews.com/ node/436)

Secondary Structure of Wood. Woods can be classified into two major groups: soft and hard. Softwoods have vertical structures mainly comporised of long tapering cells known as tracheids (Figure 2.3) [Smook, 1999]. Rays are another main feature that occur as a horizontal structures several cells high. The wall of a typical tracheid is an actual ‘fiber’, has numerous layers, and measures about 20-40 μm in diameter. The tracheid is composed of three main layers: 1) the middle lamella, mainly lignin bonds between fibers; 2) the primary wall, a thin (.05 μm) permeation resistant layer; and 3) the secondary wall, which makes up the bulk of the cell wall with three different fibril alignments. Hardwoods are mainly composed of libriform fibers, long narrow cells and much wider and shorter cells called vessels (Figure 2.4). Vessels are large enough to be detected with the human eye and occur as pores in cross-sections or a series of long channels on surfaces. The diameter of vessels varies in earlywood to latewood within the ring structure. One major difference between softwoods and hardwoods is the weight and volume percentages of the contained fiber cells. Another important difference between the two is in the lengths of the fibers. Softwood fibers are more than twice the length of hardwood fibers.

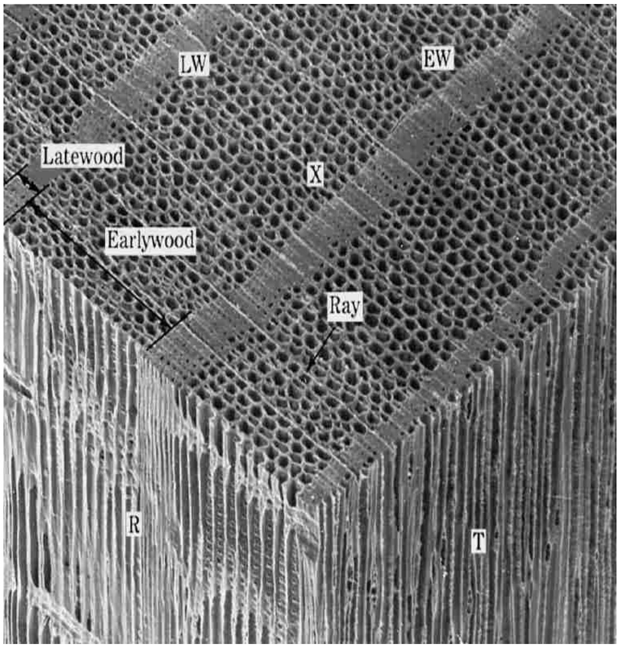


Figure 2.3 Microscopy image of softwood features. Visible are tracheids (T), and rays (R) (from: *www.ce.berkeley.edu/~paulmont/CE60New/wood.pdf)*

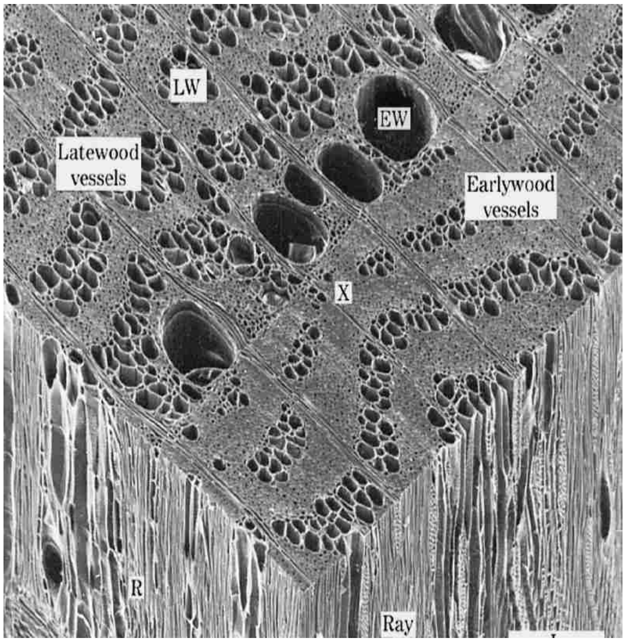


Figure 2.4 Microscopy image of hardwood features. Both large and small vessels are visible (from: *www.ce.berkeley.edu/~paulmont/CE60New/wood.pdf)*

Wood fiber has many attributes that make it a suitable choice as a polymer additive. Wood fiber has an inherently high tensile strength, is resistance to deformation, has inherent bonding ability, has the ability to absorb modifying additives and is chemically stable.

For plastic amendments, wood fiber is most commonly produced mechanically from reclaimed sources. Once acquired, the material is ball-milled to create smaller fibers and then screened to attain desired mesh size (holes/inch). WPCs can have a variety of wood-types (pine, maple, oak, etc.) and fiber sizes ranging from 10 to 80 mesh [Clemons, 2002]. Wood fiber is one of the most cost effective ways to produce a composite material [Stark, 1997]. It is often derived from a waste stream, comes from a renewable resource and has been shown to perform like talc filled plastics [English et al., 1997].

Coupling Agents

Addition of coupling agents (CA) in low percentages (~3%) is a common method to compatibilize unlike polymers and also bind additives to the plastic. In both cases, CAs lower the interfacial tensions between unlike materials. The cellulose portion of wood is a polar material and olefin plastics are nonpolar. These two materials are considered incompatible without amendment. Weak interaction between the plastic matrix and the wood fiber can work against the composite, reducing strengths. It is common practice to add a coupling agent compatibilizer (like MAPE) to enhance the interaction of fiber with polymers. When the fibers are well dispersed among the plastic matrix, stress is distributed more evenly throughout the bulk material, which also can improve strength [Keener et. al., 2004].

To improve wood particle-polymer interactions one needs to: 1) make the plastic less hydrophobic, or 2) make the wood fiber more hydrophobic. So far, attempts to make plastic more hydrophilic have not gained much attention. Methods to make wood more hydrophobic, however, are well developed. These initially include treating the wood with isocyanates, anhydrides, and silanes. Maleic anhydride, for example, has a polar half that can bond with cellulosic hydroxyl groups and a nonpolar ethylene that can open and attach to an olefin resin (Figure 2.5). Anhydride coupling agents attach to the wood fiber via two carboxylate ($-COO^-$) functional groups [Lu et al., 2000] mainly through esterification, but probably some hydrogen bonding as well. Maleic anhydride (MA) is a cyclic, unsaturated carbonyl compound, containing one carbon-carbon double bond (C=C) and, once opened, two carboxylate groups ($-COO^-$). This conjugated structure greatly increases the reactivity of the carbon-carbon double bond toward conjugate addition under a radical initiator [Morrison & Boyd, 1992]. By bonding to the wood fiber, MA transforms the wood surface for stronger adhesion to plastics. If conjugate addition occurs, the two components are chemically cross-linked. However, the molecular size of MA is much shorter than that of the polymer matrix and wood fibers. This discrete nature makes MA less effective than coupling agents based on longer chain molecules [Maldas et al., 1988; Maldas & Kokta, 1990].

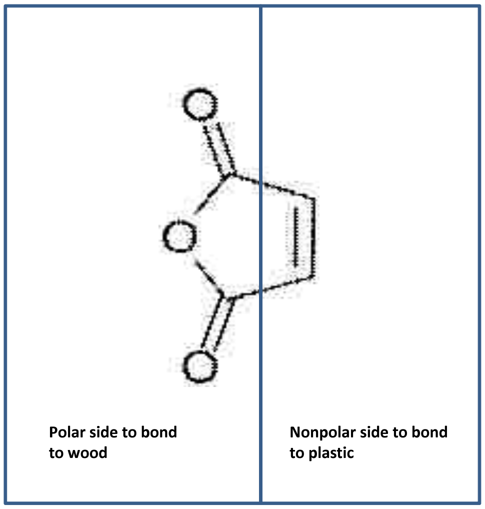


Figure 2.5 Maleic anhydride's polar character

More advanced techniques have evolved in which a copolymer is attached to an anhydride (e.g., maleated PE, maleated PP), further enhancing its ease of compatibility with plastics [Oksman et al., 1998; Simonsen et al., 1998]. For this dissertation, the use of an anhydride-modified copolymer (maleated polyolefin) has been adopted. It is a current, popular approach in industry because the coupling agents are readily available and existing processing equipment can easily incorporate it without modifications.

During graft co-polymerization, coupling agents either crosslink part of the polymer matrix to the wood surface and/or modify the polarity of the polymer matrix by virtue of the anhydride carboxylate groups [Lu, 2000]. This results in the improvement of the interfacial adhesion. It has been suggested in some cases that this MAPE can act as a dispersing agent instead of a true coupling agent in melt blending formation because of its low-molecular weight [Wegner et al. 1992]. When acting only as a dispersant coupling agents fail to either graft to the wood fiber or more likely not have good interaction with the nonpolar polymer.

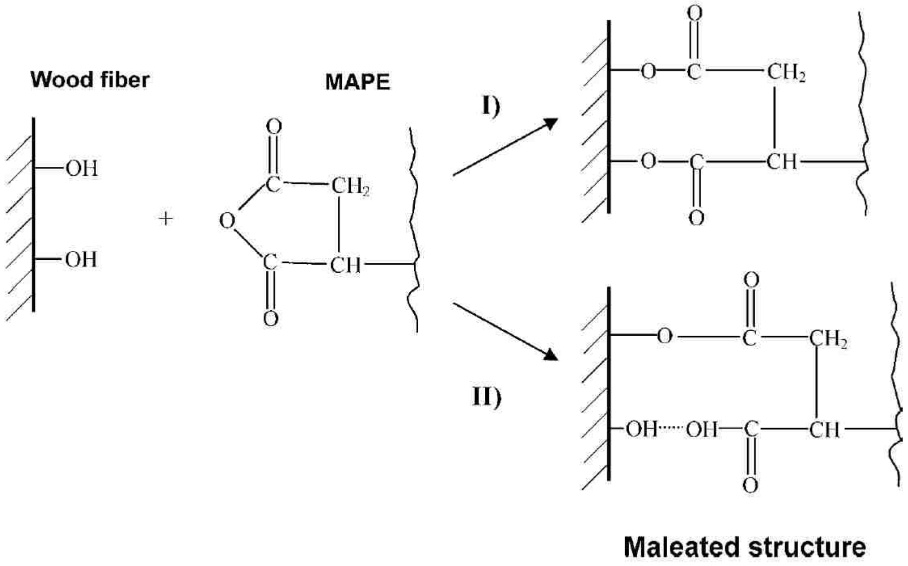


Figure 2.6 Common PE- wood flour- MAPE coupling mechanisms [Lu et. al., 2000]

Other Plastic Additives

Cement Fillers. The technical literature contains no background on cement as a polymer additive. Based on cement's composition (Table 2.2), however, it can be considered similar to silica and calcium carbonate that have been studied. Cement particles occur as a fine (1-100 μm) amalgam of mostly silica and calcium (Figure 2.7).

Cement Composition	Mass %
Tricalcium silicate $(CaO)_3 \cdot SiO_2$	45-75%
Dicalcium silicate $(CaO)_2 \cdot SiO_2$	7-32%
Tricalcium aluminate $(CaO)_3 \cdot Al_2O_3$	0-13%
Tetracalcium aluminoferrite $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	0-18%
Gypsum $CaSO_4 \cdot 2\ H_2O$	2-10%

Table 2.2 Common composition of Portland cement [Hewlett, 1998]

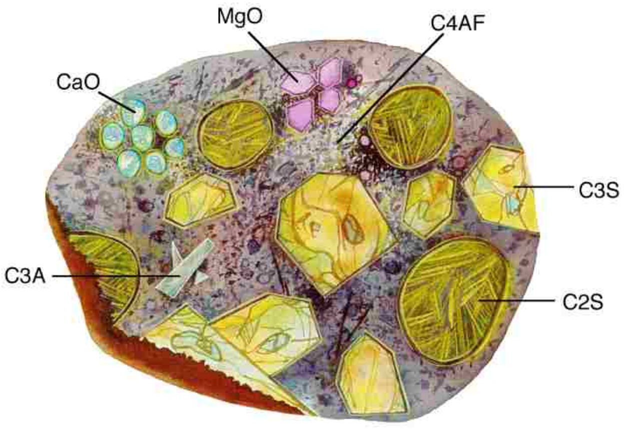


Figure 2.7 Cement particle CaO: Calcium oxide, MgO: Magnesium oxide, C_4AF: Tetracalcium alumminoferrite, C_3S: Tricalcium silicate, C_2S: Dicalcium silicate, C3A: Tricalcium aluminate (from: http://cnx.org/content/m16445/latest/)

Silica and calcium carbonate materials have been investigated as amendments to plastics to improve strength, enhance chemical resistance, reduce cost and act as carriers of pigments and other additives through the plastic matrix [Deniz et al., 2009; Gordzka, et. al., 2002]. They were investigated as separate polymer fillers, and their resulting morphologies reported by Deniz et al., 2009. Both fillers dispersed in the plastic but that silica was well embedded within the polymer matrix whereas calcite existed in discrete cavities. They infer that this phenomenon is due to the lack of wetting of the calcite by the polymer during processing, indicating limited or no calcite-polymer interaction. Calcite materials possessed lower tensile strengths. Calcite can be used to decrease costs in the production of non-strength-demanding materials. Silica, on the other hand, can be used as a reinforcing agent in polymeric materials.

Ash Fillers. The only previously reported use of ash as a filler in plastic materials involved ash from the combustion of coal [Hasset, 1995]. Because coal ash can be laden with heavy metals, the US EPA is concerned about leaching from products that are produced from the waste ash. The ash material pertaining to this research is from a ‘multi-fuel’ boiler that combusts a mixture of wastes, mainly wood and a small amount of plastic. Coal ash and multi-fuel boiler ash are expected to impart similar characteristics to the final product. Hasset found ash-plastic composites to exhibit higher strengths and durability, better skid resistance, and lighter weights. Based on this result, it seems that ash from coal combustion integrates well into some plastics.

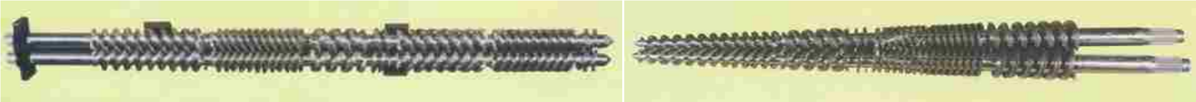
CHAPTER 3

Analytical Tools of Processing and Assessing Material Properties

Chapter 3 provides background and rationales for the processing and analysis techniques used in this thesis project. First, is a discussion on processing of plastic materials. Second, the thermal analysis techniques, mechanical testing equipment and spectroscopic methods are described (four sections). Finally, the use of surface morphology to characterize product quality is outlined.

Compounding and Processing

The most common method of processing thermoplastics is profile extrusion. In this method, the plastic is heated to a melt temperature with good flow and the material is pushed through a die, forming a constant stream. This method can be used with pre-compounded material and a single-screw extruder or compounding and extruding in one step using a twin-screw extruder. Twin-screw extruders come in an assortment of screw configurations each with a different purpose (Figure 3.1). A parallel, co-rotating screw is best known for its compounding ability, creating shear forces to aide in mixing and dispersion of solids, such as wood fiber. Conical counter-rotating screws are utilized in systems where additives such as liquid monomers and pelletized plasticizers/colorants are added to the processed material. These screws are utilized when the material is sensitive to shear forces and good mixing is still needed. Lastly, parallel counter-rotating screw configurations are used to disperse additives in applications that need good elongation. Pictures of conical and parallel screws have been included in Figure 3.1.



Parallel screws

Conical screws

Figure 3.1 Example of twin-screw types (from: http://www.jigarindustries.com/TwinParallelScrews.htm)

Sample preparation for samples discussed in Chapters 4 - 6 were carried out in a Lestritz 18-mm co-rotating twin-screw extruder model at 100 rpm (Figure 3.2). All barrel zone temperatures were set at 170°C. The compounded material was extruded into a rod and then ground into pellets to pass through a 4-mm diameter screen.

Figure 3.2 The Lestritz 18-mm twin-screw extruder

Thermal Analysis

Differential Scanning Calorimetry (DSC). DSC is a very useful analysis technique for analyzing polymer blends and polymer composites. This method measures the energy absorbed and released from a material as it is heated. Energy transitions appear as phase changes occur in the sample. These chemical reorganizations can be due to crystallization, melting or glass transitions. In DSC, a reference and a sample pan are used to calibrate the change in heat flow detected by the instrument. When an event releases or absorbs energy, heat compensation is necessary to maintain the temperature balance between the sample and reference pans. This difference in heat, measured as an electrical current (J/g), is recorded as a function of either temperature or time. The resulting thermogram will have peaks and valleys corresponding to the crystallization (Tc), melting (Tm), glass (Tg) and decomposition (Td) transition events. An example of each event type is illustrated in Figure 3.3.

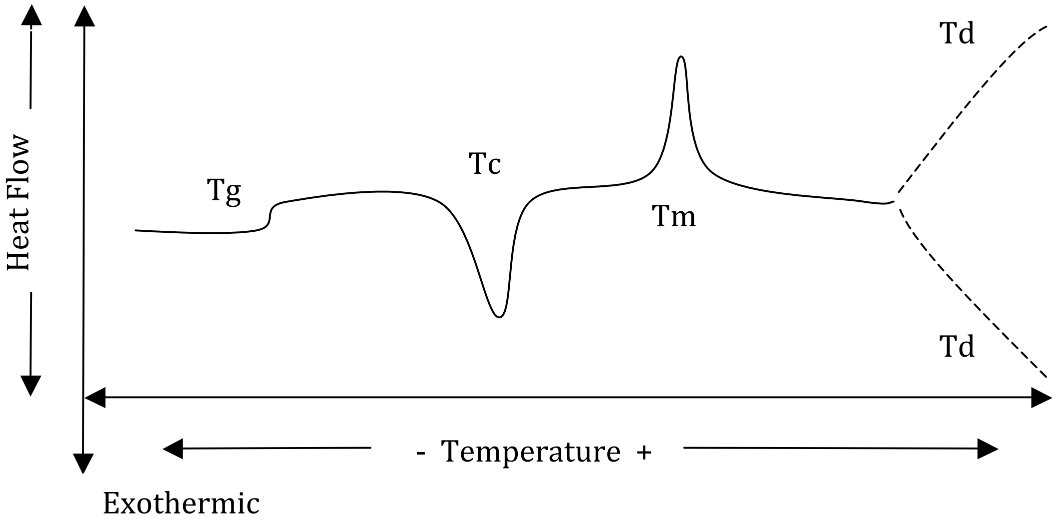


Figure 3.3 Example DSC thermogram showing different transitions glass (Tg), crystallization (Tc), melting (Tm), decomposition (Td) (from: http://www.flemingptc.co.uk/our-services/dsc-tga/)

In polymers, the Tg is a second order transition corresponding to the temperature at which the polymer chains of amorphous regions go from a glassy to a rubbery state while remaining solid. This signifies a change in the local degrees of freedom by increasing chain mobility and registers as an increase in the heat capacity of the polymer. Amorphous polymers will only exhibit a Tg in DSC as they have no real crystallinity. Semi-crystalline polymers have two other main transitions: a crystallization transition (Tc) and a melt transition (Tm). These transitions are due to reorganizations in their more crystalline regions (Figure 3.4). Both Tc and

Tm are first order transitions where the internal structure is rearranged occurring first with a latent heat step yielding a transition that is not continuous. In the Tc energy is released (exothermic) as the polymer builds up sufficient energy to align into a higher crystal form. A Tc will occur in the scan if the polymer has not been fully crystallized before the first heat step and also in the cooling step. As heating continues the polymer will next reach its melting temperature (Tm). In order to reach Tm, energy must be added to the system (endothermic) breaking weaker intramolecular forces that adhere polymer chains until the entire polymer is melted. At first there is no change in temperature as all the heat is going into melting the polymer and the temperature will not increase until the entire polymer is melted. A final transition is at the polymer's decomposition temperature (Td). This is an irreversible step at which the polymer begins to degrade when the side chains on the polymer backbone are cleaved.

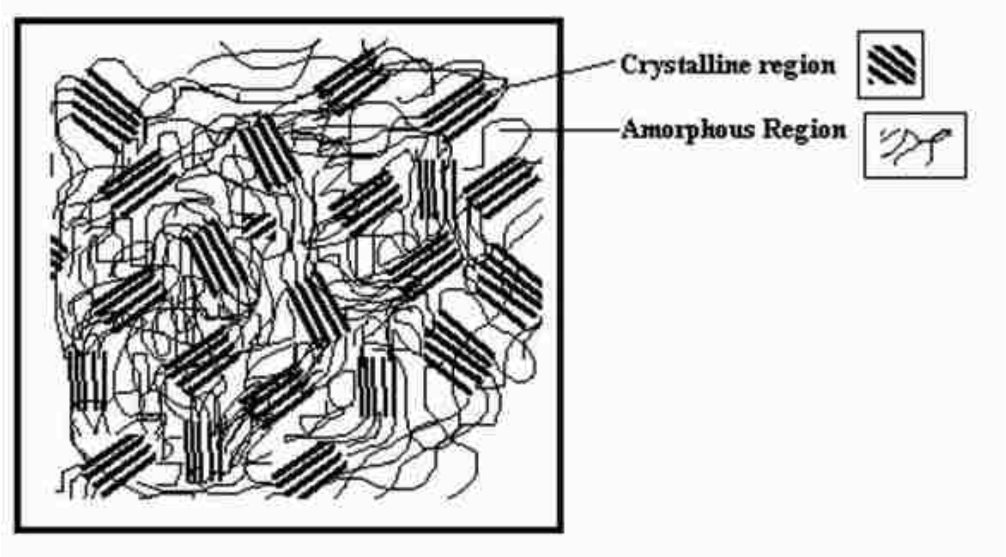


Figure 3.4 Amorphous and crystalline regions of a semicrystalline polymer (from: http://web.utk.edu/~mse/Textiles/Polymer%20Crystallinity.htm)

Percent crystallinity of a polymer can be calculated by considering the area bounded by the Tc or Tm peaks and a known value for that polymer at 100% crystalline.

Since the bulk of the plastic mix studied consists of complex materials (i.e. the tape is both polypropylene and an adhesive layer, and the hot melt adhesive is a three component material), a known value does not exist for a crystallinity calculation. Therefore, enthalpy required to either melt (ΔHm) or crystallize (ΔHc) a sample can be calculated by the integration of their peaks. These values can be then be compared over formulations yielding insight into crystallization kinetics due to the fillers and loading. DSC was done on a TA Q200 instrument (Figure 3.5).

Figure 3.5 The TA Q200 DSC instrument

Thermogravimetric Analysis (TGA). TGA is a quantitative technique that follows the mass of a sample as a function of temperature in a controlled environment. This method is useful in determining many properties of a sample such as: compositional analysis of multi-component materials or blends, thermal stability, decomposition kinetics, estimation of product lifetimes, moisture, and volatile content.

Thermogravimetric analysis was performed on a Perkin Elmer TGA-7 instrument with a heating rate of 10 °C/min (Figure 3.6). Samples, initially ~ 9 mg, were heated from room temperature to 600 °C under an inert N_2 atmosphere. Data were analyzed using the Perkin Elmer Pyris v8 software. The main purpose of the thermograms was to determine the effect of additives in each formulation through the onset of degradation temperature and overall curve shape.

Figure 3.6 The Perkin Elmer TGA-7 instrument

Tensile Testing

Determination of a polymer's mechanical properties is one of the most common techniques in characterizing strengths of the material. In tensile testing the force is monitored as a sample is subjected to axial pulling at a constant rate. Often, auxiliary units (extensometers) are used to help control the rate of loading or strain. The output of this testing is a stress-strain curve. Stress of the applied force is measured over a cross-sectional area. Strain is the normalized displacement. There are many important material properties that can be determined from the curves that are generated (Figure 3.7). Most plastics exhibit an initial linear region, which corresponds to the modulus of elasticity (MOE). The upper limit of the curve corresponds to the maximum force the material can resist before rupture. The area under the curve is the amount of 'toughness' or energy at break. This is the total energy stored by the specimen during its deformation. Tensile testing offers important information on the properties of the material that aids in design and engineering of products.

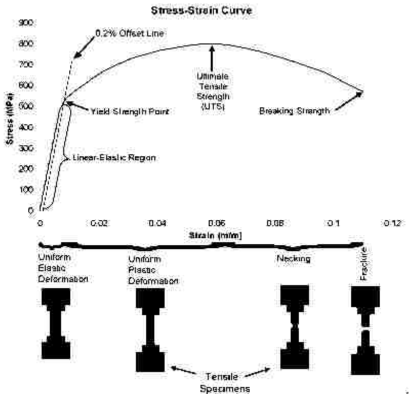


Figure 3.7 A tensile stress-strain curve with various events noted

(from: http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Mechanical/Tensile.htm)

All tensile specimens were mixed and formed in a Dynisco Mixing Molder using a certified ASTM D 1708 mold (Figure 3.8a). The mixer and mold temperatures were 180 °C and 90 °C, respectively. Samples were mixed at 50 rpm for 3 minutes, then injected into the mold and cooled to room temperature. Samples were tested using an Instron 5500R-1122 Universal Test Machine (Figure 3.8b) using a 5 kN load cell. A strain rate of 1 mm/min was applied according to ASTM D 1708 protocol. Strain was measured using an extensometer (Epsilon model 3442). Eight replicate specimens were measured for each sample type.

a. b.

Figure 3.8 Tensile strength testing equipment: a. The Dynisco Mixing Molder used for fabrication of micro-dog bone sample preparation; and b. Instron 5500R-1122 Universal Test Machine used for tensile tests

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR is an accepted technique used to determine polymer type (e.g., PP, PE, PS) based on the infrared stretching modes of the molecular structure. The ATR accessory is used to simplify sample preparation to obtain reproducible spectra from solid materials (Figure 3.9). In ATR, the IR beam is not transmitted through a sample, but interacts with the material's surface. The ATR crystals are dense with a high refractive index. A series of internal reflections creates an evanescent wave extending beyond the surface of the crystal and into the sample's outer layers. Good contact is needed between the sample and the crystal because the wave extends only about one micron beyond the crystal's surface (but depends on the choice of crystal and its refractive index).

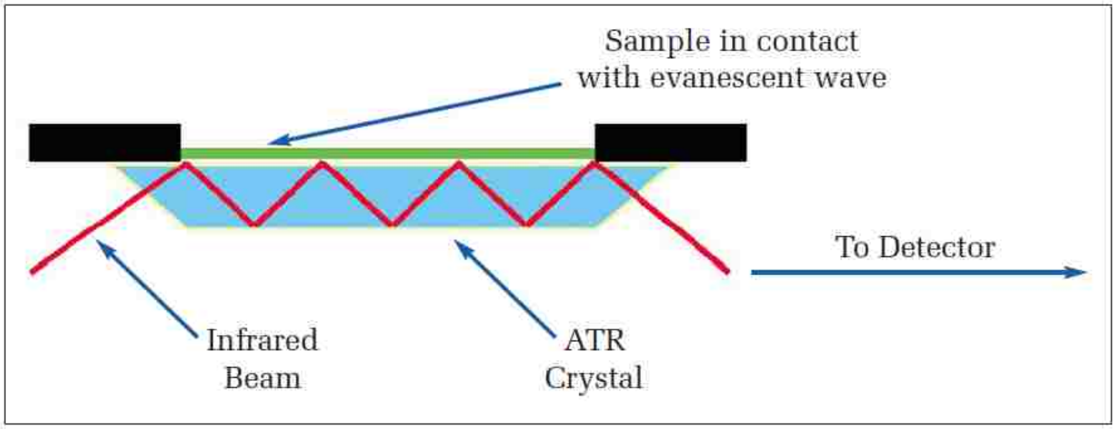


Figure 3.9 Schematic of how ATR works [Perkin Elmer, 2005]

Fourier transform infrared spectroscopy (FTIR) measurements were performed by a Thermo Nicolet Avatar 370 DTGS spectrometer (Figure 3.10) using a single-bounce ZnSe attenuated total reflectance (ATR) probe (Smart Performer). A set of 64 scans was obtained over a range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1}. The spectra were ATR and baseline corrected, averaged as triplicates and then matched to a spectral library using the OMNIC v7.4 software (Thermoscientific).

Figure 3.10 The Thermo Nicolet Avatar 370 DTGS FTIR. The entire instrument appears at left, a detailed view of the ATR attachment is on the right

Morphology

Morphology in materials is the study of their surface features. This method is commonly employed in composites to identify the changing surface features that result from additives. Furthermore, visualizing the faces of tensile fractures can provide insights regarding the additives. Interactions with the plastic matrix may be reinforcing, compatibilizing or ill-mixing.

Microscopy. Magnification of 400x is sufficient to identify large-scale surface features, the general level of component mixing, and identification of voids. A Celestron Handheld Digital Microscope was used to capture 400x images of the samples (Figure 3.11).

Figure 3.11 The Celestron Handheld Digital Microscope

Scanning Electron Microscopy (SEM). SEM is a powerful visual technique that produces an image by scanning a sample with a beam of electrons. In a back-scatter electron set mode, electrons interact with the surface of the sample's topography and are reflected to a detector.

Differences in electron voltages can be translated into an image. Images for samples were produced using a Tescan Mira XMU scanning electron microscope with a resolution of 3 nm at 30 kV and an accelerating voltage of .2-30 kV detected by secondary electron back-scatter (Figure 3.12). Samples were sputtered with gold prior to imaging to increase their conductivity.

Figure 3.12 The Tescan Mira XMU SEM

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CHAPTER 4

Characterization of a Cardboard Recycling Facility's Mixed Plastic Waste for Beneficial Use

Tova Sardot, Armando G. McDonald, Garon Smith

An issue with old cardboard container (OCC) recycling is the generation of a plastic waste stream that currently either gets land-filled or burned. The contents of this rich plastic waste, which constitutes 35% of the exiting stream, are not well documented. This study is aimed at characterizing the plastic waste stream for engineering new second life products. The plastic waste from a Wandel screen-processing unit was composed typically of hot melt adhesives (37%), polypropylene (32%), polyethylene (17%), and polystyrene (9%). Proportions varied 10% or less in each polymer category. The plastic waste was compounded, milled and injection molded into test specimens. DSC analysis showed that the polymers exist generally in separate phases. TGA thermograms determined that the onset degradation (405°C) of the mixed stream is an average of its components. In tensile tests, the mixed plastic waste stream performed comparably to its starting materials with a modulus of 9.6 MPa, ultimate strength of 8.7 MPa, and toughness of 52.6 J.

Introduction

Of all products shipped in the US 90% are in cardboard boxes and over 70% of those boxes get recycled every year [Corrugated Packing Alliance, 2008]. During the manufacturing of kraft pulp for cardboard boxes, there is often reclamation of secondary fiber from cardboard recycling. This secondary fiber is used in new cardboard manufacturing at a rate of 30-35%. In the reclamation facility, waste bales are conveyed into a pulper and broken down into a slurry [Smook, 1992]. The slurry is then fed into a system of pressure screens, deflakers, cyclones, and other cleaning devices aimed at separating the higher quality kraft fibers from all other contaminants. Common contaminants include dirt, rocks, tramp metal, low tear-strength kraft paper, packing material and the more difficult to remove contaminant 'stickies'. Stickies is the general term reserved for glues, hot melts, and latexes.

In the Smurfit Stone Container Missoula mill, the process of complex separations ends up in four streams: useable fiber, and three waste streams. These waste streams are known as the hydradenser, select purge and Wandel screen. The hydradenser waste stream contains about 90% unusable fiber and 10% mixed plastic (e.g., polystyrene pellets, stickies and thin film plastic). The select purge waste stream is generally a 70/30 mix of plastic to fiber but has considerable variation. The Wandel screen has over 90% mixed plastic content and includes some fiber and wood chips at ~ 5%. The usable fiber moves on from the recycling facility to the paper making process and the three waste streams come together and then go to the Freeman Press where water is squeezed out down to about 35% moisture content. Next, the waste stream is sent to a multi-fuel boiler and is burned for energy reclamation. Every day 7-14 tons of waste exit this facility. Similar quantities emerge from other cardboard recycling facilities around the country and the world. EPA (Environmental Protection Agency) is currently considering changing its regulations on what can be considered fuel for multi-fuel boilers and in the future this waste may have to be land filled.

According to the EPA, at least 7.6 billion tons of industrial solid waste and 243 million tons of municipal solid waste end up in United States landfills every year [EPA, 2011]. Surprisingly, as wastes increase, the number of landfills is rapidly decreasing [EPA, 2009]. Furthermore, plastic commonly ends up as litter in the environment even after being land filled [EPA, 2005]. As litter, plastic migrates to waterways where birds and fish get tangled or mistakenly ingest the waste. It is estimated that 100,000 mammals die every year due to plastic waste [Fowler, 1983]. In the oceans, we are just beginning to understand the scope of the plastic and waste problem. By broadening our scope of what is recyclable, a stronger market is created for all polymers. A higher value on plastic waste means that less will end up loose in the environment.

Plastic generation and subsequent disposal has increased 10-fold from 1960 to 2000 and continues to be the largest growing segment of the country's municipal solid waste pie [EPA, 2009]. In 2009, 30 million tons of plastic waste was generated and the recycling rate was only 7% of production. Recycling rates are low due to the limited scope of plastic recycling. Currently, high-density polyethylene (HDPE) and polyethylene terephthalate (PET) are the only polymers recycled on a large scale and are from post consumer waste (PCW). PCW plastics are difficult and costly to recycle due to inconsistent impurities as well as inefficient collection and separation. Investigating industrial processes that produce plastic wastes cleanly and consistently should be a priority. Although there is not accessible data on the industrial solid waste contribution to the plastic population of US landfills, areas of industry that that fit this criterion do exist. Both an example and the subject of this research, cardboard recycling has an inherent mixed waste stream including a substantial amount of plastic. The plastic in these streams are unusually clean for PCW. During the extensive fiber recovery, the plastic waste endures warm water and cyclone processing that removes sand, dirt and other impurities (Figure 4.1). Many of these facilities burn these wastes and recover high British thermal units (BTU) contents to aid in powering their processes. Obviously, burning creates air quality issues and squanders an opportunity for beneficial use. Furthermore, EPA is considering banning this practice and the cost of land filling the over 10 tons/day waste stream per facility is not economical.

The aim of this study was to establish the polymeric composition of industrial plastic waste stream and the mechanical strength and thermal properties of the compounded material. The mixed stream was separated into specific plastic classes, characterized separately and compared with reference plastics.

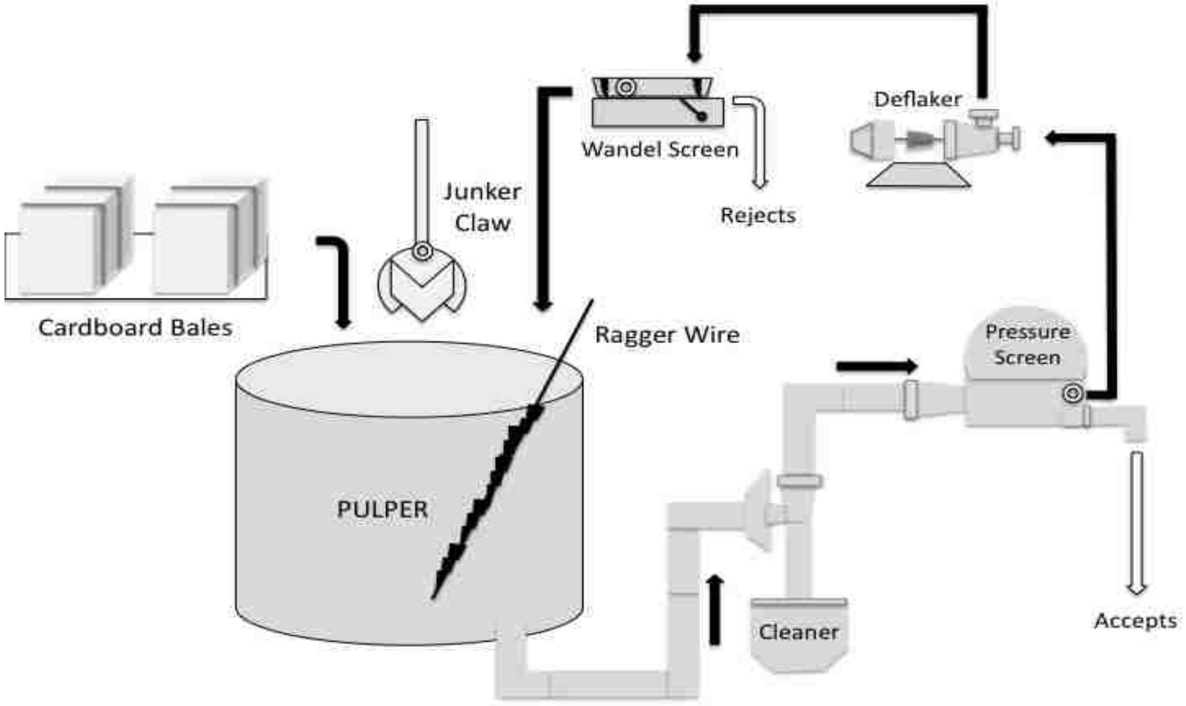

Figure 4.1 Schematic of fiber recovery and subsequent mixed plastic waste generation

Materials

The subject of this research was a mixed plastic waste stream from the Smurfit Stone Container Cooperation's old corrugated container (OCC) cardboard recycling facility in Missoula, MT. Three reject streams exit this facility, but the stream from the Wandel vibrating screen was the subject of characterization because it had the easily observable higher plastic content. A general diagram of the OCC process has been included in Figure 4.1.

The Wandel waste stream (WWS) was chosen for characterization as it embodied 75% of the plastic content that exits the OCC facility. Figure 4.2 shows the WWS. The other two waste streams visually had far higher fiber contents. This waste stream leaves the OCC facility with about 55-60% moisture content (before entering the Freeman press). Samples were gathered on 9-20-07, 9-25-07, 5-12-08, 5-13-08, 7-6-09, and 7-7-09. All plastic material was air-dried on bench top screens for about one week.

Figure 4.2 Photograph of dried Wandel Waste Stream

The following polymer materials were used as control samples due to their similarity to identified plastics. These controls were chosen to mimic the different product polymer types allowing isolation of found properties of the mixed waste. Woodworking hot melt glue sticks,10 cm x 1.1 cm, from the Ace Hardware Cooperation were used for comparison with cardboard box adhesive (hot melt sample). Recycled low-density polyethylene (LDPE) pellets (postindustrial thin film bags) from the Rainer Plastics, Inc plastic processor were used as a control for the thin film LDPE (LDPE sample). Hytop polystyrene (PS) foam plates (22 cm) from the Federated Group, Inc. were the material used as the *atactic* PS control (PS sample). Two types of tapes were utilized to account for possible differences in generic brand film or adhesive thickness: Carton Sealing Tape (48 mm x 10.1 m) from the 3M™ Stationary Products Division (3M™ tape sample) and Carton Sealing Tape (48 mm x 45.7 mm) from Greenbrier International, Inc (generic tape sample).

Two additional plastic controls were employed as virgin polymer comparisons: HDPE (Equistar Petrothene LB01000) and polypropylene (PP, Fortilene HB 9300 by Solvay). These samples were included in the characterization to determine quality characteristics for possible applications and general reference.

In the study to determine thickness of the tape control film and adhesive layers, Goo Gone® was used to soften the adhesive for removal.

Methods

Fourier transform infrared (FTIR) spectroscopy measurements were performed by a Thermo Nicolet Avatar 370 DTGS spectrometer using a single-bounce ZnSe attenuated total reflectance (ATR) probe (Smart Performer). The scans were obtained with 64 scans, range of

4000-400 cm^{-1}, and a resolution of 4 cm^{-1}. The spectra were ATR and baseline corrected, spectral library matched and processed using the OMNIC v7.4 software (Thermoscientific).

The WWS was compounded in a Lestritz 18-mm co-rotating twin-screw extruder model at 100 rpm. All barrel zones were set at 180°C. The compounded material was extruded into a rod and then ground to pass through a 4-mm diameter screen.

All tensile specimens were mixed and molded in a Dynisco Mixing Molder using an ASTM D 1708 mold. The mixer and mold temperatures were 180°C and 90 °C, respectively. Samples were mixed at 50 rpm for 3 minutes, then injected into the mold and cooled to room temperature.

Thermogravimetric analysis (TGA) was performed using a TGA-7 instrument (Perkin Elmer) with a heating rate of 10°C/min. The samples were heated from room temperature to 650°C under an inert atmosphere (N_2). Data were analyzed using the Pyris v8 software (Perkin Elmer).

Differential scanning calorimetry (DSC) was performed using a TA instrument model Q200 DSC coupled to a refrigerated cooling unit. The samples were cooled from room temperature to -20 °C, then a second cycle of heating from -20 °C to 250 °C at heating/cooling rate of 10 ^{o}C/min. Data were analyzed using the Universal Analysis 2000 software (TA instruments).

A Celestron hand held reflective digital microscope was used to capture 400x images of the WWS sample.

An Instron 5500R-1122 universal test machine was employed for tensile tests using a 5 kN load cell. A strain rate of 1 mm/min was applied according to ASTM D 1708. Strain was measured using an extensometer (Epsilon model 3442). Eight replicate specimens were measured for each sample type.

For determination of average adhesive content for tape samples, removal of the adhesive layer for tape controls was accomplished using a petroleum distillate-type solvent to soften the adhesive (Goo Gone®). First the sample was weighed, then place in a vial of solvent and shaken for four days. The samples were removed and the adhesive was soft enough to easily peel off. Samples were weighed again and the mass difference was the weight of the adhesive layer. Three replicates were made for each tape.

Results and Discussion

WWS Plastic Identification and Speciation

WWS samples were taken on six different days and separated into polymer-type (PP, HDPE, PS, etc). The identities of the separated plastics were confirmed through ATR-FTIR spectroscopy by spectral library matching and comparison with reference polymers.

Infrared Spectra. Figure 4.3 shows representative FTIR spectra of separated plastics from the WWS. Spectral library matching was used to determine the class of plastic from the segregated WWS plastic fragments. PE was identified through its characteristics C-H stretching and bending vibrations of methylene (CH_2) groups in the polymer backbone [Serranti et al., 2010]. The methylene C-H asymmetric and symmetric stretches occur at 2917 and 2852 cm^{-1}. Additionally, there is a scissoring vibration at 1468 cm^{-1} and a rocking vibration at 718 cm^{-1}.

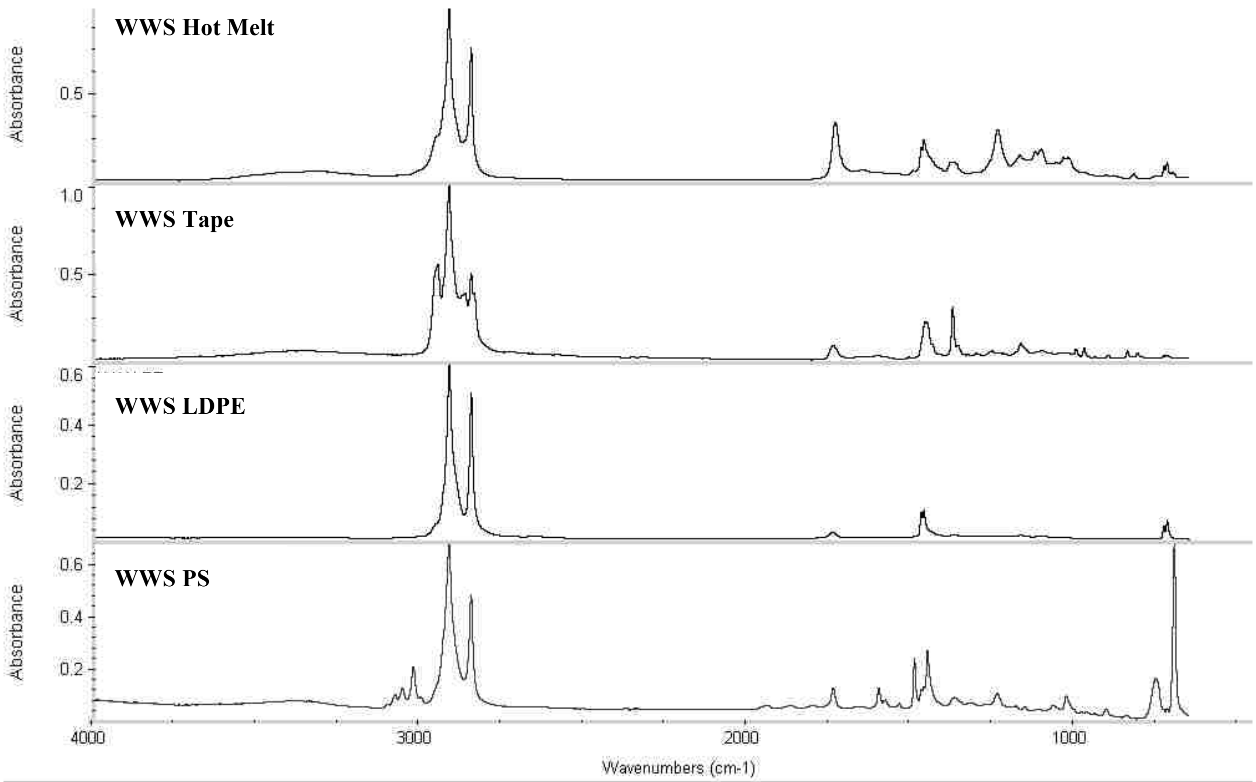

Figure 4.3 FTIR spectra of separated plastic material from the WWS: (1) tape (PP), (2) hot melt (EVA), (3) PE, and (4) PS (top to bottom)

In order to look for possible differences in the bulk adhesive of the tape, spectra were taken of the adhesive side of tapes found in the WWS, 3M™ and generic brand controls. These spectra show no significant differences between the two chosen controls and the WWS tape sample. The adhesive material in all samples has been identified as a polyacrylate-type adhesive.

PP was also identified in the WWS. PP has strong C-H methylene stretching bands at 2921 and 2840 cm^{-1} [Serranti et al., 2010]. There were also asymmetric and symmetric C-H stretches at 2956 and 2875 cm^{-1} and a C-H symmetric deformation mode at 1377 cm^{-1} from methyl groups. These bands were all characteristic of PP.

A small amount of PS was found and identified in the WWS. The IR spectra of PS had weak aromatic C-H stretching modes above 3000 cm^{-1} and also methylene C-H stretching bands at 2925 and 2850 cm^{-1} (Figure 3) [Mayo, 2004]. Out-of-plane C-H bending and puckering vibrations were observed between 750 and 690 cm^{-1}. Weak bands between 2000 and 1650 cm^{-1} were associated with benzene mono-substitution. Lastly, doublets near 1600 and 1500 cm^{-1} can be attributed to aromatic in-plane stretching.

Hot melt adhesive was identified as polyethylene vinyl acetate (EVA) in the bulk waste stream and this was confirmed by FTIR spectral matching. The spectra of EVA show similar absorbance bands to PE and PP in the 3100-2800 cm^{-1} due to similar C-H stretching of methylene groups [Mathias, 1992]. The characteristic carbonyl absorbance peak for EVA are associated with the acetate group at 1737 cm^{-1} and an ester C-O stretch at 1020 cm^{-1}.

Figure 4.4 displays the approximate composition of plastics in the WWS. Since the densities of each polymer are close to 1 g/cm^3, speciation based on volume would be very similar. Percentages of each polymer type varied <10% over all replicate samples taken. The variation range in plastics were: PP and EVA (hot melt) between 8.5 and 9.0%; PE about 6%, PS 5% and the ‘other’ category 5%. The ‘other’ category was reserved for random material, which was comprised generally of pulp fiber, paper, string, foil and wood shards.

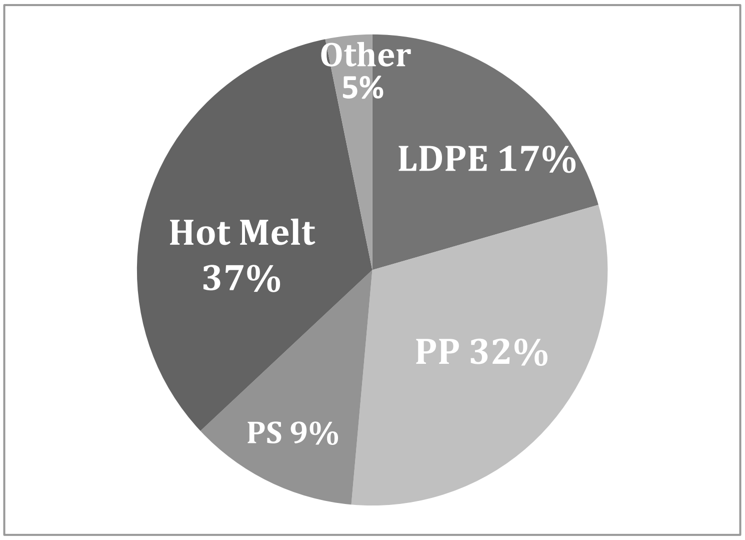

Figure 4.4 Approximate plastic composition by weight percent of WWS

Background on the Identified Polymers. Hot melt glues are common cardboard box adhesives with a substantial contribution to the WWS waste stream. Glues for this application are commonly made from ~30% EVA with 20-30% tackifiers and 20-30% wax [Special Chem, n/a]. The polymer and the tackifier ingredients influence the molecular interaction both with each other and the substrate while adjusting the wax component tunes the melting temperature [Nardin, 1993].

The vast majority of PP found in the WWS is packing tape from cardboard boxes. Packing tape used as controls for this study consists of about 52-60% biaxially oriented PP (BOPP) thin film and 30-38% acrylic-based adhesive layer [FBI, 2008]. Percentages were determined by removal of the adhesive layer by hydrocarbon solvent. The fragments were approximately 5 mm x 60 mm x 0.5 mm in size.

The polyethylene contribution was a thin film amalgam of LDPE and LLDPE. These thin films are generally from packing bags and shipment receipt bag. The fragments were approximately 50 mm x 10 mm x 10 μm in size.

The majority of PS in the mix is expanded PS from packing material with very few thin films or solid substrates. The fragments varied from more intact pieces at approximately 15 mm x 20 mm x 2 mm in size to single beads at approximately 2 mm diameter.

Control Samples. The spectra of the chosen reference samples and WWS samples were highly similar. A comparison of the recycled LDPE and WWS PE sample spectra shows good correlation. A few of the individual WWS PE spectra exhibited an interesting shoulder at 3050 cm^{-1} and peak at 1750 cm^{-1}. These two bands are likely due to the EVA and possibly inherent wax in the hot melt adhesive. During the OCC separation of ‘stickies’ from fiber, the slurry is kept at a temperature higher than the melting point of the wax (about 65° C) [Doshi, 2003]. This process creates dissolved and colloidal stickies, known as secondary stickies. These are rejected from the fiber that is being reclaimed for repulping and end up in the facility's waste stream [Douek, 1997]. It seems that the secondary stickies may have an affinity for the PE film.

Samples from the WWS are designated with a WAN prefix. The weighted average spectra of the controls in Figure 4.5, when compared with the WWS spectra, are very similar. In the spectral average for all control samples, the 3000-3100 cm^{-1} region seems to have some stronger artifacts related to weak aromatic C-H stretching modes of PS. This may be absent from the WWS spectra because the partitioning of PS to the WWS may be poor or 9% isn't a significant contribution. Other artifact differences in the fingerprint region are more difficult to define but are minimal.

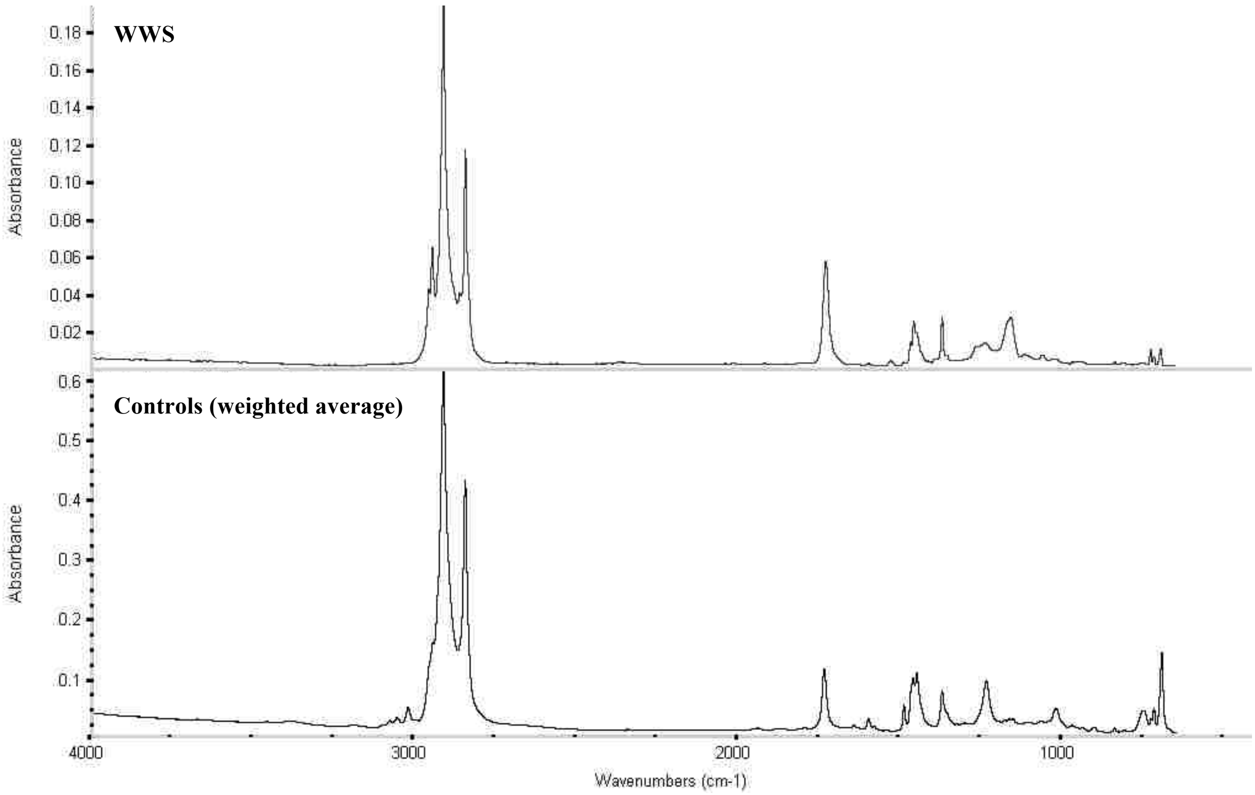

Figure 4.5 FTIR spectral comparison of averaged controls with compounded mixed waste stream

Thermal Analysis

Thermal Gravimetric (TG) Analysis. Figure 4.6 displays the thermographic curves of the control samples. Table 4.1 displays the onset degradation temperatures of all control samples compared to the WWS sample. All samples except for the hot melt are one-step degradation curves. Generally, polymers undergo degradation mechanisms associated with free radical processes [Wilkie, 1999]. These processes begin with bond dissociations at the temperature of pyrolysis. The recycled LDPE sample degrades via random chain scission where the initial fragments produced are pieces from the original molecule. The greater the degree of branching off the backbone, the greater the chance for hydrogen transfer and increased degradation at lower temperatures. PP has more tertiary carbons off the main chain in comparison to PE and, therefore, has lower thermal stability [Chan, 1997]. TG analyses on PP polymers can reveal an early volatization event related to the evaporation of water and this may be the early event on the virgin PP thermogram. As for the tape, it is comprised of a PP thin film with an acrylic adhesive bottom layer. There also exists a very thin release layer on the top-side of the tape, normally made of a silicon based substance. Both the adhesive and release layers are hydrophobic; hence there is a lack of indication of water loss.

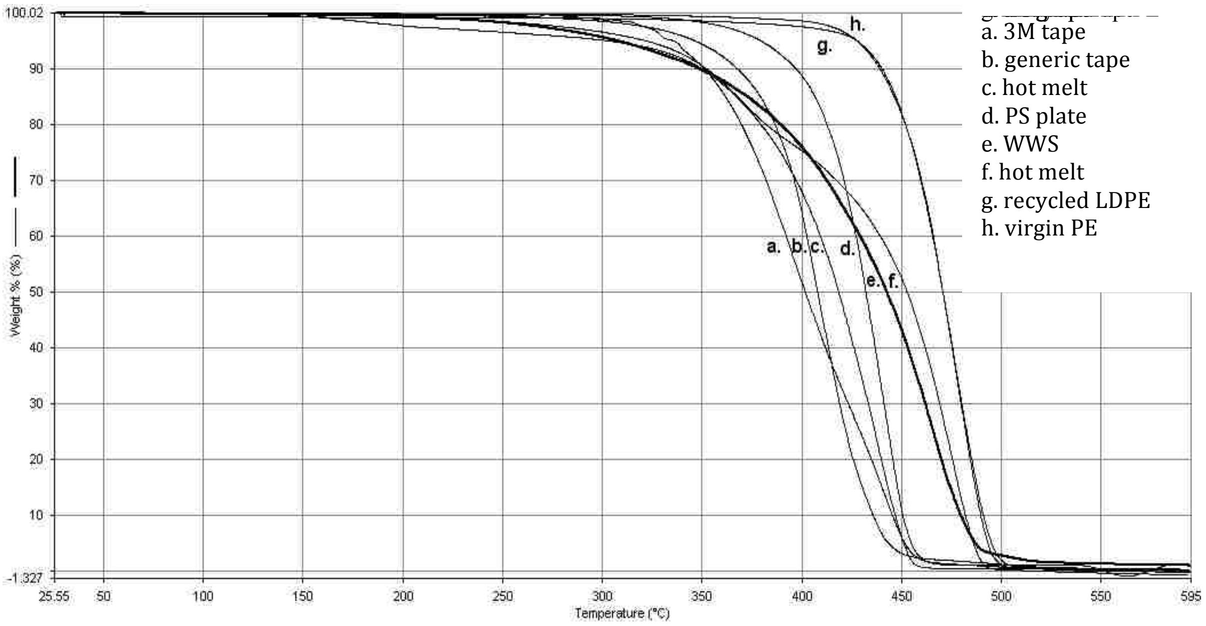

Figure 4.6 TG thermograms of WWS and control samples: (a.) 3M tape, (b.) generic tape, (c) holt melt (EVA), (d.) PS plate, (e.) WWS, (f.) hot melt, (g.) recycled LDPE, (h.) virgin PE

	Degradation onset temperature (° C)	Degradation onset temperature published values (° C)
WAN 0900	405	---
3M™ tape	347	*Not available*
Generic tape	380	*Not available*
Recycled LDPE	445	500 [Wilkie, 1999]
PS plate	403	399 [Chan, 1997]
Hot melt (EVA)	437	430 [Fernandez, 2001]
Virgin PP	388	380 [Emhart Canada, n/a]

Table 4.1 Onset degradation temperatures for WWS, reference plastics, and reported values determined by TGA

The PS has early degradation of weak chain links, then above about 302 °C, depolymerization occurs. The hot melt (or EVA type polymer) degrades in a 2-step process. The first event is due to loss of an acetic acid from the vinyl acetate [Fernandez, 2001]. Since these bonds are the weakest within the molecule, these groups get stripped from the chain before the backbone is broken into more fragments.

If you consider a simple weighted average thermogram by taking the percent contribution of each control sample, as found by the Wandel polymer speciation, multiplied by the degradation onset temperature (T_d), a 'theoretical' onset temperature for the WWS sample is 408 ° C. The measured degradation temperature was 3.9 °C lower for the compounded WWS sample and this is likely due to micro-sized unmixed segments or areas of incompatibility in the polymer mix. The overall degradation of the mixed polymer sample takes on attributes of all the included polymers and ends up having stability similar to virgin PP and tape samples.

It is useful to use the first derivative of the TG curve to better observe where the greatest degradation occurs for each sample (Figure 4.7). In Figure 4.7, the WWS sample peak and depth is between that of its two greatest components: tape and hot melt. Also worth noting, the early first step degradation event of the hot melt sample does not appear as distinct in the WWS sample. Although, the curve for the WWS sample in the same temperature range does seem to have a few small events, the other polymers must be stabilizing the mixed hot melt within the system.

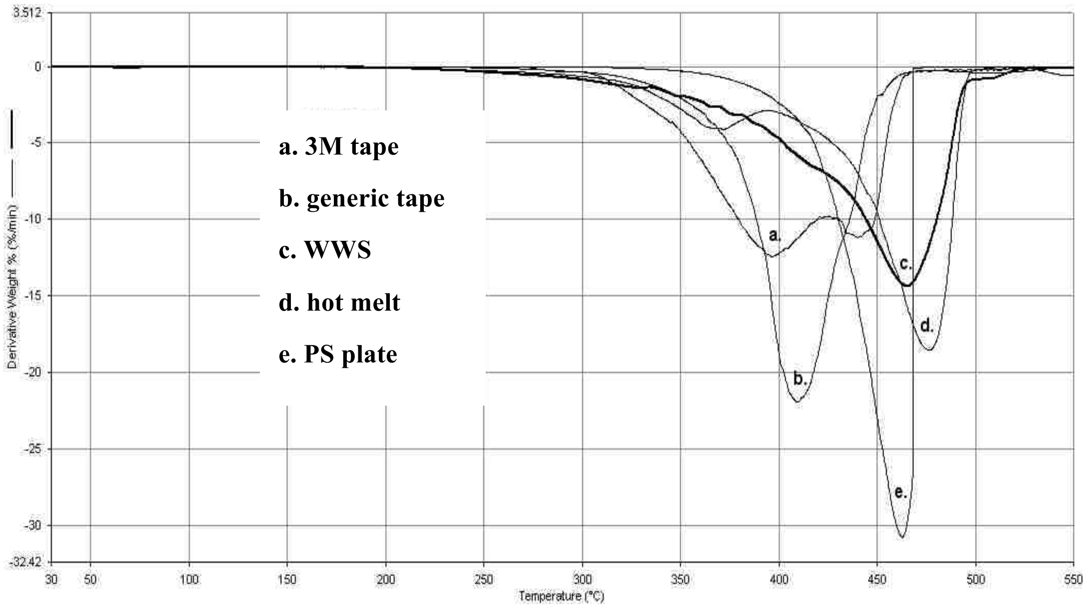

Figure 4.7 First derivative of the TG thermograms for (a.) 3M tape, (b.) generic tape, (c) WWS, (d.) hot melt (EVA), (e.) PS plate

The first derivatives of the thermograms for virgin PP and the generic tape (Figure 4.7 and 4.8, respectively) have strikingly similar shapes and like peak values. The peak of generic tape sample is lower by 30^{o}C due to the presence of adhesive. While the curve for the 3M™ tape clearly has two distinct degradation steps. This suggests that the adhesive coating may be far thinner on the generic brand of tape and/or more possible volatization of the adhesive fragments occurs during sample preparation. Additionally, in comparing the two control tape samples, we see the first signs of a difference in the first derivative. This is likely due to slightly different adhesive formulations between brands. For example, the difference may result from a methyl acrylic versus a butyl acrylic based adhesive.

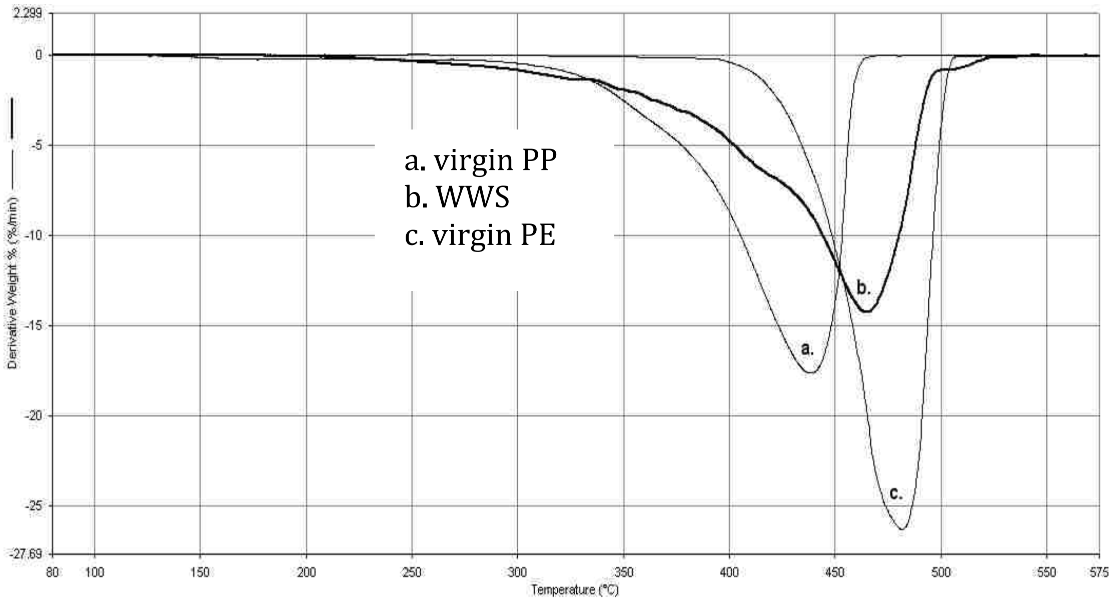

Figure 4.8 First derivative of the TG thermograms WWS and virgin polymers: (a.) virgin PP, (b.) WWS, (c) virgin PE

Differential Scanning Calorimetry. The DSC melt peaks of the WWS sample show a striking correlation to the melt peaks of the control samples (Figure 4.9, Table 4.2). This indicates phase separation and some incompatibility of the different plastics within the WWS. Although, it has been observed that melt blended immiscible polymers show mixture behavior due to the micron-scale mixing morphology [Thirtha, 2006]. Another feature of the thermograph that should be noted is that PS is an amorphous polymer and has no specific melting temperature, but PS does have a known glass transition point in the range of 74-109°C [Brandrup, 1999]. In the DSC of the PS control sample, a glass transition point at 104.2°C was seen. In the LDPE control sample had a narrow melt peak at 105.5^{o}C. It is possible that the first peak attributed to LDPE (2) in WWS at 105.5°C includes a glass transition from PS that is broadening the curve. The feature at 69.6°C relates well to the reported melt peak of EVA in the range of 62-73°C [Emhart Canada, n/a]. Finally, peak 4 (at 156.6°C), correlates to the reported melt peak of PP.

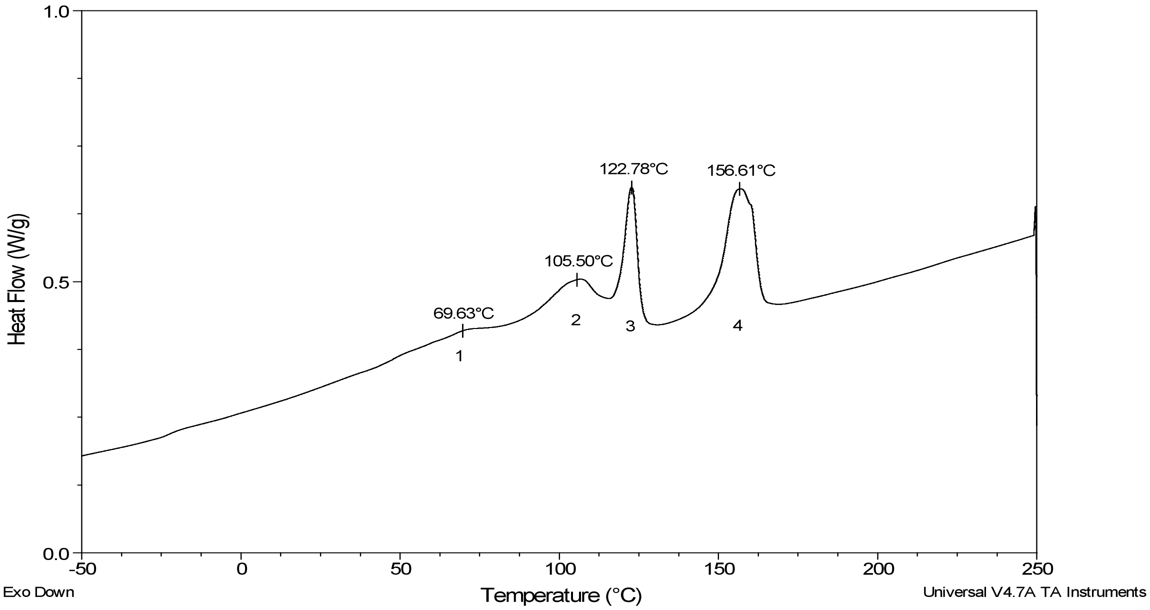

Figure 4.9 DSC thermogram of compounded WWS sample

Sample	Reported melt peak °C	WAN corresponding melt peak °C
PP (3M™ tape and generic tape)	157.4 [Maier, 1998]	156.6 (4)
Hot melt (EVA)	62-73 [Emhart Canada, n/a]	69.6 (1)
LDPE	108.7/122.1 [Brandrup, 1999]	105.3 (2)/ 122.8 (3)
PS	74-109 (Tg) [Brandrup, 1999]	104.2 (2)

Table 4.2 Comparison of melt temperature determined by DSC of the WWS to reported values of the WWS's known plastic ingredients

Microscopy

Micrographs in Figure 4.10 show the cross sections of compounded WWS samples. Particles of wood and fiber are noticeable in all the images of Figure 4.10. Finer milling of the WWS after compounding would be useful to better distribute cellulose-type materials. Image 10a shows the surface of the mixed polymer does include an occasional void. Figure 4.10b shows legs indicative of some ductile-type tensile failure in the tensile break cross section. Tensile failure occurs with legging (from LDPE components) and abrupt breakage (from PP and EVA components). This performance signifies the effect of the mixed system by displaying characteristic properties from each polymer.

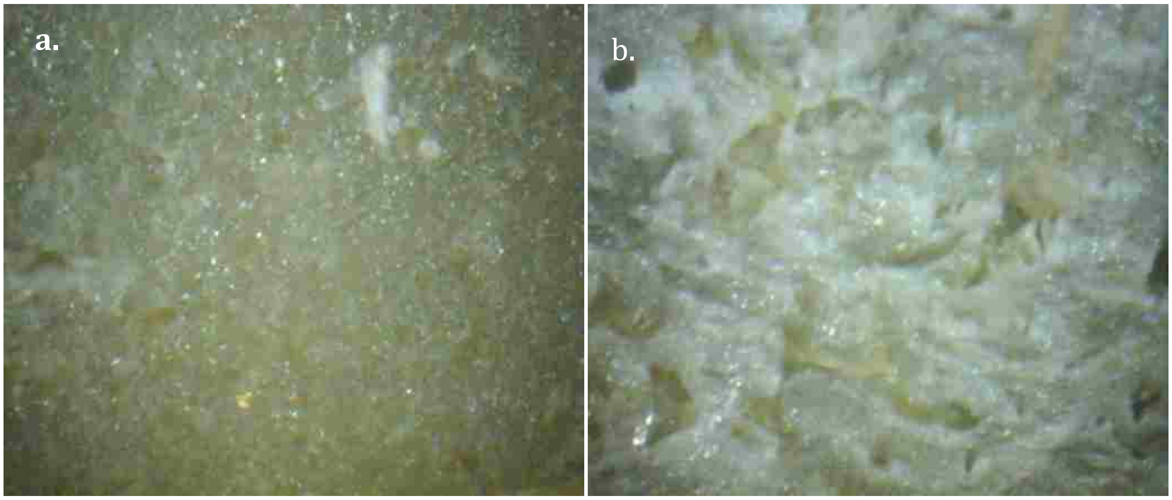

Figure 4.10 Micrographs (400x) of twin-screw compounded WWS sample cross section (a) and tensile fractured surface (b)

Tensile Tests

Table 4.3 shows the relative tensile modulus of WWS compared with its polymer constituents. Tested tensile samples do not include a control for hot melt. There was difficulty in releasing the hot melt sample from the specimen-mold as this material is a very good adhesive. The value for hot melt included in Table 4.3 is a published value [Silquest, n/a]. The WWS includes materials from the 'other' segment of speciation. These impurities were seen to cause early breaks during tensile tests and these data were thrown out. At least six samples were kept for each formula. More consistency and even slightly higher tensile strengths could be attained with the use of full sized dog-bone samples and/or finer grinding of the extruded and compounded WWS.

	Tensile modulus (MPa)	Tensile modulus Published Value (MPa)	Ultimate strength (MPa)	Ultimate strength Published Value (MPa)
WAN 0900	10.0	---	8.7	---
Hot Melt (EVA)	**Not available*	3.2 [2]	**Not available*	3.1[2]
3M Tape	16.3	***Not available*	10.3	.23-.45
Generic Tape	20.7	***Not available*	17.5	****Not available*
RLDPE	9.0	12.2[1]	11.16	10.3[1]
PS	92.3	3000[1]	45.5	40.0[1]
Virgin PE	43.9	800-1400[1]	25.8	19-30[1]
Virgin PP	42.8	1380[1]	12.5	35.5[1]

Table 4.3 Tensile strength and modulus values for tested plastic samples with comparison to published data

*Hot melt was not viable for sample preparation. Published values have been included for comparison.

**Modulus for both tape samples are not included. This property is not typically determined for tape-type products by manufacturers.

*** Generic tape manufacturer did not have available data for the ultimate strength of their product.

[1] Brandrup et al., 2003; [2] 3M Corporation, n/a

All components of the WWS except for the hot melt have greater tensile modulus values than the mixed system. The tensile modulus of hot melt materials is generally very low due to its amorphous structure and high wax content. Its strength lies in the ability to form networks of hydrogen bonds with other substrates [Chemquest Group, 2011]. The relative softness of the

WWS system is due to high hot melt content (32%) and phase-separated polymers. The PS contribution to the WWS compared with the other components is low (9%) and likely has little effect on the overall polymer mix. Interesting to note is the lower modulus value for the 3M™ tape compared to the generic tape. This is further evidence for volatization of the adhesive components during sample preparation of the 3M™ tape, hence a lower modulus value. The modulus of the WWS sample had a similar stiffness to its tape components with a slight lowering due to the hot melt and polymer phase separation that DSC data suggest.

A published value of 3.10 MPa for the ultimate strength of hot melt has been included in Table 4.3 [3M, n/a]. The WWS sample has a strength close to that of its 3M™ tape control. It is stronger than both the brittle PS plate sample and the hot melt value. Again, the PS contribution to the WWS compared with the other components is low (9%) and likely has little contribution to global plastic properties of the WWS. Again, the generic tape shows a slightly higher strength than the 3M™ brand. The overall strength of the mix comes from the tape and thin film PE components that then get diminished by the hot melt adhesive.

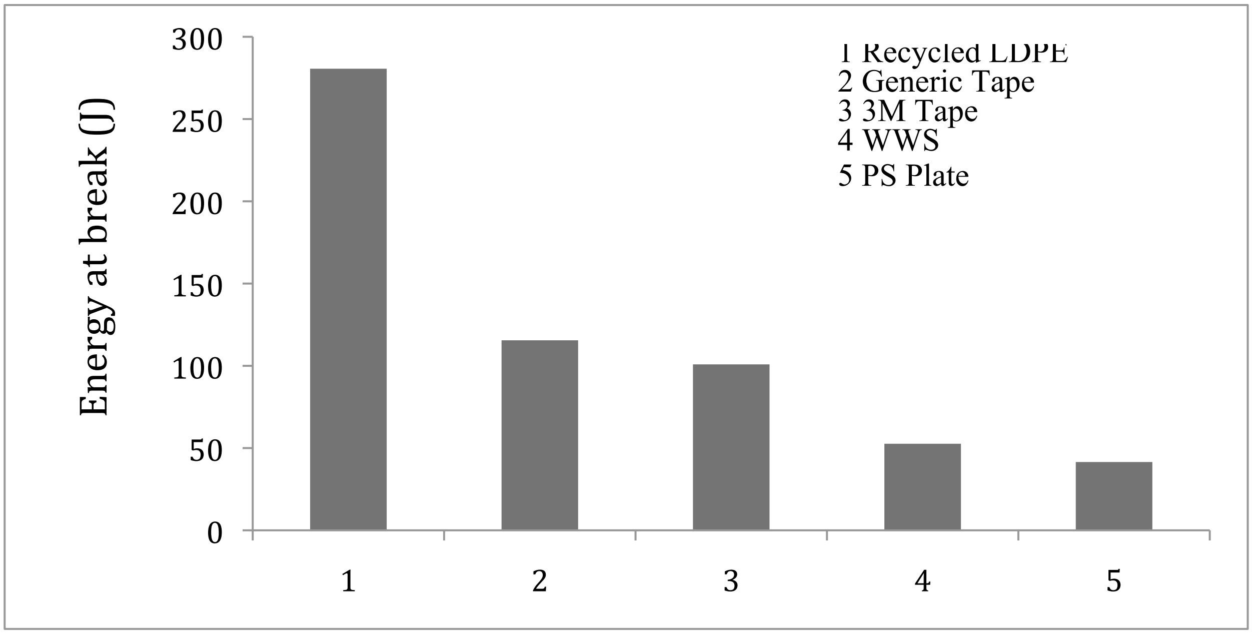

Figure 4.11 Average toughness (tensile energy at break) of control samples and WWS

Toughness (Figure 4.11), also known as the energy at break, is a measure of the area under a sample's tensile stress-strain curve. A suitable published value for hot melt toughness was not found and was left out of Figure 4.11. A similar trend is seen in toughness as was observed with the generic and 3M™ brands. This figure shows that the WWS sample was not as tough as its thin film ingredients. Again, this is probably due to both polymer incompatibility, which yields more free volume in the matrix [Meran, 2009], and the hot melt adhesive adding weaker properties.

Control and Virgin Sample Comparison with Published Values. Table 4.4 is a comparison of the WWS sample with PP and PE virgin polymers. The WWS sample is not expected to reach strengths and hardness of these two polymers. This is due to phase separation from inadequate mixing/incompatibility and lower strength components Post consumer recyclates commonly have lowered properties [Meran, 2009]. These values have been included for overall reference.

	Tensile modulus (MPa)	Ultimate strength (MPa)	Energy at break (J)
Virgin PE	43.9	25.8	141.2
Virgin PP	42.8	12.5	52.6
WWS	10.0	8.7	8.1

Table 4.4 Tensile modulus, ultimate strength and toughness (energy at break) of virgin samples and WWS

In order to confirm the validity of the control and WAN sample tensile data, a comparison to published values has been included (Table 4.4). The value for the ultimate strength of the 3M™ tape sample was acquired from the company of origin but was not available for the generic tape. Information on the modulus of tapes is not provided because it is not a value that is typically useful for this particular product. Furthermore, 3M™'s acquired value for the ultimate strength is based on the performance of the intact tape: one consistent layer of thin film PP coated with an intact layer of adhesive. The sample produced for this study's test was made by mixing the tape and adhesive together via melting and injecting the molten mix into a mold. This is the reason the 'published value' is so different from our measured value. It is surprising that the molten-mixed tape produced strengths on par with the other controls. Tensile data was not available from the manufacture of the generic tape.

Conclusions and Future Work

Characterization of the main components of a mixed plastic waste stream from a cardboard recycling facility revealed the source of its lowered strength properties. FTIR spectra identified plastic materials in the waste stream. DSC analysis showed separate melt peaks for each polymer constituent, uncovering a phase separated behavior of the mix. Strength tests illuminated the effects of high hot melt adhesive content in the waste stream.

Although the mixed plastic WWS samples do perform well compared to individual additives, there is much room for possible improvements. Future work will be aimed at increasing strengths and achieving better compatibilization of the mixed polymers. An LDPE graft copolymer will be used to attain better miscibility of the blend. Removal of the hot melt adhesive would increase strength and hardness considerably but would most usefully be accomplished before drying the waste. As the WWS dries, the mobility of the hot melt is decreased due to hydrogen bonding with paper, LDPE thin film and adhesion to the sticky side of packing tape. Elimination of all the hot melt may not be necessary, as at lowered content it may act as a compatibilizer to some effect. The extracted hot melt may be recyclable. Additionally, the WWS would be a good candidate for wood plastic composite (WPCs) materials, which should increase modulus and toughness. This waste stream might also fare well as a 50% additive to virgin or recycled HDPE with a graft copolymer. Minimally, the WWS could be pyrolyzed into a transportation fuel or oil.

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CHAPTER 5

Investigating PP/LDPE/EVA Miscibility of Cardboard Recycling's Mixed Plastic Wastes by DSC and SEM

Tova Sardot and Garon Smith

The feasibility of using mixed plastic wastes from cardboard recycling was investigated by looking at the miscibility of its components – 37% polyethylene-vinyl acetate hot melt adhesive (EVA), 32% polypropylene tape (PP), 17% low density polyethylene thin film (LDPE), 9% polystyrene packing material and 5% others. The plastic mix was dried and compounded. The resulting material was subjected to characterization by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). DSC analysis revealed three principal phases corresponding to the three major components. The EVA hot melt appears to promote miscibility between itself, the smaller granules of LDPE and some of the PP. SEM images show that the components blend into a topography with mostly small to intermediate phase regions. The large phase granules, seen in previous studies, are LDPE. Since miscibility was incomplete, the use of finer grinding and addition of compatibilizing agents is suggested.

Introduction

Mixed commodity plastics, which account for ~ 70% of all consumed resins, are considered not recyclable on a large scale [Ajja, 2002]. Rationales for this notion include: inconsistent impurities from product life, variations in day-to-day levels of polymer-type, and the debated miscibility of some polymers mixtures. The existing infrastructure that recycles plastic consumer waste (PCW) is antiquated at best. Collection and separation of polymers is costly and inefficient. There do however exist plastic wastes from industrial processes that are produced cleanly and consistently. Cardboard container recycling generates a waste stream that has a significant amount of *clean* plastic with a consistent mix of polymer-types and is the subject of this research. The plastic in the mixed waste stream is mostly commodity resins (PP, LDPE, PS) with EVA (hot melt adhesive).

Plastic wastes are a problem world-wide. As plastic generation continues to increase exponentially and land-fills decrease, recovery of polymeric wastes hovers at a mere 7% [EPA, 2009]. In land-fills, plastics leach their toxic additives into waterways [Linther, 2011] and often still end up as litter in the environment. As litter, plastic migrates to waterways where birds and fish get tangled or mistakenly ingest the waste. It is estimated that over a million animals die every year due to discarded plastics [Derriak, 2002]. In the oceans, we are just beginning to understand the scope of plastic litter and quantify the problem. Large plastic streams are also burned for energy recovery. Burning creates and releases toxic emissions [Simoneit, 2005]. Incineration wastes an opportunity for beneficial use of a material that has a nearly endless potential to be recycled. By broadening the scale of what is recyclable, a stronger market is created for all polymers. A higher value on plastic waste means that less will end up neglected, creating problems for the environment.

Waste plastics can be converted to useful polymer alloys. This practice has been proven attainable by the wood plastic composite industry. Miscibility of mixed polymer systems is a complex issue that depends largely on processing, the percentage of each starting polymer, and interfacial tensions. Although, most combinations are considered incompatible, use in non-critical applications or compatibilization to improve interfacial adhesion of polymer phases is possible [Ajja, 2002]. Treatment by shearing is another way to achieve better mixing of otherwise immiscible polymers. This method has been successful in blending different grades of polyethylene (PE) leading to improved clarity, abrasion and stress crack resistance.

The mixed plastic waste material for this research came from the Smurfit-Stone Container Missoula mill. This mill had an Old Corrugated Container (OCC) facility that reclaimed high tear-strength fiber for reuse in their linerboard product. The OCC rejects emerged in three streams known as the hydradenser, the select purge, and the Wandel screen at a rate of 7-14 tons per day. These streams were de-watered and sent to a multi-fuel boiler for energy reclamation. Cardboard recycling facilities worldwide have analogous waste streams. In the near future these waste may have to be land-filled as EPA is reconsidering what is safe to burn. The Wandel waste stream (WWS) was chosen for this research because it had the highest plastic content of the exiting OCC streams and accounted for 75% of the total plastic rejects.

The aim of this study was to establish general miscibility/immiscibility of the identified polymers of the WWS. An understanding of the miscibilities allows one to identify the best phases on which to concentrate for improving compatibilization. Ultimately, this will create a higher quality starting material and broaden its potential for reuse. Differential scanning calorimetry (DSC) can reveal information on phase interactions. Scanning electron microscopy (SEM) provides images from which to assess polymer identification and phase behavior. Together, the two techniques help illuminate the miscibility of the three main polymer types in the WWS.

Materials and Methods

The mixed plastic waste stream investigated in this research was from the Smurfit-Stone Container Corporation's OCC cardboard recycling facility in Missoula, MT. Previous studies reported that the composition of the Wandel waste stream (WWS) by weight is: 37% hot melt adhesive for boxes, 32% polypropylene (PP) carton sealing tape, 17% low density polyethylene (LDPE) thin film, 9% polystyrene (PS) packing material, and 5% other [Sardot, et al., 2012]. Hot melt cardboard adhesive is composed of ~35% ethyl vinyl acetate (EVA), ~ 30% wax, and ~ 35% tackifiers. Actual percentages vary slightly based on manufacturer formulation. The 'other' category includes wood shards, low tear-strength fiber, foam, staples or any material that has a small contribution to the waste stream.

Plastic consumables were used as control sample analogues for identified plastics in the WWS mix. Woodworking hot melt glue sticks, 10 cm x 1.1 cm, from the Ace Hardware Corporation were used for comparison to cardboard box adhesive (EVA hot melt sample). Recycled low-density polyethylene (LDPE) pellets (post-industrial thin film bags) from Rainer Plastics, Inc. were used as a control for the thin film LDPE. Two types of tapes were utilized to account for possible differences in generic brand film or adhesive thickness: Box Sealing Tape (48 mm x 10.1 m) from the 3M™ Stationary Products Division (3M™ tape sample) and Carton Sealing Tape (48 mm x 45.7 mm) from Greenbrier International, Inc (generic tape sample).

The WWS was compounded in a Lestritz 18-mm co-rotating twin-screw extruder at 100 rpm. All barrel zones were set at 180°C. The compounded material was extruded into a rod and then ground to pass through a screen with 4-mm diameter openings. The compounded WWS was subsequently re-compounded, re-ground and re-screened.

Differential scanning calorimetry (DSC) was performed using a TA instrument model Q200 DSC coupled to a refrigerated cooling unit. The samples were cooled from room temperature to -20°C, then subjected to a second temperature cycle from -20°C to 250 °C at heating/cooling rate of 10^{o}C/min. Data were analyzed using the Universal Analysis 2000 software (TA instruments).

Images were produced using a Tescan Mira XMU scanning electron microscope (SEM) with a resolution of 3 nm at 30 kV and an accelerating voltage of .2-30 kV detected by secondary electron back-scatter. Samples were sputtered with gold to increase their conductivity.

Results and Discussion

Differential Scanning Calorimetry (DSC). DSC thermograms illuminate melt phase behavior, offering some insights into miscibility of the WWS mixture. EVA, PP and PE have low interfacial tensions and any immiscibility between them stems from differences in branching and melting temperatures [Li, 2001]. Figure 5.1 shows the DSC scans of the WWS mix (Curve 1) compared with control samples and isolated WWS polymer ingredients. The second and third curves in Figure 1., shows the EVA (hot melt adhesive) samples. A typical WWS hot melt sample shows a two peak phenomenon, the first of which occurs at ~70°C and the second at ~ 112°C. The second is probably the PE copolymer of the hot melt. Formulations vary greatly among manufacturers and with product applications. The control used for this sample differs from the WWS hot melt, showing only one peak at ~ 70°C.

The wax and tackifier components of the EVA hot melt adhesive are expected to mix well with olefins. Wax has been shown to bond well with LDPE and to increase mechanical properties [Rassiah, et al., 2010]. Tackifiers are used in PP- and PE-based hot melts. The hot melt adhesive should also be compatible in the WWS. Tackifiers are most commonly terpene-phenol resins (TPR). TPRs are responsible for the adhesion of the EVA to the substrate, forming bonds between its phenol groups and materials like aluminum, paper/fiber and glass [Nardin, et al., 1993]. They remain stable in excess of 260°C and are expected retain integrity during compounding at 180°C [Ruckel, n.d.]. The combination of wax and TPRs may be responsible for some of the unexpected adhesion and dispersion of polymers in the WWS.

The fourth and fifth curves in Figure 5.1 isolate the LDPE contribution to WWS. The appearance of two peaks suggests that this phase contains LLDPE, but it is likely that LDPE also exists in the mix. Industry does not differentiate between these two grades of PE even though they have different branch lengths that cause very different material properties. PEs of differing crystallinities (e.g., HDPE, LDPE, LLDPE), can be immiscible even though interfacial tensions are low [Li, 2001]. This is due to the different melting temperatures (Tm) and extents of branching. During melting, liquefaction of the higher-Tm PEs can be impeded as they become encased by already molten material.

In the WWS mix, the first peak of the LDPE phase and the second peak of the hot melt phase have overlapping Tms and should have low interfacial tensions – a good environment for partial miscibility. Additionally, the first peak of the hot melt in the WWS is significantly smoothed over and broadened. The hot melt, some LLDPE and some PP is expected to comprise the main bulk of the polymer system. The longer branched LDPE fractions and most of the PP exist separately. The miscibility of PP and PE (of varying crystallinity) has been studied extensively, but their miscibility is debated. PP has been shown to exhibit limited miscibility with LDPE with evidence of some portions of PP dissolved in the LDPE phase [Dong, et al., 1998]. Blends of PP and LLDPE, however, have been shown to achieve miscibility [Dumoulin, et al., 1989a, Dumoulin, et al., 1987b, Flaris, et al., 1992a, Flaris, et al., 1992b, Li, 2001, Ultracki, 1989]. Further miscibility improvements could be attained through the use of compatibilizers.

The last four curves in Figure 5.1 show PP behavior. Virgin PP and two different tape control samples are included with the WWS to account for possible differences in brand, although these seem small. The PP peak of WWS is broadened over that for the other PP samples, indicative of some slight miscibility in the mix. Ethylene vinyl acetate has been employed to compatibilize PP and wood flour [Dikobe, 2009].

There may be other phases due to the PS and other trace polymers in the WWS. The occurrence of these materials is below 10% and any contribution that deviates from the three main polymer constituents will not be evident in the DSC thermograms.

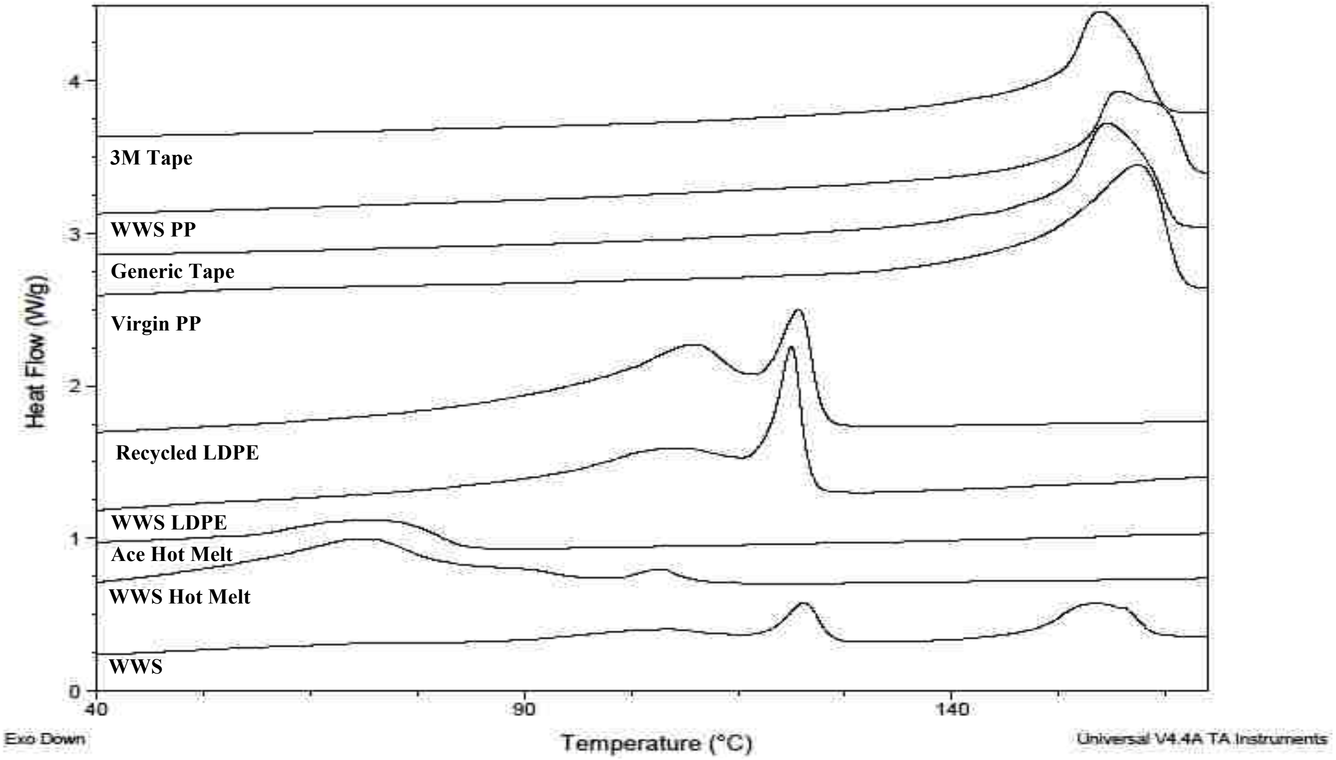
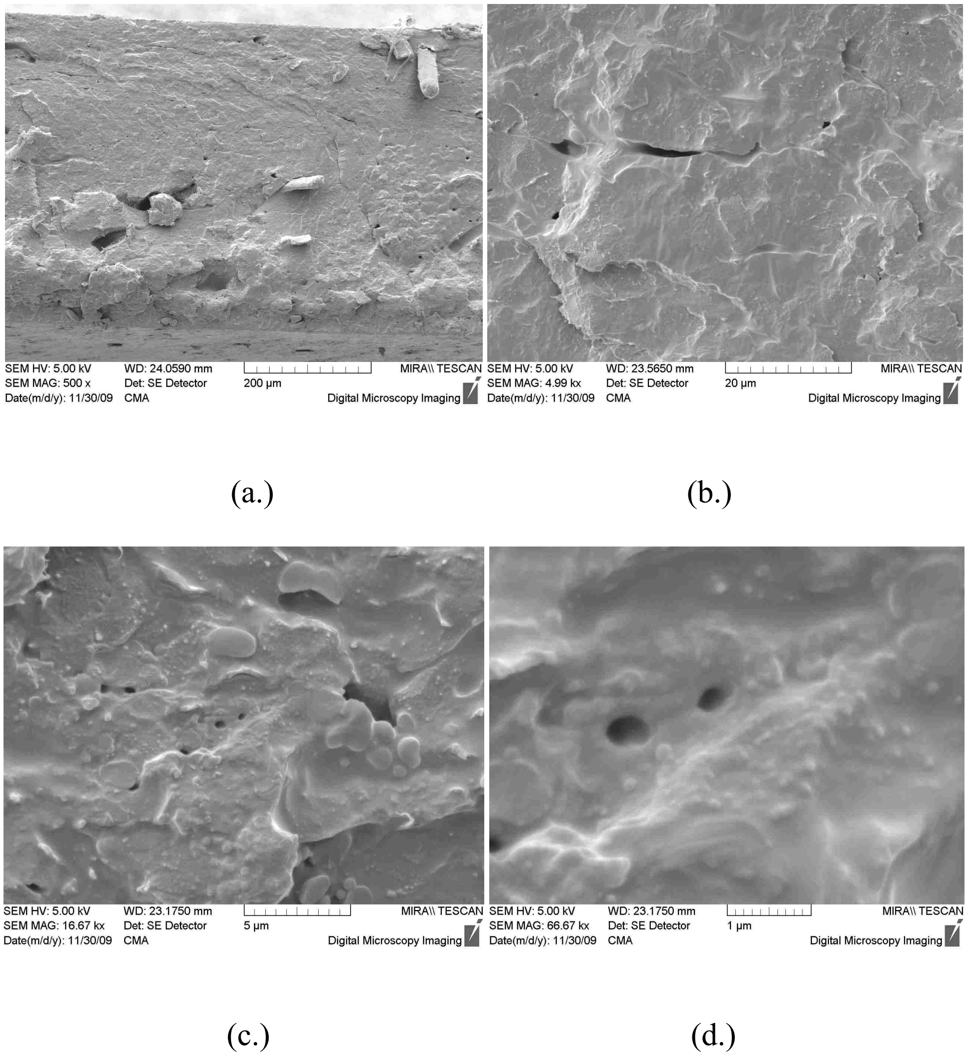


Figure 5.1 DSC scans of the WWS mix compared with hot melt sample from the WWS and the Ace hot melt, LDPE sample from the WWS and a recycled LDPE, tape sample from the WWS, generic packing tape, 3M packing tape and virgin PP

Scanning Electron Microscopy (SEM) Morphology. Even when polymer phases exist separately, they still can have a great effect on one another. The existence of two polymer phases can inhibit spherulite growth. Since the WWS mix is a many polymer system, the existence of very small phases may be partially due to restricted growth of the crystalline structure, as there is no discernable spherulite structure in images with ~ 1 μm resolution (Figure 5.2). The main matrix material is composed of EVA hot melt adhesive. Previously reported tensile values showed that the WWS exhibited a 181% higher value for ultimate strength in comparison to hot melt adhesive values [Sardot, et al., 2012]. The improved performance indicates some intermediate miscibility in the mixed polymers. Possible interactions could include: 1) miscibility of the shorter branched fractions of LLDPE and LDPE with the shorter branched fractions of EVA hot melt adhesive (Figure 5.1); 2) partial miscibility of PP with LLDPE [Li, 2001]; and 3) bonding of the tackifier component with the PP and PE phases. Previously published 400x micrographs of the WWS showed legging due to the visible presence of LDPE phases [Sardot, et al., 2012].

SEM micrographs of the WWS mix are shown in Figure 5.2. at increasing magnifications – 500x, 4.99kx, 16.67kx and 66.67kx. Panel 2c. is the best image for viewing polymer phases. There is a smooth bulk matrix background upon which small, intermediate and larger granules are seen. The polymer content of the smallest grains is most likely from wax fractions in the EVA hot melt adhesive (≤ 200 nm seen easily in many areas of the lower half of Panel d.). This finding is consistent with previous morphology findings of similar hot melt adhesives [Lui, 2010]. Some fractions of short-branched LLDPE and PP are likely part of the main matrix. PP will experience the greatest interfacial tensions with the hot melt phase and is the best candidate for the larger granules of Figure 2c (about 1-2 μm in dimension). This leaves LLDPE as the prime candidate for the intermediate grains. LLDPE has been shown to achieve partial miscibility with PP due to similar chain lengths (Dong et al., 1998; Shanks et al., 2000). This lends further support for this analysis as the larger phases (PP) tend to aggregate with the intermediate phases (LLDPE). It is very likely that the PP and LLDPE phases are somewhat mixed. Large, ill-mixed LDPE rods are seen protruding from the sample face in Figure 5.2a, consistent with previous studies.

Overall, morphology findings were surprising in that the phase grains were generally smaller than expected. This is likely due to low interfacial tensions, shear mixing, and partial miscibility of most of the polymers in the system. The proportion of PP to hot melt adhesive in the mix (32% to 37%) and the low occurrence of larger phase granules support partial miscibility of much of the mix. A few phases may be due to PS and other trace polymers in the WWS. Identification of these minor phases was beyond the scope of this study's methodologies and instrumentation. No anomalous phase regions were noted in any SEM image, so trace polymers seem to have little influence on the final material.



(a.) (b.)

(c.) (d.)

Figure 5.2 SEM images of WWS mixed plastic alloys at (a.) 500x (b.) 4.99kx (c.) 16.67kx (d.) 68.67kx magnification

Conclusion

Partial miscibility has been identified in the mixed polymer system of the WWS. Given the overall WWS composition, the EVA hot melt seems to be promoting miscibility among other components, especially LLDPE and PP. Utilizing a compatibilizing agent geared towards increasing interactions between the two least miscible polymers in the mix, PP with PE, would be beneficial in increasing the overall properties. The WWS may also be a good candidate for a rubber additive. Many ternary PP/PE/rubber composites have been investigated that exhibited good miscibility and improved properties [Hemmati, et al., 2001]. Furthermore, fine grinding and a second compounding run (with or without an additive) may enhance dispersion by decreasing phase sizes [Moreira, et al., 2001]. This can also be done at an elevated temperature to entice mixing of dissimilar branched polymers.

Acknowledgements

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CHAPTER 6

Valorizing Mixed Plastic Wastes from Cardboard Recycling by Amendment with Wood, Cement and Ash

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Chapter 6 seeks to improve over all properties of the Wandel waste stream through amendment with various materials. The mixed plastic was compounded with wood flour (WF), cement, ash and maleated polyethylene (MAPE). WF and MAPE increased the tensile modulus by 65%, ash and cement increased moduli by 49% and 39%. MAPE decreased crystallinity and compatibilized both mixed polymers and additives. Samples were characterized by DSC and TGA. Additives decreased phase separation. TGA analysis showed wood flour, ash, cement and MAPE thermally stabilized the plastics. These improvements make this mixed plastic waste more attractive for reuse.

Introduction

According to the US Environmental Protection Agency (EPA), at least 7.6 billion tons of industrial solid waste and 243 million tons of municipal solid waste end up in US landfills every year [EPA, 2011]. As wastes increase, the amount of landfill space is decreasing [EPA, 2009]. Furthermore, plastic often ends up as litter in the environment even after being land filled [EPA, 2005]. Great strides have been made to recycle pure polymer types by source-sorting according to the recycling code numbers molded into products. A more challenging problem is created when resin types cannot be easily segregated. Substantial mixed plastic waste streams exist in industry and need to be evaluated for potential product reuse. Innovative methods of utilizing mixed plastics can stimulate a stronger market is for all plastics, diverting them away from disposal or litter fates.

Plastic generation and its subsequent disposal has increased exponentially from 1960 to 2000 and continues to be the fastest growing segment of the country's municipal solid waste [EPA, 2009]. In 2009, 30 million tons of plastic wastes were generated and the recycling rate was only 7% of production. The only polymers recycled from post consumer waste (PCW) on a large scale are high-density polyethylene (HDPE) and polyethylene terephthalate ester (PETE). PCW recycling poses many hurdles that the industry is not yet well equipped to handle. The main reasons for these difficulties are: 1) inconsistency of PCW composition with respect to both polymer resins and impurities, and 2) inefficient collection and separation. Investigating industrial processes that produce plastic wastes cleanly and consistently should be a priority. There is not accessible data on the quantities of industrial plastics in US landfills. Although, it is clear that some industries generate sizable plastic waste streams.

Both an example and the subject of this research, cardboard recycling has an inherent mixed waste stream including a substantial amount of plastic. The plastics in this instance are unusually clean and consistent compared to most PCW. Furthermore, similar waste streams are found anywhere that boxes are recycled. Of all products shipped in the US, 90% are in cardboard boxes and over 70% of those boxes get recycled [Corrugated Packing Alliance, n/a]. During fiber recovery, the plastic waste is subjected to repeated agitation in warm water plus multi-stage cyclone processing. This removes sand, dirt and other impurities. Many of these facilities ultimately burn these wastes to recover their high-energy contents and supplement production of steam and electricity. Not only does burning plastic squander an opportunity for beneficial reuse, it also creates air quality issues. EPA is considering banning this practice. Research has identified high concentrations of a wide variety of organic tracer compounds in the emissions from burning plastic [Simoneit, 2005]. The release results in human and environmental exposures. Gaseous components and particulate matter contain products from depolymerization, volatilized additives and decomposition. Airborne species such as these are not currently considered in ambient air emission inventories. Open burn smoke from plastic can discharge 47 times the amount of phthalates in comparison to surface extraction in hexane. Also emitted are polycyclic aromatic hydrocarbons (PAHs) as well as a handful of alkanes.

Without burning, the cost of land filling the over 10 tons/day waste stream from each facility is not economical. Some new disposition for the material needs to be found. Initial characterization of the Wandel waste stream (WWS) showed that this plastic material ‘as is’ has a relatively low modulus and tensile strength due to components with lower melting points and lower crystallinities [Sardot et al., 2012]. Differential scanning calorimetry (DSC) analysis showed evidence of some phase separation of polymers in the mixture. Thermal gravimetric analysis (TGA) revealed that there is good thermal stability of the mixture; the WWS’s plastic is similar to virgin tape components. Utilizing wood fiber and a compatibilizer should address the weaknesses of the WWS, making the ultimate material more attractive for use.

Wood plastic composites (WPCs) have grown in popularity in the past decade because they offer many benefits [Clemons, 2008]. These materials are not new, and more recent formulations have tended toward higher wood content, improved processing technologies and additives that help new generation WPCs outperform their predecessors. WPCs extend forest resources by providing substitutes for dimension lumber that are required for solid planks and poles. Furthermore, the wood components used to make them would otherwise have ended up in a slash pile [Prichard, 2007]. Wood flour (WF), considered fillers within the polymer, reinforce and stiffen the plastic matrix. At the same time, the plastic components impart moisture barrier properties to the wood fiber. Therefore, wood plastic composites display beneficial hybrid properties between wood and plastic.

Chemically, the plastic matrix acts to bind the WF so that forces placed on the composites are transmitted evenly throughout its bulk. Often, the interaction between the hydrophobic polymer and the hydrophilic wood fibers is weak. Maleated polyolefin compounds, in this case maleated polyethylene (MAPE), are often employed during compounding aid in the adhesion of the wood to the polymer. This is accomplished via a reaction of the hydroxyl groups on the wood surface with the maleated groups of the MAPE. The properties of the individual constituents as well as the interactions between them play an important role in the WPC's final properties [Ellsworth, 1999]. Other factors that influence the degree of reinforcement are wood particle size, type of mixing, and WF loading. Wood flours (80 mesh and smaller), have been shown to increase modulus the most with or without compatibilizer and dispersion [Wolcott, 2001]. Polyolefins are well suited for use in wood composites because their melt temperatures are below 200^{o}C where degradation of wood begins. The WWS is an amalgam of polyolefin-type immiscible and semi-miscible polymers. Compatibilizers can also be used to improve mixing of unlike polymers.

Other additives explored in this study were Portland cement and intermediate ash from pulp mill multi-fuel boilers. Adding cement to polymers increases compressive and flexural strengths, decreases water absorption, and imparts good weather resistance [Assad, 2011]. Ash from coal combustion has been previously considered as an amendment to plastics with possible application in recycled waste [Hasset, n/a]. This study showed that the ash amendment increased strength of the plastic material. Ash from a combusted wood and plastic waste source has not yet been investigated. Cement and ash particles sizes are expected to be on the order of about 1-20 µm. While they are not ultra fine, they are over an order of magnitude smaller than the WF (80-mesh maple flour is about 177 µm in length). This allows the cement and ash to interact more intimately with the polymer matrices.

The aim of this study was to increase the mechanical strength and thermal properties of the compounded mixed industrial plastic waste stream by adding reinforcing agents (WF, cement, ash) and a compatibilizer (MAPE). The WF, cement and ash should increase stability in the plastic by reinforcing the matrix. The compatibilizer (MAPE) is used to improve interaction in the plastic mix, notably low-density polyethylene (LDPE), polypropylene (PP) and ethylene vinyl acetate-hot melt (EVA-HM) adhesive, separately and with reinforcing agents. MAPE is expected to promote better blending of the mixed polymers in the WWS.

Materials

The subject of this research was a mixed plastic waste stream from the Smurfit-Stone Container Corporation's old corrugated container (OCC) cardboard recycling facility in Missoula, MT. The OCC plant recovers usable fiber from other materials present in the boxes. The stream from the Wandel vibrating screen (Figure 6.1) was the subject of characterization because it was 90% plastic and comprised 75% of the total plastic exiting as rejects. The Wandel waste is ~37% EVA-HM based box adhesive, ~32% PP from packing tape, ~17% LDPE from thin film, ~9% PS (polystyrene) from packing material, and a ~5% 'other' category [Sardot et al., 2012]. Each polymer category varies less than 10% making it a consistent starting material for new product generation. Hot melt cardboard adhesive is composed of ~35% EVA, ~ 30% wax, and ~ 35% tackifiers. Percentages vary slightly based on company formulation. The 'other' category includes wood shards, low tear-strength fiber, foam, staples or any material that has a small contribution to the waste stream. The waste stream comes out of the OCC facility with a 37-40% moisture content. A drying step is necessary before reuse can occur.

Figure 6.1 Dried Wandel waste stream (WWS)

Composite additives included intermediate ash from the Smurfit-Stone mill's multi-fuel boiler, commercial 80-mesh maple wood flour (American Wood Fibers, Columbia, MD), Portland cement (Moscow Building Supply, Moscow, ID) and MAPE (Polybond 3029, Crompton, Middleburry, CT).

Methods

The WWS was dried on bench-top screens and then compounded in a Lestritz 18-mm co-rotating twin-screw extruder model at 100 rpm. All barrel zones were set at 180°C. The material was extruded as a rod and then ground to pass through a screen with 4-mm diameter apertures.

The compounded WWS was blended with WF (30%), ash (10%), cement (10%), and MAPE (3%) (see Table 6.1) before being re-compounded, re-ground and re-screened.

All specimens for tensile strength tests were mixed and molded in a Dynisco Mixing Molder using an ASTM D 1708 micro-dog bone mold. The mixer and mold temperatures were 180°C and 90°C, respectively. Samples were mixed at 50 rpm for 3 minutes, then extruded and mixed again for 3 minutes. This process was repeated a third time to insure complete mixing. Finally, the material was injected into the micro-dog bone mold and cooled to room temperature.

Thermogravimetric analysis (TGA) was performed using a TGA-7 instrument (Perkin Elmer) with a heating rate of 10°C/min. The samples were heated from room temperature to 650°C under an inert N_2 atmosphere. Data were analyzed using the Pyris v8 software (Perkin Elmer). Three TGA replicates were run for the WWS sample; little difference was observed in the three thermograms. This further signifies the waste stream's consistency.

Differential scanning calorimetry (DSC) was performed using a TA Instrument's model Q200 DSC coupled to a refrigerated cooling unit. The samples were cooled from room temperature down to -20°C, then a second cycle of heating from -20°C to 250°C at a heating/cooling rate of 10°C/min. Data were analyzed using the Universal Analysis 2000 software (TA instruments). Three DSC replicate samples were run for the WWS; little difference was observed in the three thermograms. This observation also signifies waste stream's consistency.

An Instron 5500R-1122 Universal Test Machine was employed for tensile tests using a 5 kN-load cell. A strain rate of 1 mm/min was applied according to ASTM D 1708. Strain was measured using an extensometer (Epsilon model 3442). Eight replicate specimens were measured for each sample type.

A Celestron hand held reflective digital microscope was used to capture 400x images of the WWS-based samples.

Results and Discussion

Thermal Gravimetric Analysis. In general, additives to WWS increased its thermal stability. Figure 6.2 shows thermograms of the WF samples. The addition of 3% MAPE to the WWS in Trace (b), increases overall thermal stability. This trace is offset 10-20^{o}C higher over much of the weight-loss range. When WF is added, a different scenario is seen. Some components of WF are more volatile than the plastics and weight loss begins at lower temperatures (Trace (c)). Eventually, however, the remaining WF components are less volatile than the WWS. Thus, Trace (c) crosses over Trace (a) and remains higher thereafter. Mineral ash in the WF is probably responsible for weight loss in Trace (c) slowing at about the 8% weight level (the transition of potassium carbonate, K_2CO_3, to K_2O). The addition of MAPE to WWS + WF mix, Trace (d), has a less pronounced thermal stability effect than it had with WWS alone. Trace (d) seems to be dominated by the WF behavior, rather than the MAPE. MAPE cleans up the small noisy events that arise around 300^{o}C and continue to its completion. This demonstrates that MAPE works well to compatibilize the WF within the WWS matrix. Trace (d) shows the same mineral ash behavior at its end.

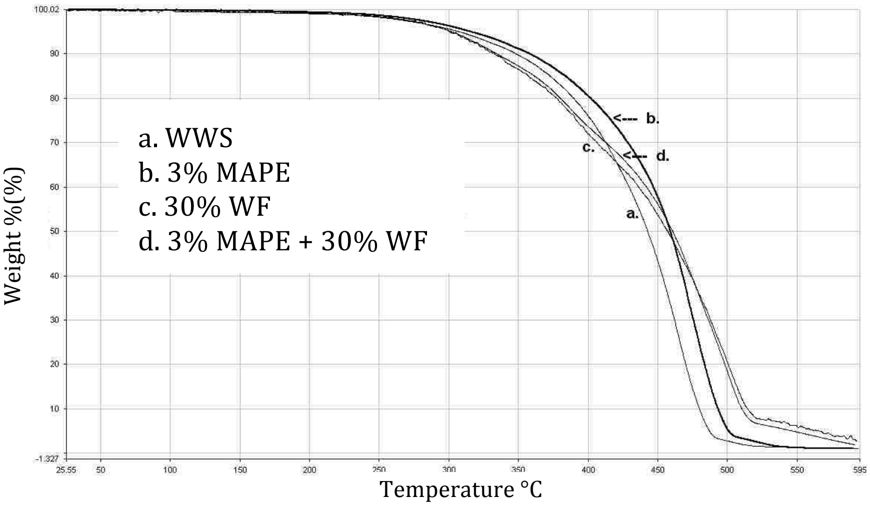


Figure 6.2 TGA thermogram results of (a) WWS alone, (b) with 3% MAPE, (c) with 30% WF, (d) with 3% MAPE + 30% WF

TGA curves for formulations with ash and cement are not included in Figure 6.2. Their important TGA results are more apparent when noting their onset temperatures and viewing their TGA differential forms. The TGA onset degradation temperatures and derivative peak temperatures for all samples are shown in Table 6.1.

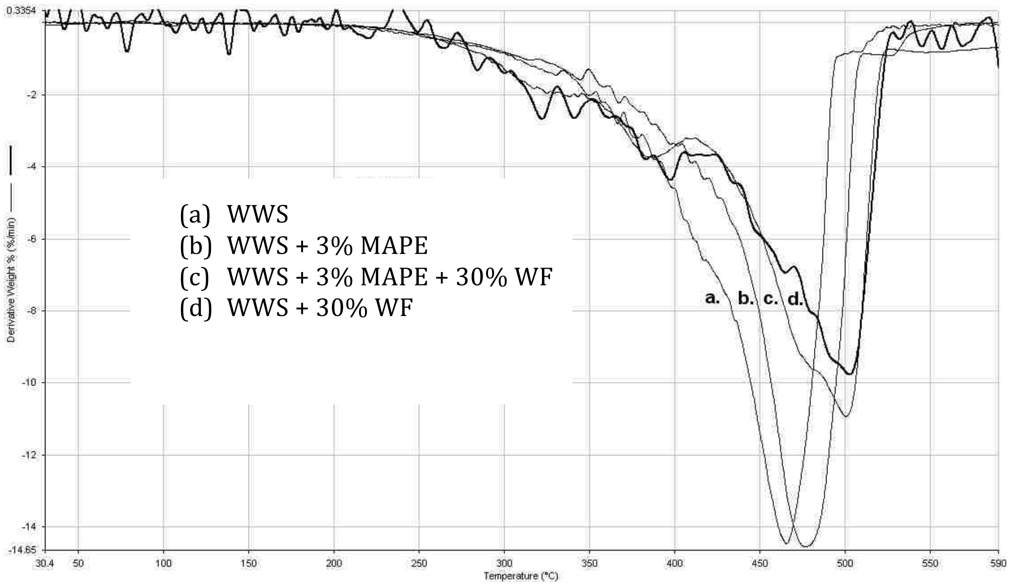
Sample	Onset degradation (°C)	Derivative peak temperature (°C)
WWS	404.7	465.5
WWS + 3% MAPE	412.3	476.6
WWS + 30% WF	393.2	505.1
WWS + 3% MAPE + 30% WF	402.5	499.2
WWS + 10% Ash	431.2	485.2
WWS + 3% MAPE + 10% Ash	414.0	476.4
WWS + 10% Cement	419.0	467.8
WWS + 3% MAPE + 10% Cement	416.9	478.3

Table 6.1 TGA onset degradation temperatures and first derivative peak temperatures for all sample formulations

The addition of all materials except WF increases the temperature at which degradation begins. This demonstrates that the other two amendments offer an increased protection of the mixed WWS plastic. The 30% WF addition lowers the onset temperature due to the decomposition of the WF itself beginning above 200°C. WF contains volatile organic substituents not present in the totally inorganic cement and ash. Supplementing the WF with MAPE compatibilizes the fibers and brings the onset temperature up to a near-baseline WWS value. The ash and cement samples have higher increases in onset temperature. Since both have already gone through a high temperature process, they are already more thermally stable.

Figure 6.3 shows derivative curves for the TGA analysis. Panel I shows the derivative curves of the WF formulations. The overall shapes of the WF derivative curves are saw-toothed and contain a shoulder around 400°C. These are consistent with TGA derivative curves seen for hardwood flour by itself [Gronli, 2002]. Hence, the WF traces are more like wood than plastic. TGA derivative curves for WF are also typically noisy due to the wide temperature range over which the complex structure of lignin decomposes. This is clearly seen in Trace (d) of Panel 3I. The addition of MAPE (Trace (c)) smoothes out much of the WF noise especially during the larger events around 330°C and 390°C.

I.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Derivative Weight % (%/min)
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550
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Temperature (°C)
(a) WWS
(b) WWS + 3% MAPE
(c) WWS + 3% MAPE + 30% WF
(d) WWS + 30% WF
a.
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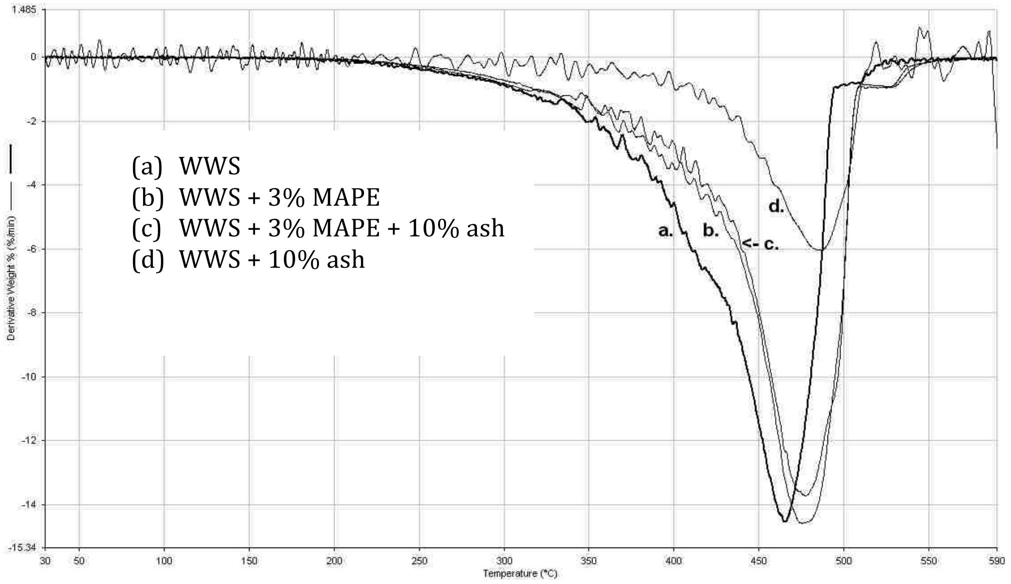
c.
d.

II.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Derivative Weight % (%/min)
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350
400
450
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550
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Temperature (°C)
(a) WWS
(b) WWS + 3% MAPE
(c) WWS + 3% MAPE + 10% ash
(d) WWS + 10% ash
d.
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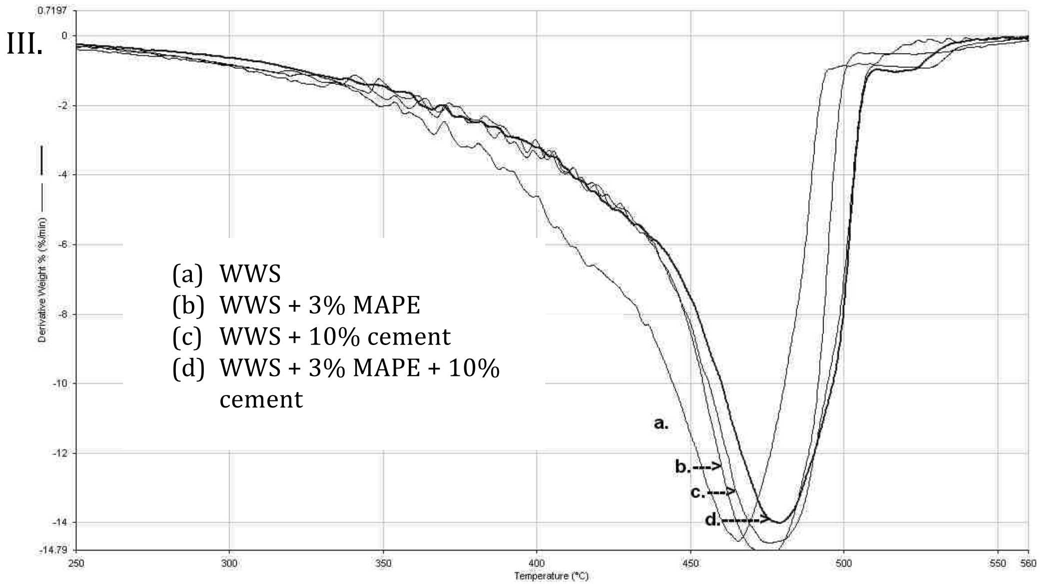
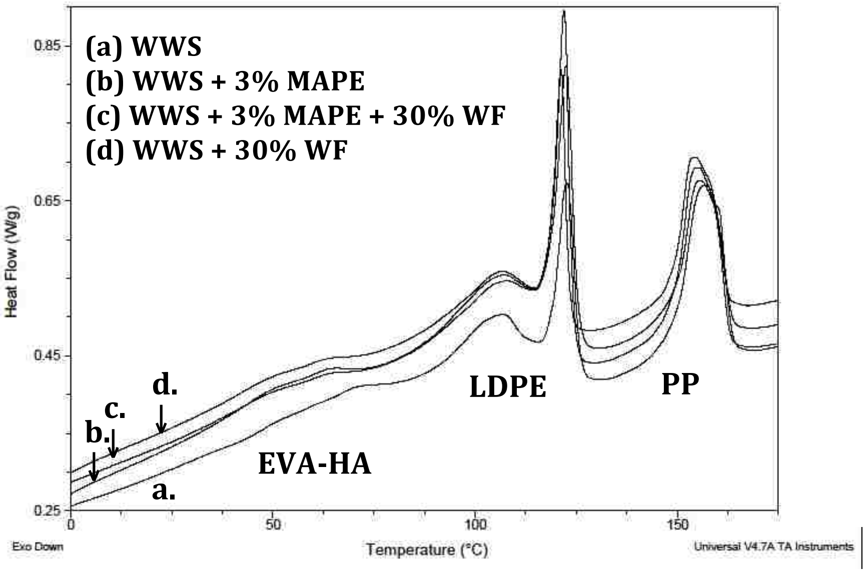


Figure 6.3 Derivative curves for TGA plots I. WF formulations, II. ash formulations, and III. cement formulations

The peak temperature for the derivative curves (Table 6.1), shows the temperature at which the greatest mass loss event occurs for each sample. MAPE slightly increases the resistance of the WWS to thermal degradation. The sample with both MAPE and WF has a higher corresponding peak temperature, suggesting that the MAPE is encasing the WF to some extent and protecting it from breakdown. Overall the ash increases stability. Addition of MAPE to the ash lowers the derivative peak temperature and increases the rate of thermal degradation. Lastly, the cement formulas also improve resistance to thermal degradation but to a slightly lesser extent than the ash. The cement increases the onset temperature but not the peak derivative temperature. The cement seems to interact with the MAPE better, shifting the peak to higher temperatures.

Differential Scanning Calorimetry (DSC). All additives investigated with the WWS decrease crystallinity. DSC scans that include amendments to WWS are displaced upwards in the endothermic direction and represent changes in enthalpy over phase transitions. This behavior has been previously associated with strong intermolecular interactions between wood fiber, clays, and ash with polymers [Liang, 1995;Lei, 2007; Deepthi, 2010]. Mechanisms of this decrease are generally due to the particles of the additive inhibiting close packing of the polymer chains, which reduces mobility during a transition. The double-peak phenomena in the DSC scans is attributed to LDPE, but is likely a mix of LDPE and linear low density polyethylene, LLDPE [Thomas, n/a]. WWS and MAPE samples have been included in each panel in Figure 4 as a reference for comparisons with the different additives, namely, WF, Ash, and Cement.

I.



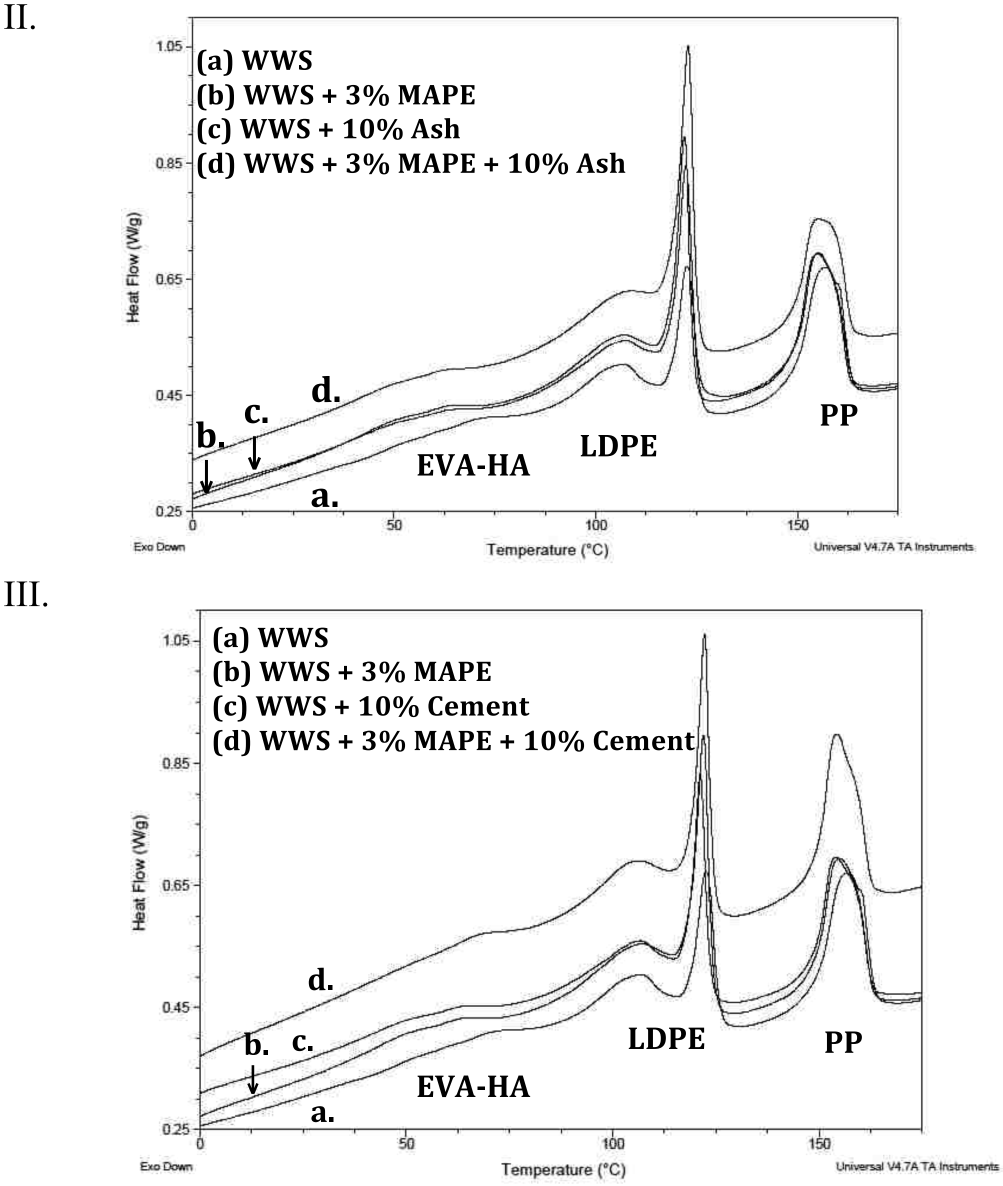


Figure 6.4 DSC thermograms of samples: I.WF formulations, II. ash formulations, and III. cement formulations

Addition of WF decreased crystallinity of the composite by at least a third, indicating strong interactions between the WWS and the amendments. The curves in Figure 6.4(a) and the change in enthalpy for each transition in Table 6.2 show that for WF samples crystallinity decreases following: MAPE > MAPE + WF > WF. Adding 30% WF may increase viscosity at the transition, reducing chain mobility of the polymers and effectively lowering the rate of crystallization [Deepthi, 2010]. The slowed mechanics likely result from poor nucleation of polymer crystals at the WF sites. MAPE increases crystallinity slightly, which is evidence that the interaction of the WF with the WWS is improved by its presence.

Sample	EVA-HA ΔEnthalpy (J/g)	EVA-HA T_m (°C)	LDPE Peak #1 ΔEnthalpy (J/g)	LDPE Peak #1 T_m (°C)	LDPE Peak #2 ΔEnthalpy (J/g)	LDPE Peak #2 T_m (°C)	PP (Tape) ΔEnthalpy (J/g)	PP T_m (°C)
WWS	6.1	62.4	4.4	103.1	11.6	122.7	19.2	157.1
WWS + 3% MAPE	5.8	62.6	0.84	103.3	8.0	122.5	14.2	159.1
WWS + 30% WF	6.3	62.2	1.3	102.3	7.8	122.5	11.3	158.2
WWS + 3% MAPE +30% WF	4.2	50.9	3.1	104.4	9.7	123.0	13.3	158.6
WWS + 10% Ash	4.6	61.1	0.45	102.6	11.4	123.2	12.2	159.7
WWS + 3% MAPE + 10% Ash	3.2	56.7	1.2	105.5	12.7	123.2	14.1	158.1
WWS + 10% Cement	5.0	60.9	0.79	101.8	8.8	121.5	15.5	158.1
WWS + 3% MAPE + 10% Ash	5.2	62.4	2.7	104.0	8.8	121.4	16.2	157.2

Table 6.2 DSC melt transition enthalpies and temperatures for the three main constituent polymers in all WWS fomulations

Ash formulations exhibit a similar trend in the change in enthalpy for melt transitions seen in Figure 4(b) and Table 6.2. The crystallinity trend in the data is MAPE > ash >> MAPE + ash. Here the addition of the MAPE with the Ash decreases crystallinity the greatest and impairs chain mobility. The ash alone allows for more chain mobility than when compatibilizer is present. This suggests that a different compatibilizer might be more suitable for ash.

The highest decrease in crystallinity over all formulas and additives was MAPE + Cement (Figure 6.4(c) and Table 2). The crystallinity trend for cement was: MAPE > Cement >> MAPE + Cement. Similar to the ash samples, it is the MAPE + Cement together that cause the greatest reduction in the change in enthalpy for the transitions. The addition of cement to the WWS allows for better nucleation of the polymer during a melt transition. The cement and ash additives follow what appears to be a ‘quasi nanocomposite’ trend more so than the WF blends. Their smaller particle size allows more intimate contact. This trend has been reported with particles typically in the 1-100 nm range where it is believed that columbic charges, quantum confinement and confined polymer matrices are responsible for improved properties in the resulting composite materials [Yuan, 2006].

Tensile Testing

Additives generally increase the modulus (stiffness) of the WWS but impart only small gains in tensile strengths. The MAPE compatibilizer, true to its role, improves the consistency of behavior when materials are subjected to tensile testing. Table 6.3 holds the measured values for both modulus and tensile strength and their associated precisions. For comparison purposes, modulus and tensile strength data for recycled LDPE, virgin HDPE and virgin PP are also included. Rather than use reported values, they were measured under identical protocols and on the same equipment.

Sample	Modulus (MPa)	Coefficient of variation (%)	Tensile Strength (MPa)	Coefficient of variation (%)
WWS	9.9	18	8.7	14
WWS + 3% MAPE	11.8	10	9.1	8.4
WWS +30% WF	16.4	32	8.6	2.3
WWS + 30% WF + 3% MAPE	16.5	14	8.1	6.5
WWS + 10% Ash	14.8	15	9.4	15.2
WWS + 3% MAPE + 10% Ash	14.0	6.3	10.2	5.9
WWS + 10% Cement	13.8	36.9	7.9	6.4
WWS + 3% MAPE + 10% Cement	13.3	13.9	9.6	8.9
Recycled LDPE	9.0	6.9	11.2	10
Virgin HDPE	43.9	5.2	25.8	1.6
Virgin PP	42.8	3.9	12.5	8.4

Table 6.3 Modulus and tensile strength data for WWS-based samples, recycled LDPE and virgin HDPE and PP samples

WF is the best of the three additives studied for increasing the modulus of the composite material. It demonstrated a 66% increase in modulus compared to 50% for ash and 34% for cement. MAPE was important with regard to improvements in sample consistency. In every case, be it WWS alone or WWS with an additive, the coefficient of variation when MAPE was present was half or less than that in its absence. Without MAPE, ash and cement modulus data varied greatly between one sample and another, an indication that dispersion of additives was an issue. MAPE nicely resolved the issue. The composites' moduli are better than recycled LDPE, a control material in this comparison study. Virgin HDPE and PP both exhibit substantially higher moduli.

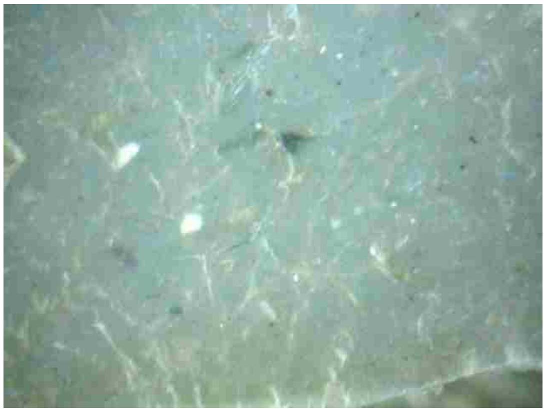
Tensile strengths are little affected by most of the amendments. The MAPE, when added to WWS alone, increased tensile strength by 5%. With WF formulations, MAPE decreased tensile strength very slightly. This behavior has been reported in other plastic composite work

[Cai, n/a], and is due to the differing polarities between the polymer chains and the particles of the amendments. All polymers contained in the WWS are hydrophobic polyolefins while cellulosic materials are highly polar. Adhesion between the wood flour and the plastic may be weak. Furthermore, EVA has been shown to compatibilize WF to PP in a previous study 2008 [Dikobe, 2009]. In the WWS mix the EVA-dominated hot melt may act as a compatibilizer between wood fibers and plastic due to it polar and non-polar parts. The largest gains in tensile strength were noted with the MAPE + Ash (17% stronger) and MAPE + Cement (10%). These tensile values are on par with the tested samples of recycled LDPE and virgin PP.

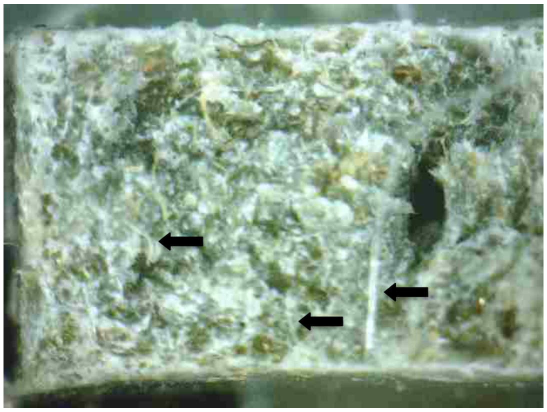
With the exception of the WWS + Ash composite, the coefficients of variation with additives and MAPE were substantially below that of WWS alone (14%). The WWS sample was expected to have fairly inconsistent failure due to its mixed polymer nature and high occurrence of voids within samples. The most dramatic consistency in measured values was noted with WWS + WF for which it was a mere 2.3%. It is possible that the hot melt is compatibilizing the WF in the sample better than MAPE in terms of adding strength. The coefficients of variation for tensile strength of wood composites is similar to that for both recycled LDPE and virgin PP. Only virgin HDPE is truly consistent.

Morphology

Micrographs of the composite surfaces and tensile-strength break faces help to understand some of the testing results and general properties. Figure 6.5 shows pairs of micrographs for WWS itself and with each additive. The tensile strength break faces are more illuminating.



(a)

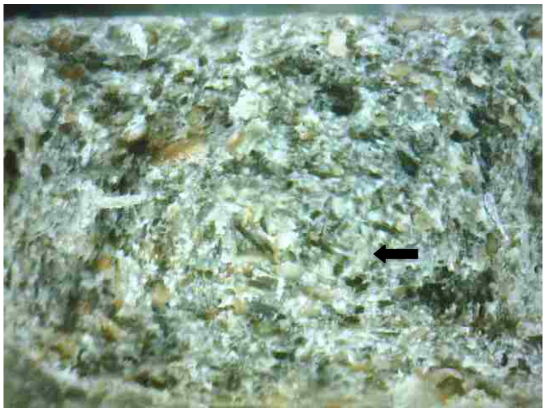


(b)

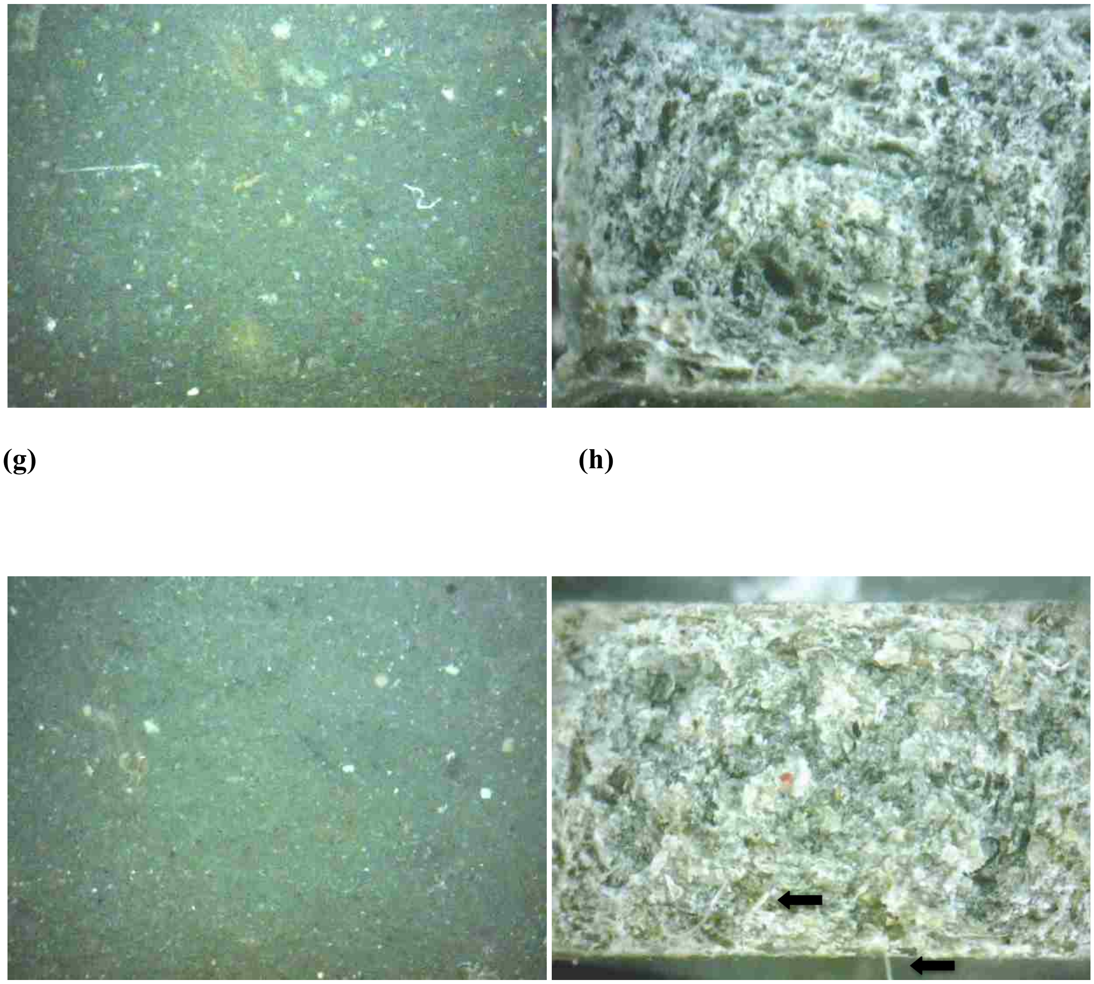
(c)

(d)

(e)



(f)



(g) (h)

(i) (j)

Figure 6.5 Micrographs (400x) of sample surfaces (left column) and tensile breaks (right column): (a) & (b) WWS, (c) & (d) WWS + 3% MAPE, (e) & (f) WWS + 30% WF, (g) & (h) WWS + 10% Ash (i) & (j). Arrows designate LDPE legging. Micrographs have not been included MAPE + additives since they were indistinguishable from the corresponding samples without MAPE

The addition of 3% MAPE to the WWS increases bulk consistency. This is readily apparent in looking at the occurrence of large voids in WWS compared to WWS + MAPE break faces (Figure 6.5(b) compared to 6.5(d)). Larger voids occur in most of the WWS samples. The inconsistent number and distribution of voids in WWS by itself helps explain its high coefficients of variation in tensile testing. Although not immediately apparent given the micrograph-viewing angle, addition of 3% MAPE also decreases overall break face topography. This indicates some compatibilization within the mixed system. Both WWS and WWS + MAPE samples exhibit some legging due to LDPE regions in the mix and are indicated by arrows in images.

The micrographs of WWS and additives lend further evidence for some better phase interactions in the final composite material. The surface views are largely similar in appearance except for that with WF added (Figure 6.5(e)). The distinctly larger WF shards display an orientation trend from upper left to lower right. Break face views for all three additives show far fewer and much finer LDPE legs (see arrows). Their break face topographies are also more consistent. The 30% WF sample in Figure 6.5(e) shows that there is good distribution of wood fibers within the WWS system. The smoothest break faces are seen with WWS + ash and WWS + cement micrographs (Figure 6.5(h) and 6.5(j)).

Conclusions and Future Work

A cardboard recycling facility's waste stream with a high content of mixed plastics was successfully used to prepare a series of potential composite materials. MAPE, WF, cement, and ash all dispersed well within the plastic matrix, yielding a more uniform final material. The resulting product displayed an increase in beneficial thermal and mechanical properties. These materials show promise for utilizing this mixed plastic to make new products from a waste stream that has been traditionally incinerated and land filled. Even better, the cardboard recycling procedure pre-cleans the mixed plastic stream such that minimal preparation is required beyond drying. Adding recycled or virgin PE (20-30%) and or higher WF content should substantially improve the tensile strength of the resultant composite materials.

Several additional procedures could improve upon our findings. Finer milling of the starting WWS would improve interactions both between the mixed plastics themselves and with the additives. Finer milling was difficult to achieve, as the WWS tends to "gum up" blades. Cryogenic milling or heat-resistant blades would be useful. Ash and cement could be acid treated to etch surfaces and promote better dispersion and even adhesion within the polymer matrix. Finally, removal of some hot melt adhesives will also improve strengths. Removal could be accomplished by density separation at the mill site before drying.

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CHAPTER 7

Conclusions and Future Work

The WWS is a good candidate for reuse in the generation of new products – unamended, compatibilized, or as a part of a composite. This waste stream could be used 'as is' in nonstructural applications. Fortuitously, its separation from wood fiber nicely pre-cleans it. It might also be added in various percentages to recycled homopolymer waste streams with or without amendment to produce stronger materials.

Characterization of a cardboard container facility's mixed plastic waste has been accomplished. Speciation of the WWS and comparison with similar ingredient products revealed the polymer source components of the mixture. An asset to this waste stream is that the polymer types in the mixture are unusually consistent, compositional variations being less that 10% for each polymer category. DSC revealed two obvious peaks (LDPE, PP) and a third more dispersed peak (EVA hot melt). This indicated some compatibility within the mix itself. TGA revealed the degradation behavior of the WWS to be between that of the two main components: PP tape and EVA hot melt adhesive. In tensile tests the WWS acts more like the recycled LDPE sample in terms of modulus and ultimate strength. The WWS is more similar to the PP tape sample in terms of toughness as opposed to the much weaker EVA hot melt sample. The WWS was also found to perform well compared to the behavior of individual components. This surprising internal compatibility of the mix may be due to the more polar parts of the hot melt adhesive and adhesive from the tape interacting well with the other hot melt components and forming the main bulk of the material. As good as the mixed WWS was by itself, its strengths and weaknesses made it a good candidate for improvement through compatibilization and amendment with other materials.

Analysis of the DSC thermogram coupled with SEM images of the WWS surfaces gave further information regarding the miscibility of the mixed polymer system. The EVA hot melt was identified as the main matrix material due to its low melt temperature and wide low peak in the DSC thermogram. Some lower branched fractions of the PP and LLDPE polymers with the acrylic-based adhesive from tape are likely dissolving together and forming the main phase. This conclusion is based on: 1) previous studies of partial miscibilitity between hot melt type components with PP or LLDPE or PP with LLDPE [Krupa et al, 2001; Hlangothi et al., 2002; Dong et al., 1998; Shanks et al., 2000]; and 2) the lack of many PP and LDPE phases.

Composite materials were produced using the WWS with MAPE, WF, cement and the Smurfit-Stone mill's multi-fuel boiler intermediate ash. All materials dispersed well within the WWS's mixed plastic matrix. These amendments all displayed beneficial thermal and mechanical properties. The addition of MAPE only increased tensile strength slightly (5%) but had more of an impact on improving its modulus and dramatically reducing variability in break strengths. It is possible that MAPE is not achieving covalent bonding with either the polymer or WF substrates. The choice of a different MA compatibilizer based on an LDPE of LLDPE co-polymer may improve interaction. The addition of WF also increased the modulus/ consistency of breaking but not the overall tensile strength. It is possible that higher wood loading is necessary to achieve better alignment of the wood fibers in the plastic matrix. The ash + MAPE sample attained the highest tensile strength with a value similar to a recycled LDPE sample. Cement dispersed well as an additive but interacted less strongly with the polymer matrix than all other additives. The addition of MAPE made for a slight improvement.

Good dispersion of the amendments within the WWS is not a problem. DSC data indicated an overall decrease in crystallinity and micrographs showed good dispersion. It is likely that adhesion of amendments to the polymer could be improved. It is important to remember that strengths did not decrease with the addition of the amendments – an indication of some adhesion. This may be promoted by the hot melt adhesive in the WWS.

Future work with the WWS would further enhance its properties. Finer grinding of the WWS after initial compounding is an important step in improving this waste stream. Machinery to accomplish this goal was not available for this research. The difficulty stems from the hot melt adhesive in the mix which tends to 'gum up' blades. Cryogenically cooled or carbide-coated blades would prove useful in finer grinding. A second way to improve properties of the WWS would be to remove some of the EVA hot melt adhesive. This could be accomplished via floatation as part of the process equipment at the OCC facility. Not all EVA needs to be removed because some evidence exists that suggests it promotes adhesion between polymers and between polymers and amendments. Lowering the percentage of EVA will provide space for the more crystalline polymers to form spherulites.

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