Expanding the Use of Compostable Plastics: A Novel Approach to Corrosion Inhibiting Films

Kristy A. Gillette
Michael J. Morin
Boris A. Miksic

Cortec Corporation
St. Paul, MN 55110

Abstract

Worldwide there is an overwhelming concern with the vast amount of waste production and overflowing landfills. To combat this, several waste diversion programs have been installed including recycling and incineration; however, these programs suffer from their own limitations and can be deleterious to the environment as well. Biodegradable products have received an overwhelming consideration as a solution to aid in the battle for a greener tomorrow. Companies today are striving to provide an environmental footprint that not only reduces their waste but also their reliance on petrochemicals as well as an overall reduction in their carbon footprint. Options for packaging, service ware, durables and organic waste collection are at the forefront of this campaign.

Related to this, another worldwide concern is the longevity and efficiency of equipment and infrastructure. One of the causes that shortens the life cycle of these materials is corrosion. It is estimated that the cost of corrosion in the United States is roughly $276 billion per year. In effort to provide a corrosion inhibiting solution while being environmentally conscious, a biobased compostable corrosion inhibiting film, Eco-Corr®, has been developed.

In the paper herein, the corrosion inhibiting performance as well as the physical properties of Eco-Corr, a compostable corrosion inhibiting film, will be discussed. The utility of this film will be demonstrated through real life case studies.

Introduction

According to the most recent study published by The National Institute of Science and Technology[1] the annual costs of corrosion were estimated to be about $300 billion, which relates to 3.1% of the Gross Domestic Product (GDP). Of this total, the cost associated with corrosion within the manufacturing and production sector is estimated to have cost companies $17.6 billion annually. To combat this issue $121 billion per year is spent on methods to prevent and control corrosion. Some of the techniques implemented include: material selection, cathodic protection, protective coatings, and corrosion inhibitors.

Before focusing on preventative techniques, the basic chemistry of corrosion must first be understood. In order for corrosion to occur, an electrochemical cell must be established. There are four requirements for this to occur: (1) an anode, (2) a cathode, (3) an electrolyte, and (4) an electronic pathway (Figure 1). All metals, similar and dissimilar, naturally align themselves into an anode and cathode. In order for the corrosion cycle to occur, the anode and cathode must be electrically connected and there must be a conductive environment (electrolyte) for ions to flow. In most cases, the electrolyte is water, but it could also be in the form of soil, concrete, saline, other liquids, or gases. When these four elements are established the anode will begin to corrode through transfer of electrons (e^-) to the cathode. Oxidation, or corrosion, always occurs at the anode and the cathode remains intact. It is important to note that controlled corrosion is a good thing, as this is the technology used in the construction of batteries.

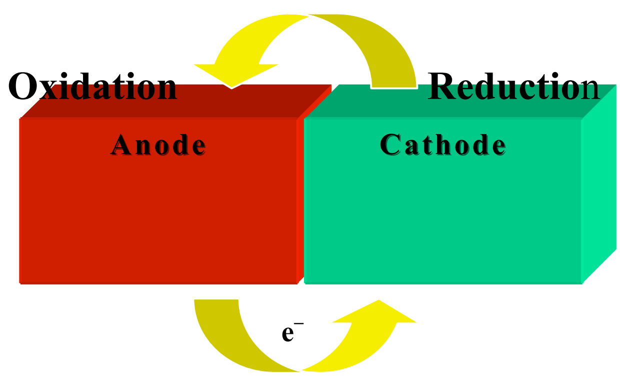

Figure 1. Representation of the corrosion cell

One class of corrosion inhibitors commonly used to prevent or slow corrosion are vapor phase corrosion inhibitors (VpCI®* or VCI); which account for an estimated $0.4 billion of the total annual cost associated with preventing corrosion.[1] Vapor phase corrosion inhibitors are a class of chemicals with unique properties such that in the gas phase they have an affinity for and

* VpCI® is a registered trademark of Cortec Corporation

adsorb onto metal surfaces providing a protective layer that prevents oxidation. These chemicals must exhibit a fine balance of chemical properties in order to be effective corrosion inhibitors. Their ability to sublimate or evaporate into the gas phase is a property of their sublimation or evaporation rate. If the phase change, from solid or liquid to gas, occurs too quickly the VpCI source may be depleted and provide a short protective life. In contrast, if this rate is too slow the material may not sublimate/evaporate fast enough to provide ample protection before the corrosion cycle begins. Another key property is the vapor pressure of the chemical which directly relates to the quantity that is required to saturate the space. If this is high, it takes a large quantity of that chemical to saturate the air. Conversely, a low vapor pressure means that a small amount of a chemical is needed to saturate the air; however, if this value is too low the molecules will not exhibit a gas phase. VpCI molecules are also polar and have an affinity for metallic surfaces. This property allows them to physically adsorb (physisorb) onto other polar surfaces such as metal. VpCIs work to inhibit and decrease the corrosion rate by forming a protective barrier layer of molecules on the metal surface.

VpCIs can be used in many different forms and incorporated into a variety of substrates and products. The substrate of focus herein is protective packaging and plastic films. Most manufacturers use some form of packaging to protect, ship or store their parts. In effort to combine corrosion prevention with packaging materials corrosion inhibiting films and papers have been developed. Corrosion inhibiting films can be produced using one of two methods by either coating a substrate or directly incorporating the corrosion inhibitors in the extrusion process. The latter of the two is the process commonly employed in manufacturing corrosion inhibiting films such as Eco-Corr®[†].

Another worldwide concern revolves around the vast amount of waste production and depletion of nonrenewable resources. A major contributor to this issue is related to the over usage and abundance of petroleum-based plastic materials common to everyday life. One particular concern is that of plastic bags. It is estimated that one trillion plastics bags are consumed annually.[2] Of this number, only one percent are recycled[3] leaving the majority to be discarded in landfills and improperly disposed causing damage to the environment. It is estimated that 80% of the litter collected from our roadways and waterways is from plastic materials.[4] In the northwest Pacific Ocean, marine pollution from plastics has become such an enormous problem that the area has been coined "The Great Pacific Garbage Patch."[5] In addition to environmental impacts, plastic bags cost US consumers an estimated 4 billion dollars which is reflected in increased goods cost and often overlooked and unnoticed.[3]

To address the growing problems associated with plastics, and waste in general, several diversion programs have been initiated. These include recycling, reuse, incineration, composting, and increased awareness and education. However, recycling and incineration suffer from limitations and have also been shown to contribute to environmental pollution. Reusable woven plastic or canvas bags have emerged as a short term solution for plastic bags; however the cost of these are substantially greater than traditional plastic bags and they are somewhat inconvenient. The end of life of these bags is also no different as they will eventually end up in a

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[†] Eco-Corr® is a registered trademark of Cortec Corporation.

landfill. Another option which is increasing in popularity is utilizing compostable materials as a replacement for traditional plastic goods. In order for this route to be advantageous consumers must be aware of what biodegradation truly means and which materials can or cannot be composted. A common misconception is that biodegradable materials will break down in landfills. However, scientific research has proven that this is not the case and very little biodegrades in modern landfills.[6] Even organic materials such as fruits and vegetables or newspapers have been found intact after years of exposure in a landfill. Unlike landfills, compost facilities are regulated and the soil is churned and kept moist to facilitate aerobic biodegradation by microorganisms. Even with the influx of composting facilities some materials will always need to be disposed of in a landfill; however, with material selection and education the extent to which we rely on landfills can be reduced.

Today's overwhelming concerns about the environment have caused an emergence in bioplastics as potential alternatives to petroleum based polymers. Bioplastics are a class of plastics that are derived from renewable resources such as cellulose, plant and vegetable oils, starch, and sugars. Bioplastics have received increased attention and experienced rapid growth over the past few years, as the growth rate increased 38% globally from 2003 to 2007.[7] In Europe alone, the growth rate was approximately 48% over the same time period. It is estimated that the global capacity for bioplastics will increase from 0.36 million metric tons (Mt) in 2007 to 2.33 Mt in 2013 and further yet to 3.45 Mt by 2020.[7] The most prevalent bioplastics today include starch-based polymers, polylactic acid (PLA), polyhydroxyalkanoates (PHA), polyamides (PA), and biobased polyethylene. Bioplastics are typically produced through modification of natural polymers or some form of fermentation. These biobased materials aid in the reduction of fossil fuel usage but do not directly address the issues relating to plastic pollution and waste. It should also be noted that while the source for these materials is not derived from fossil fuels, most manufacturing facilities and processes involved in their production are still fueled by fossil fuels. Companies are becoming increasingly more conscious of their carbon footprint and green energies are starting to be implemented to address this.

Another divergent class of materials receiving much interest as a solution to petroleum-based plastics and waste are those that are designed to biodegrade. Biodegradation is defined by the aerobic degradation of materials and complete conversion into carbon dioxide and water. There are many materials which naturally degrade but it's the conversion to CO_2 and H_2O that is key. Biodegradable plastics include both biobased materials as well as petrochemical materials. A common misinterpretation is that all biobased materials are biodegradable which is not accurate. For example, polyethylene derived from sugar is no more biodegradable than polyethylene derived from petroleum. On the other hand, some petroleum based materials, such as EcoFlex.®[‡] a copolyester resin, are fully biodegradable and compostable.

To address both of these global concerns, a certified compostable VpCI film has been developed. The material selection for the development of this film took into consideration the following parameters: material cost, environmental impact, stability, and mechanical properties. Eco-Corr was developed to optimize these features. The film is comprised of a blend of certified

‡ EcoFlex® is a registered trademark of BASF Corporation.

compostable copolyester resins and proprietary corrosion inhibitors. The unique construction of this film allows for optimal mechanical properties to be achieved through alteration of the resin structure. For these purposes, Eco-Corr is available in various formulations ranging from zero biobased content up to 40% to provide a flexible or more rigid film respectively.

One specific customer application that aided in the conception of this product was a military war readiness program. This project required three to five years of preservation for military vehicles. It was essential that the vehicles be readily accessible at any moment with little to no preparation necessary for deployment. The incumbent process entailed protection of the internals with additives followed by shrouding with VpCI-126®[§], a polyethylene based film. The problem with this method was that when the vehicles were unwrapped the film was buried as a means for disposal. During the burial the personnel discovered previously buried films fully intact. Although this is not a commercial composting environment, there was value in replacing the non-biodegradable polytheylene film with a biodegradable film. It has been demonstrated that the film discussed herein will degrade in backyard compost and within active growing soil within a few months, albeit slower than in a commercial composting faciltiy.

Experimental Procedures

To fully evaluate corrosion inhibition three different tests are conducted to assess the contact-, barrier- and vapor-phase corrosion inhibiting abilities. Contact-phase corrosion inhibition evaluates a product's ability to protect metallic components while in direct contact with the metal surface. This is assessed by the Razor Blade test[8] and is carried out as follows: carbon steel panels, constructed of CRS SAE 1008/1010, are cleaned in methanol and dried. Two drops of deionized (DI) water are placed on the metal panel and covered with the substrate of interest. After two hours, the substrate is removed and the panels inspected for any sign of corrosion, pitting or staining. This test can be adapted to other metals such as copper, galvanized steel or aluminum with a slight modification in the test solution used for each metal (0.005% sodium chloride, 3.5% sodium acetate or 3.5% sodium chloride respectively) and the exposure time.

Barrier-phase corrosion inhibition tests a product's ability to inhibit corrosion and act as a barrier when exposed to corrosive gases such as SO_2 and H_2S. This property is tested according to the SO_2 Test[9] which evaluates the substrate's performance as a barrier against an aggressive sulfur dioxide (SO_2) environment. The test is conducted by wrapping carbon steel panels within the substrate and allowing them to condition in a gallon jar for 20 hours at ambient temperature. After pre-conditioning the panels, an SO_2 gas environment is created within the jar and the wrapped panels are exposed to this environment at elevated temperatures (50°C) for 16 hours followed by room temperature for 8 hours in a cycling oven. The jars are then removed from the oven, panels unwrapped and visually inspected for any sign of corrosion. The panels are graded on a scale from 0 to 4, where grade 0 is heavily corroded (covering >25% of the panel) and grade 4 means no visible corrosion on the panel surface.

[§] VpCI-126® is a registered trademark of Cortec Corporation.

Perhaps the most important criteria for a good VpCI film is the vapor-phase corrosion inhibiting ability (VIA).[10] This tests a product's ability to protect metals from corrosion without coming into direct contact, relying only on the sublimation of VCI vapors and subsequent adsorption as a means for protection. The VIA test is performed as follows: carbon steel plugs are sanded in one direction with 120 grit silicon-carbide sandpaper and rinsed in methanol. The plugs are then polished at a 90° angle to the initial grind with 320 grit paper, rinsed in methanol and dried. The test apparatus consists of a quart jar with a modified lid (Figure 2). The cleaned plugs are then inserted into the rubber stoppers (Figure 2-B, F). Strips of the test substrate (1" x 6") are hung from the inside of the lid, being sure not to come in contact with the plug. The lids are screwed on tight and the jars are left to condition for 20 hours at ambient temperature. After conditioning, a glycerol/water solution is added to the jars to accelerate corrosion and left to sit at ambient temperature for two hours. The jars are then placed in a 40°C oven for an additional two hours and after which, they are removed from the oven and the surface of the plugs inspected for corrosion. The plugs are rated on a scale of 0-3 where grade 0 is heavily corroded (showing no corrosion inhibition), while grade 3 means no visible corrosion and good inhibiting effects.

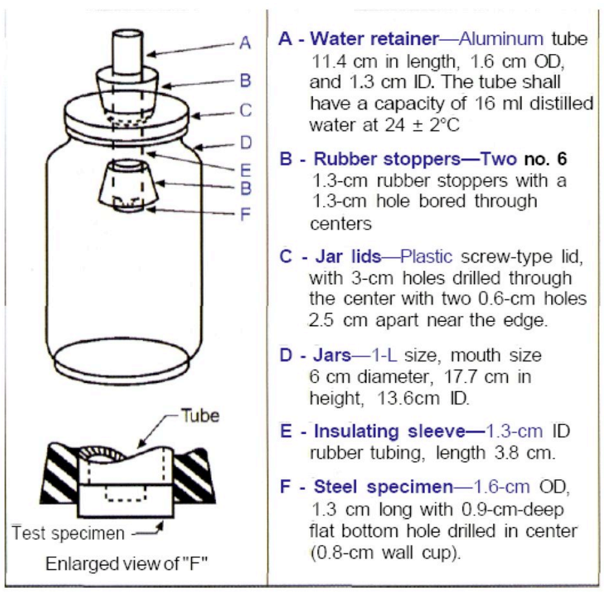

Figure 2. VIA test apparatus

In addition to the corrosion inhibiting properties, Eco-Corr® was evaluated in accordance to ASTM D6400[11] by the Biodegradable Products Institute (BPI). ASTM D6400 is the American standard specification for compostable plastics. In order to be considered compostable a material must meet the following three criteria: (1) satisfactory rate of biodegradation and subsequent conversion to carbon dioxide; (2) satisfactory disintegration such that no more than 10% of its original weight remains after sieving on a 2.0 mm sieve; and (3) biodegradation does not result in the production of toxic materials and does not adversely impact the ability of the resultant compost to support plant growth. As part of the BPI evaluation metals analysis and FTIR spectroscopy were conducted and reviewed. In addition, the construction and components of the film were evaluated by peer review and determined to be compliant with ASTM D6400[11].

In addition to the BPI review and evaluation, a simple laboratory biodegradation study was conducted replicating home composting conditions. Compost was generated using a home compost device. Samples of film were buried within the mature compost and kept in a 50°C oven. The samples were checked on a regular basis and the progress noted and recorded with photography. This test was not meant to replicate any standardized testing such as ASTM D5338[12] but for demonstration purposes only.

The mechanical properties of Eco-Corr film were also analyzed and compared to traditional VCI films. The properties that were measured include: breaking factor, tensile strength at break, elongation at break, yield strength, dart drop impact resistance and tear resistance. The breaking factor determines the load required in order to rupture a material. Tensile strength at break measures the stress at which a material permanently deforms or breaks. Elongation at break computes the strain on a sample when it breaks and depicts how much a material will stretch when put under stress. The yield strength is similar to tensile strength but measures the exact stress at which a material strain changes from elastic deformation to plastic deformation. Stress exceeding the yield strength is not recoverable. These were all evaluated according to ASTM D882-02[13] using an Oakland Series 500 Force Test Stand. Tear resistance measures the force required to propagate a pre-cut slit across a sheet specimen and was assessed according to ASTM D1922-06a[14] using a Thwing-Albert pendulum. Finally, impact resistance measures the toughness or shatter resistance of a film and was evaluated with an Oakland Series 8000 Dart Drop Impact Tester according to ASTM D1709-04, Method A[15].

Results and Discussion

The corrosion inhibiting properties of Eco-Corr film is outlined in the tables below. The results are reported in comparison to VpCI-126 film, an industry standard corrosion inhibiting film, based upon linear low density polyethylene (LLDPE). Table 1 describes the contact-phase corrosion protection as determined by the Razor Blade test for ferrous metals (carbon steel) while the protection afforded to non-ferrous (copper) metals is demonstrated in Table 2.

Table 1. Carbon steel Razor Blade test results

Sample	Panel 1	Panel 2	Panel 3	Control
Eco-Corr®	Pass	Pass	Pass	Fail
VpCI-126®	Pass	Pass	Pass	Fail

Table 2. Copper Razor Blade test results

Sample	Panel 1	Panel 2	Panel 3	Control
Eco-Corr®	Pass	Pass	Pass	Fail
VpCI-126®	Pass	Pass	Pass	Fail

Table 3 depicts the barrier-phase corrosion inhibiting ability evaluated according to the SO_2 test described above.

Table 3. SO_2 test results

Sample	**Panel 1**	**Panel 2**	**Panel 3**	**Control**
Eco-Corr®	Grade 4	Grade 4	Grade 4	Grade 0
VpCI-126®	Grade 4	Grade 4	Grade 4	Grade 0

The vapor-phase corrosion inhibition performance of Eco-Corr® in comparison to VpCI-126 is reported below in table 4.

Table 4. VIA test results

Sample	Plug 1	Plug 2	Plug 3	Control
Eco-Corr®	Grade 3	Grade 3	Grade 3	Grade 0
VpCI-126®	Grade 3	Grade 3	Grade 3	Grade 0

These test results verify that Eco-Corr film performs as well as its traditional polyethylene counterpart. It is clear that Eco-Corr exhibits excellent corrosion inhibiting abilities in all three phases: contact-, barrier-, and vapor-phase.

As part of the BPI review process metals analysis was conducted on Eco-Corr by a third party testing facility, Legend Technical Services, Inc.[16] The results from the metals analysis are outlined in Table 5. An infrared spectrum was also collected for analysis and is shown in figure 3 below.

Table 5. Eco-Corr® metals analysis as conducted by Legend Technical Services, Inc.

Analyte	**Test Method**	**Units**	**Results**	**BPI Limits**
Arsenic	EPA 6010B	mg/kg	<0.50	21.5
Cadmium	EPA 6010B	mg/kg	<0.25	19.5
Calcium	EPA 6010B	mg/kg	2100	NA
Chromium	EPA 6010B	mg/kg	<0.50	NA
Cobalt	EPA 6010B	mg/kg	<0.25	NA
Copper	EPA 6010B	mg/kg	<1.0	750
Iron	EPA 6010B	mg/kg	20	NA
Lead	EPA6010B	mg/kg	<1.0	150
Mercury	EPA 7471A	mg/kg	<0.10	8.5
Molybdenum	EPA 6010B	mg/kg	<2.5	NA
Nickel	EPA 6010B	mg/kg	<0.50	210
Selenium	EPA 6010B	mg/kg	<1.0	50
Zinc	EPA 6010B	mg/kg	2.4	1400

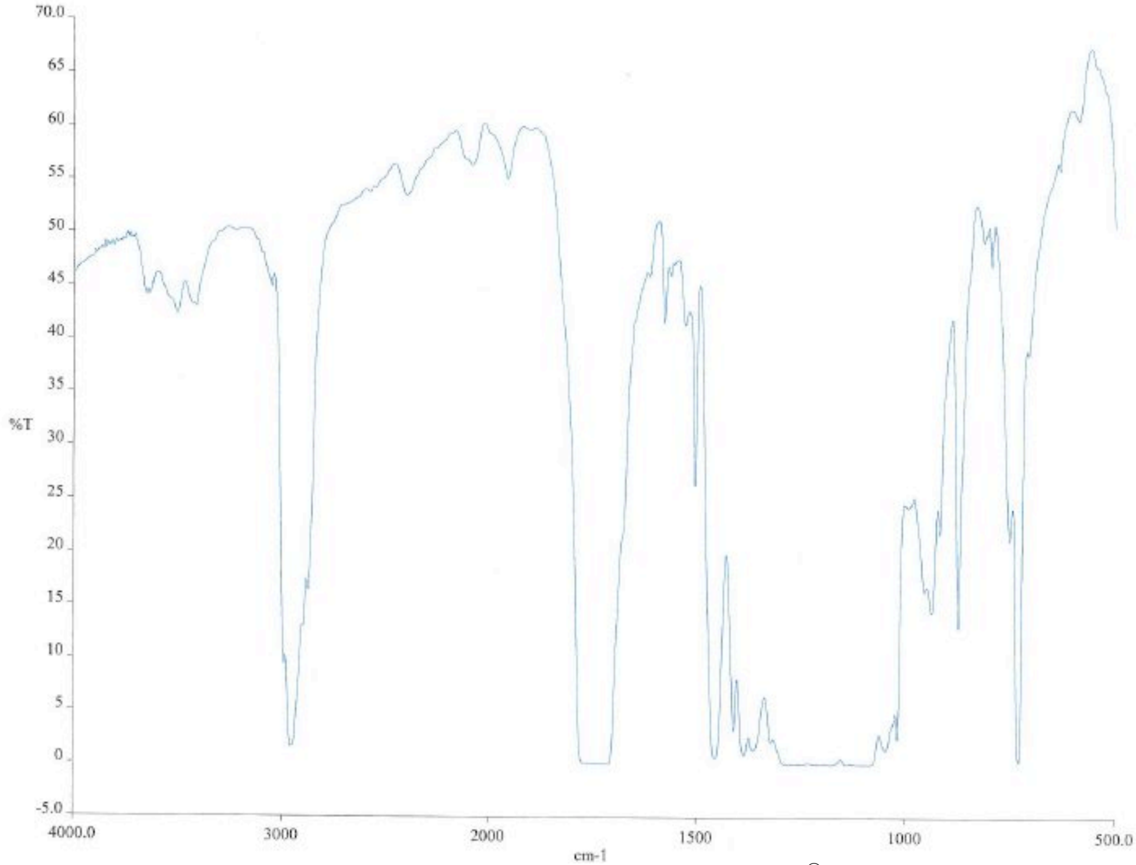

Figure 3. FTIR spectrum of Eco-Corr®

The images shown in Figure 4 illustrate the rate of biodegradation in a home composting environment. Within one month signs of degradation are evident. After 3 months of exposure in compost significant degradation has occurred and within 4 months only small particles of film remain.

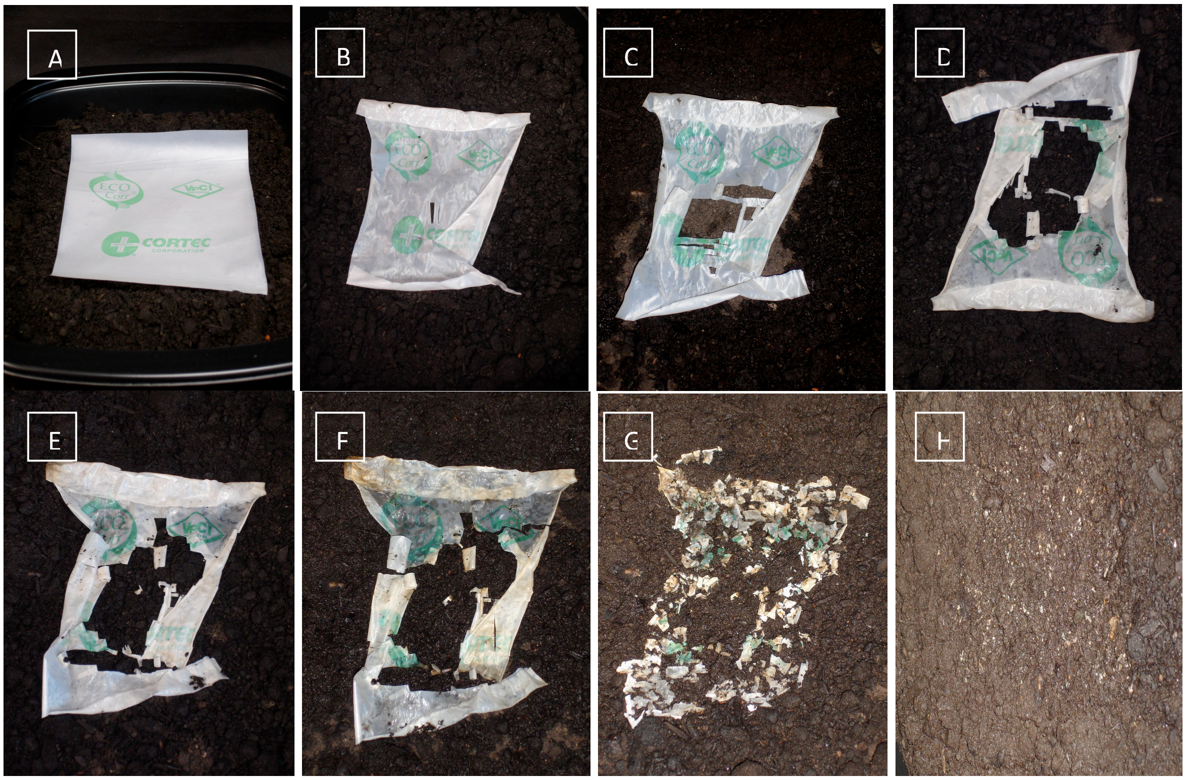

Figure 4. Illustration of Eco-Corr biodegradation as time elapsed; A, time = 0; B, time = 15 days; C, time = 30 days; D, time = 43 days; E, time = 62 days; F, time = 76 days; G, time = 93 days; H, time = 112 days.

The mechanical properties of EcoCorr® were evaluated and compared to a LLDPE based VpCI film to demonstrate the differences from material selection (Table 6).

Table 6. Mechanical properties of Eco-Corr® versus traditional PE VpCI film (VpCI-126®).

Property		Test Method	Units	Eco-Corr 40*	Eco-Corr 0*	VpCI-126
Caliper		ASTM D6988	mil	2.00	2.00	2.00
Breaking Factor	MD	ASTM D882-02	lbs/in	11.77	10.40	18.88
	CD			9.32	10.81	18.25
Tensile Strength at Break	MD	ASTM D882-02	psi	5774.65	4728.20	3184.35
	CD			4451.90	4699.10	3109.60
Elongation at Break	MD	ASTM D882-02	%	300.21	759.38	770.37
	CD			340.68	795.89	833.65
Yield Strength	MD	ASTM D882-02	psi	2321.62	991.44	793.85
	CD			2285.99	1093.1	1425.18
Tear Resistance	MD	ASTM D1922-06a	mN	156.96	3719.95	15852.96
	CD			470.88	4959.94	20279.24
Dart Drop Impact Resistance		ASTM D1709-04, A	grams	573.30	>1300	753.28

*Number signifies the biobased content in product.

These results demonstrate the "tune-ability" of Eco-Corr films in order to achieve the desired mechanical properties and performance level. From the results above it is clear that increasing the amount of biobased material results in an increased tensile strength but causes a reduction in impact and tear resistance. Eco-Corr can be optimized to provide the appropriate balance of mechanical properties. These results also prove that incorporating biobased and biodegradable materials does not significantly alter the product's integrity or performance. In fact, the tensile strength for Eco-Corr 40 is significantly greater than traditional PE based VpCI film. Eco-Corr with zero biobased content demonstrates excellent impact resistance and elongation that is comparable to PE. Traditional VpCI-126 film does, however, out-compete the two biodegradable films in tear resistance.

In addition to the laboratory evaluation, field studies have been conducted through customer trials. One specific example is a leading automotive manufacturer who utilized Eco-Corr for in-bound and out-bound packaging and protection of cam shafts. This case study was conducted over a period of eight months, after which the shafts that were protected with Eco-Corr were inspected and showed no signs of corrosion. Furthermore, the customer introduced the film into their on-site organic waste diversion program as a means for disposal.

Conclusion

A certified biodegradable compostable corrosion inhibiting film has been developed. Eco-Corr film demonstrates the ability for biobased and biodegradable materials to perform competively with traditional polymers. Eco-Corr exhibits excellent corrosion inhibiting properties in contact-phase, barrier-phase and in the vapor-phase. In addition to being an alternative to traditional corrosion inhibiting films, Eco-Corr can also serve as a direct replacement for other corrosion preventative methods such as oils, rust preventatives and desiccants. Case studies have been conducted and prove that Eco-Corr performs as good, if not better, than polyethylene films with an added benefit to decrease waste entering landfills.

References

1. CC Technologies. *Cost of Corrosion*. [cited 8 January 2010]. Available from http://www.corrosioncost.com.

2. United Nations Environmental Programme. *Report Brings to the Surface the Growing Global Problem of Marine Litter.* [cited 13 January 2010]. Available from http://www.unep.org.

3. Plastic Bag: Friend or Foe. *Consumption Externalities.* [cited 18 January 2010]. Available from www.plasticbageconomics.com.

4. Plastic Bag: Friend or Foe. *Environmental Damage.* [cited 18 January 2010]. Available from www.plasticbageconomics.com.

5. Sea Studios Foundation. *Think Beyond Plastic.* [cited 20 January 2010]. Available from http://www.greatgarbagepatch.org/index.html.

6. Environmental and Plastics Industry Council. Biodegradation Won't Solve the Landfill Crunch. [cited 14 January 2010]. Available from www.plastics.ca/epic.

7. Shen, L.; Haufe, J.; Patel, M. K. *Product Overview and Market Projection of Emerging Bio-based Plastics: PRO-BIP 2009.* **June 2009.**

8. Razor Blade Test, *Cortec Corporation Work Instruction, Test Method: CC-004*, **May 2008**, *Version 5.*

9. SO_2 Test, *Cortec Corporation Work Instruction*, *Test Method: CC-003*, **May 2008**, *Version 6*, 1-9

10. VIA Test, *Cortec Coporation Work Instruction*, **August 2008**, *Version 11*, 1-9.

11. ASTM Standard D6400, 2004, "Standard Specification for Compostable Plastics," ASTM International, West Conshohocken, PA, 2004, DOI: 10.1520/D6400-04, www.astm.org.

12. ASTM Standard D5338, 2003, "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materialas Under Controlled Composting Conditions," ASTM International, West Conshohocken, PA, 2003, DOI: 10.1520/D5338-98R03, www.astm.org.

13. ASTM Standard D882, 2002, "Standard Test Method for Tensile Properties of Thin Plastics Sheeting," ASTM International, West Conshohocken, PA, 2002, DOI: 10.1520/D882-02, www.astm.org.

14. ASTM Standard D1922, 2006A, "Standard Test Method for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method," ASTM International, West Conshohocken, PA, 2006, DOI: 10.1520/D1922-06A, www.astm.org.

15. ASTM Standard D1709, 2004, “Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method,” ASTM International, West Conshohocken, PA, 2004, DOI: 10.1520/D1709-04, www.astm.org.

16. Legend Technical Services, Inc. St. Paul, MN 55103