## ANTI-BIOFOULING POLYMETRIC WINDOWS:

## ADDITIVE EFFECTS ON MECHANICAL AND OPTICAL PROPERTIES

## THESIS

Presented to the Graduate Council of Texas State University-San Marcos in Partial Fulfillment of the Requirements

for the Degree

Master of SCIENCE

by

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## ABSTRACT

## ANTI-BIOFOULING POLYMETRIC WINDOWS:

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by

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Texas State University-San Marcos

May 2010

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The objective of this study is to investigate the effects anti-biofouling additives have on the optical and mechanical properties in several transparent polymer systems. The resulting effects on mechanical and optical properties of incorporating these additives will be analyzed in a series of studies. The materials chosen for this study were polymethylmethacrylate (PMMA), bisphenol A polycarbonate (bis A-PC), and CBDO, a co-polyterephthalate derived from 2,2,4,4,-tetramethyl-1-3-cyclobutanediol and 1,3 propanediol. The anti-biofouling agents selected were all EPA, approved biocides. Irgarol ®1051 and Diuron were incorporated by melt compounding at the biocide manufacturers' recommended dosage. Subsequently, the compounded pellets were subjected to compression molding in order to produce the test plaques. Studies were conducted using TGA, DSC, and UV spectroscopy to evaluate mechanical and optical properties. The data show that PMMA/Irgarol ®1051 material displayed an increase in mechanical properties with increasing amounts of anti-fouling agent. Optical tests indicated that PMMA/Irgarol ®1051 had the highest retained percent optical transmission of all of the combinations of polymers and biocides tested.

## **Chapter I**

## Introduction

The current trend in the world market is globalization; this includes technology people, finance, consumer goods, and business which can all be impacted by the constraint of resources. The challenge then becomes what resources are available to sustain this type of growth. The world's Oceans and coasts are invaluable cultural, environmental, and economic resources. From the data and reports of Ocean Policy Report, which was given to the U.S commission, the U.S coastal zone played an important role in the U.S economy. It was found that this zone had contributed about four point five trillion dollars to the American economy in the year 2005. (Stratigic Plan n.d.) It is easy to see that the oceans have a significant amount of potential resources that would benefit and sustain the rapid growth of the world economy. It is easy to see the importance of exploring our underwater resources, but this begs the question, "Whyhaven't we made more progress?" In spite of several achievements and accomplishments, biofouling (marine growth) of sensors is still responsible for restricting and limiting the quality of data and the efficient deployment periods of visual and optical instrumentation on independent platforms, which are used for

sampling. (Manov et al.,2004) Historically, funding offshore exploration for sustained periods has required enormous capital and funding these expeditions require research topics of great interest or importance. It is well known that, at present, scientists know more about the moon and outer space than the ocean. This seems impossible especially when we have more access to the ocean than we have access to outer space. Few researchers have unlimited resources and budgets, so, every research dollar needs to count. For those researchers that obtain the necessary funding for exploration need every action, movement, or research effort has to contribute and add value to the overall research goal. In an attempt to maximize efforts and conserve costs a solution to help make underwater research as productive and efficient as possible, is desperately needed. One possible solution that is generating considerable interest is increasing the long term sustainability and viability of autonomous scientific equipment and measuring devices.

Long-term undersea research is expanding into an increasing role but this research is limited without the protection of scientific equipment, as such, the incentive for finding solutions that prevent marine biofouling is more than apparent. (Delauney 2009) It is well known that the marine environment presents some of the harshest conditions and can be quite hostile to equipment and exposed materials.

Biofouling can be described as the accumulation of an organic and biological stratum or layer of organisms, such as algae, microorganisms, and barnacles, on underwater equipment, pipes, and surfaces, corroding and impairing structures and

systems. Typically, when biofouling is recognized, the capabilities of equipment or structures are impaired and the biofouling is in its last stage of development. As soon as the material is introduced to the marine environment, organic matter starts to settle on the surface of the material, and after about an hour, a layer of glycoprotein (biofilm) is formed. This layer of glycoprotein provides a supply of nutrients for microorganisms. Some studies suggest that in absence of algae growth, there is no macro fouling. (Kerr 2001) The submerged material often provides protection from oceanic conditions, such as current, the ebb and flow of the tide, allowing the marine fauna to colonize. Most macro organisms seek to permanently attach themselves to a surface, with a self-produced adhesive called extracellular polymer substance. The proclivity of the biofouling is also dependent on environmental conditions. Most often, it is the warm clear water of the tropics that provides the best breeding grounds for biofouling. The warmer water and the sun's ray's ability to penetrate the clearer water allows organisms to grow at deeper depths. This is the primary reason biofouling is not as prevalent at depths greater than 250 feet. (Warl 1989) This biofilm buildup is usually responsible for disrupting and changing the materials' surface energy. Biofouling most often occurs in the warm shallow coastal waters because of the combination of light penetrating the surface, high biological activity, and organic treatment from storm and agricultural runoffs, which makes an ideal environment for algae to bloom.

Reevaluations of methods are needed in order to make developments in the basic and fundamental understanding, observing, developing and organization of the ocean ecosystems. The ocean is vastly intricate, with its enormous range of measures and its

cross functional synergistic nature. In order for scientific data to be accurate and representative of the process being studied they need to be collected continuously and sustained periods of time. To achieve this goal equipment needs to maintain the preset operation parameters and calibration for the duration of deployment. Because of the need for real time measurements and the vastness of the ocean, unmanned autonomous equipment with continuous data transmission is needed. Scientists have taken a lesson learned from NASA by installing solar panels on their equipment, in how they go about sustaining long term studies. For such operations, research platforms are being developed swiftly, which include ocean observatories, observational structures which would be helpful by employing moorings, undersea vehicles, which would be autonomous (AUV's), floating platforms, and gliders to expedite research climate-scale phenomenon such as El Niño Southern Oscillation (ENSO), natural resources including oil and natural gas exploration and monitoring the oceans ecosystem by tracking phytoplankton blooms. (Chavez 1999) (Foley 1997) (Turk 2001) Once the infrastructures for research have been developed the next challenge is to maintain the infrastructure and protect the infrastructure. The use and development of this type of technology is of great interest to research organizations such as National Oceanic and Atmospheric Administration (NOAA). Most of these instruments require high transmission of UV, visible, and I.R. radiation in order to be fully engaged. (Booth 2008) Bio-optical sensors and data gather devices need clear unobstructed transmission pathways to gather accurate data, if the optical surface has the smallest imperfection this could result in skewed or erroneous data; the interjection of biased measurements through the biofouling process is a primary concern.

As previously stated, exploring and conducting research in the world's oceans and lakes is paramount to understanding what the oceans natural resources have to offer. The underwater exploration continues to advance as Planet Earth's last frontier. Technological advancements such as miniaturization of components and advances in robots are helping to accelerate underwater research. This research could permit growth and advancement of ocean floor sub-stations, which would feature wide ranging scientific sampling tools, instrumentation, and data gather devices. (NOAA n.d.) Imagine the potential of underwater exploration with ocean floor observatories that could be used as subsea-bases for docking ROV's that could then power up and download information from autonomous underwater vehicles and thereby extending underwater vehicles range, increasing equipment capabilities, and allowing real-time data-imagery to be regularly conveyed and sent out to laboratories on land. Working in a marine environment is an austere and hostile environment for most equipment. This underwater environment presents unique challenges for most data gathering devises scientific equipment during short term operations; these challenges are magnified when trying to maintain prolonged underwater operations at depth. (NOAA n.d.) Specific scientific tools and instrumentation equipment are needed to collect data such as images, long term observations, and sampling in areas ranging from the shallow coastal regions to the deepest parts of the ocean. It is essential to the success of underwater explorations to scientifically record the marine environment utilizing optical imaging devices such as video imagery and still images. (Smith 1978) Most of these instruments require high transmission of UV, visible, and I.R. radiation in order to be fully engaged. In order to maintain long-term underwater research a practical approach of protecting data gathering

equipment is desperately needed. If equipment and sensors are left unprotected in this environment, micro and macro organisms will ultimately attach themselves to the coverglass and place equipment out of operation during inopportune moments. (Delauney 2009) The fouling of expensive equipment has caused research to stall and resulted in lost opportunities, which can be costly.



Figure 1. Biological sequence of biofouling (Schleich n.d.)

There have been many research endeavors attempting to solve this systemic problem of biofouling and most have had moderate results. The most successful family of antifouling (AF) agents is the tributyl tin (TBT) based compounds. Several studies have used TBT's mixed in a silicon matrix for AF use on optical devises. (Manov 2004) The consistent deformation of the silicon matrix caused the transmission pathways to change and was well known for introducing errors into measurements. However the success of these AF agents' successes has been countered by their harmful effects to the neighboring ecosystem. Numerous studies have shown the TBT's along with other metal AF agent have a tendency to bioaccumulate and cause long term damage to the ecosystem. (Aria 2009) These unwarranted effects are part of the reason TBT's use was outlawed by the international Maritime Organization effective January 1, 2003.

For hundreds of years, copper has been utilized as an AF agent. It has a long history of success. Initially copper was applied to the hulls of ships in the form of sheets. There are records showing Paul Revere made copper sheets for ships to use. Presently, the most common delivery of copper is in paints applied for coating purposes. Copper has been added to marine paints and applied to ship hulls and other needing protection from the adherence of marine life. (Schleich n.d.) Past studies have shown using TBT accumulates in the environment and will eventually lead to increasing toxicity, resulting in the pollution of neighboring aquatic ecosystem, because of these findings, TBT is banned, and alternative anti-biofouling agents have been sought after. (Schleich n.d.) This copper sheeting method works when cuprous oxide is leached into the water. Copper has the property to interact with the enzymes, which are found on the cell membranes. It stops the division of cells. Copper corrodes in presence of seawater. During this process, the molecules, which have been oxidized, are discharged into the water. Although copper is considered to be poisonous and fatal if it is found in high concentrations for microbes and other organisms, it is not dangerous for human beings in small quantities. (Manov 2004) This technique works as long as the coating stays adhered to the applied surface. If the anti-fouling coating surface integrity becomes compromised by scratches, flaking, or degradation, biofouling will occur in a short period of time. Most of the time anti-fouling coating is an acceptable application because of periodic dry dock maintenance of ships. It has been estimated that biofouling costs the U.S. Navy over a billion dollars annually in maintenance costs. (Vietti 2009) The U.S. Navy has spent some time searching for improved anti-fouling methodology because of

the negative impact on its vessels. It is easy to see biofouling increases surface drag which has a negative effect on vessel performance and fuel economy.

Historically, anti-fouling agents have been applied to optics in the form of a thin film coating. Most often the anti-fouling agent in incorporated into organic solvent that is then either cast into a thin film or applied to the surface of the optic lens or it is applied as a coating. These methods have yielded marginal success. This method of application introduces micro-imperfections onto the surface of the now protected optic lens. As previously stated, this then allows the compromised of the optic lens to be treated with organic nutrients, which in turn promotes bioaccumulation. This then attracts micro fauna and allows them to bloom on the surface of the optic lens. The other side of this is the degradation of the coating, which, usually results in the coating flaking off, or UV degradation of the coating causing the protective coating to become cloudy and prevents the optic lens from gather data or gives false readings.

Most open ocean research sites are visited only annually because of limited operating budgets, so, the probability of failure between visits is high. Past studies have shown protective covering did improve mean failure rates of equipment when compared to the unprotected equipment. (Manov 2004) There are many successful methods of introducing anti-biofouling onto solid (non-transparent) surfaces. Preparing optics for the adherence of anti-biofouling material, however presents special challenges. Adding coatings to optical devices of still retaining the same optical and mechanical properties, is a challenge. These inherent challenges must be overcome when developing anti-

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biofouling solutions for transparent cover glasses. The most common method of reducing biofouling is to use thin transparent anti-biofouling coatings on the protective lenses of scientific instruments such as coverings for solar panels and underwater cameras. As was discussed earlier the problem with this current method becomes apparent when the protective coating becomes scratched, wears off, or otherwise compromised. This diminishes the ability of the instrument to function properly and creates a location, where marine fouling begins to grow. For years, anti-fouling agents such as antibiotics and other medicines have been incorporated into polymers or used polymers as delivery systems with great success; however, none of these have been transparent polymer applications. Long-term undersea research is expanding into an increasing role but this research is limited without the protection of scientific equipment, as such, the incentive for finding solutions that prevent marine biofouling is very apparent.

These solutions should allow for a durable, environmentally friendly, and cost effective means of a protective transparent anti-biofouling covering, producing this solution provides many challenges. However, there is great interest for protective antibiofouling coverglass. Transparent protective lenses could be used on viewports for autonomous underwater vehicles (AUV), remotely operated vehicles (ROV), underwater laboratories, aquariums, instrument, and terrestrial solar panels, just to name a few potential applications. As was discussed earlier, the traditional method of adhering antibiofouling coatings is not sufficient, mainly because this application does not provide enough durability for long term undersea exposure, for the growing demand. Several specific principal characteristics become important when selecting transparent polymers for use as protection and to endure prolonged exposure to elements; optical behavior, including UV stability, percent transmission, and mechanical properties such as impact resistance, and scratch resistance. (Booth 2008) The American Society of Mechanical Engineers(ASME) has now permitted the application of acrylic in order to construct pressure vessels under ASME Boiler and Pressure Vessel Code PVHO-1. (ASME VIII n.d.) According to current Industry safe standards, ASME VIII acrylic (PMMA) is the only material approved for underwater domes for use as a pressure vessel for human occupancy (PVHO-2). (ASME VIII n.d.) The domes manufactured for use on PVHO's usually are a minimum of a 5 thick and are created using solution casting the preferred method for manufacturing for PMMA. This method of manufacturing reduces the risk of introducing stress risers, along with structural imperfections into the material.

As previously stated, the most common anti-biofouling agents have been copper for macro organisms or animals and TBT for aquatic vegetation. There are many successful methods of introducing anti-biofouling into non-transparent polymers. For years, anti-fouling agents such as antibiotics and other medicines have been incorporated into polymers or used polymers as delivery systems with great success; however, none of these composites were used in transparent polymer applications. (Terlizzit 2001) The most common method of reducing biofouling is to use thin, transparent, anti-biofouling coatings on the protective lenses of scientific instruments such as coverings for solar panels and underwater cameras. The problem with this current method becomes apparent when the protective coating becomes compromised by abrasion and wears off. This diminishes the ability of the instrument to function properly and is primarily due to a compromised section, where marine fouling begins to grow. Long-term undersea research is expanding into an increasing role, but this research is limited without the protection of scientific equipment, as such, the incentive for finding solutions that prevent marine biofouling is apparent.

Several key characteristics become important when selecting transparent polymers for use as protection and to endure prolonged exposure to elements; optical behavior, including UV stability, and percent transmission and mechanical properties such as impact resistance, and scratch resistance.

After researching polymers that meet these criteria and are readily available, three transparent polymers, bisphenol A polycarbonate, poly methyl methacrylate (PMMA), and the above mentioned co-polyterephthalate (CBDO), were selected for their optical and mechanical properties. PMMA (Plexiglas®, Lucite®) is commonly used as a transparent polymer for use commercially and in defense of applications. (Fu 2006) PMMA is a vinyl system that is well known for its scratch resistance and UV stability. Several recent studies show how PMMA reacts when additives are compounded into the polymer matrix. (Fu 2006) The mechanical properties of PMMA such as elastic modulus, tensile strength, and it elongation and break showed significant increases when compounded with small percentages of clay nanocomposites. (Wilkie 2008) Polycarbonate (Lexan®, Zelux®) is well known for its impact resistance (Karbach 2005), poor scratch resistance and if not stabilized, poor UV stability due to its aromatic nature.

(Suriano 2003) In recent studies, changes in polycarbonates physical properties have been well documented when low molecular weight molecules are introduced. When low molecular molecules are added to polycarbonate systems a decrease in impact resistance is typically noted. When this amount is increased, the effect becomes even more apparent. (Classen 1990) CBDO (2,2,4,4 tetra-methyl-1,3-cyclobutadiol) is an amorphous polymer in the new family of PET based co-polyesters. CBDO is an aliphatic transparent polymer that exhibits excellent rigidity, thermally stability, and high glass transition temperature. (Booth 2006) (Kelsey 2000) When comparing UV stability to other polymers such as PMMA, CBDO exhibits a lower UV stability because of its aromaticity and more UV stability than polycarbonate because of its aliphatic properties. (Booth 2006) Depending on the application, the physical properties of CBDO can be modified by varying the percentages of monomer and using different catalysts. In a past study, a CBDO composite was formed by combining varying amounts of nanoclays via melt compounding. When a low percentage of additive was incorporated the composite displayed an increased stiffness, and elongation at break. These improved properties did, however, decline when larger amounts of additives were incorporated. (Beall 2007)

Irgarol®1051(2-methylthio-4-tert-butylamino-6-cyclopropylamino-S-triazine) is considered to be efficient and effective against both fresh and oceanic algae. It comes under the S-triazine family of compounds, which inhibit photo-system-II (PSII) by preventing the capture of photosynthetic in the chloroplasts; the part of the plant cell which is contains chlorophyll. (Voulvoulis 1999) Diuron, 3- (30, 40-dichlorophenyl)-1,1-dimethylurea, is considered to be one of the most important urea herbicides, which was first started being used in the fifties. It is well known for its lethality effects on plants. (Chesworth 2004) Both Irgarol®1051 and Diuron share similar methods of preventing the process of photosynthesis by impeding the transport of electron, both are not water soluble, and each herbicide come from two structurally different families of organic chemicals, S-triazines and phenylureas. Irgarol®1051 performs great to control algae and is of low biological activity to animals in general. Irgarol®1051 is easily excrete will and is not likely to bioaccumulation. (Ciba Specialty Chemical Inc. 2008) The algaecides Irgarol ®1051 and Diuron will be compounded at the manufactures predetermined percentages in the polymer matrix.

The purpose of this research is to investigate the additive effects displayed in these polymer systems. The resulting mechanical and optical effects of incorporating these additives will be analyzed in a series of studies. The optical properties, mechanical properties and anti-fouling properties of these compounded materials will be examined. These tests will help determine the best polymeric window to meet the desired polymer and biofouling properties for an anti-biofouling protective coverglass.

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## **Chapter II**

## **Materials and Methods**

The PMMA (Continential Acrylic CA-1000) and polycarbonate (Wonderlite® PC-110) used in this study was bought in resin form from TDL Plastics in Corpus Christi, Texas. Eastman Chemical Company donated the CBDO. Its *cis/trans* ratio was 46/54 and its molecular weight  $M_n$  is 55,000 g/mol. The anti-fouling agents examined were Irgarol® 1051 and Diuron. Ciba Chemical Company donated The Irgarol® 1051. The Diuron was purchased from Sigma-Aldrich Chemical Company. After complete drying, these materials were used as collected.

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**PMMA** 

Polycarbonate Figure 2: Molecular structures of polymethylmethacrylate (PMMA) and

polycarbonate (bisphenol A-PC).



Figure 3: CBDO-PDO co-polyterephthalate.



Figure 4: Structures of Irgarol® 1051 (a) and Diuron (b).

#### Characterization

In each test sample, the amount and concentration of the additives were used by implementing Beer-Lambert Law relationship.

#### Equation 1: A=α l c

A represents absorbance  $\alpha$  is the coefficient of absorption in L/mol cm, 1 is considered to be path of cell in cm and c is the concentration of the solution in mol/L. An Ocean Optics S2000 UV-Visible spectrometer to perform U.V spectroscopy, at 600 grooves/mm, and a blaze wavelength of 300nm. The ultraviolet absorption studies conducted used a deuterium light source. Several calibration curves were created, which determined the absorption coefficients for both Diuron and Irgarol® 1051. The absorption coefficient for the former was 17086 L/mol at 254 nm with a  $R^2$ = 0.9987 and for the later was 8697 L/mol cm at 251 nm with  $R^2$ = 0.9946.

For further testing, several compounded pellets were used and dissolved in  $CH_2 Cl_2$ . The intended percent incorporation values for the samples which include Irgarol®1051 were 0.25 and 0.50%. The intended percent incorporation values Diuron were found to be 2 and 4%. The UV concentration tests confirmed concentrations of 0.39 and 0.70% for the Irgarol samples and concentrations of 2.10 and 4.23% for the Diuron samples.

In order to carry out the Thermogravametric analysis (TGA), a TA Instruments Q50 TGA was used. Scans were run on samples ranging from 5-10mg at the rate of 20°C/min from room temperature to 800°C. Decomposition temperatures were reported as the value, where the sample displayed a 10 percent loss in mass.

A TA Instruments Q200 DSC was used to study the thermal behavior of the samples. 5 mg samples were utilized, with heating and cooling rate of 10°C/min under inert atmospheric conditions. Data was collected on the first heating and second cooling cycle.

Mechanical data were obtained using a, MTS/Sintech Model 1D tester, equipped with a pendulum data station, in accordance to ASTM D628.

Impact resistance was measured using a Gardner Impact Tester. This tester consists of a graduated vertical tube that guides a weighted hammer of specific mass 227g and 3632g. The 0.500 inch punch rests on the plaque position on a pedestal with a 0.640 inch hole underneath the plaque. The weighted hammer falls driving the punch into the hole. The height of the fall continues to increase until failure occurs. Failure is determined by a visible rupture of the targeted area. For PMMA, a 227g hammer was used. For PC and CBDO testing, 36232g hammer was used. The plaques test measure 2.5cm x 0.16cm.

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#### Processing

The Napco E series vacuum oven, which had a Welch 1402 mechanical vacuum pump, was used in order to dry the polymer resin for a period of 48hrs, at a temperature of 70°C under vacuum. A HAAKE Rheodrive 500, connected to a HAAKE Rheomax CTW 100 twin screw extruder, was used for the compounding the resins with anti-fouling agents. Temperature ranges of 180-210°C, were used for PMMA. PC was subjected to melt compounding at a temperature range from 180-200°C and CBDO was melt compounded at a temperature range from 150-165°C. All three polymers tested were compounded with 50% and 100% of the anti-biofouling agent of the manufacturers recommended quantity while conducting a 2-factoral designed experiment. The manufacture's recommended percent incorporation for Irgarol® 1051 is 0.5% (w/w) and the recommended percent incorporation for Diuron is 4% (w/w). (Booth 2008) By dry mixing, these materials were premixed and then subjected to melt mixing by using the HAAKE twin screw extruder. (Booth 2008) The extruder has a monofilament die head. (Booth 2008) After the process of extrusion, a water trough was used to cool the monofiliment line as it was pulled through dry ice and water and then finally into a HAAKE PP1 Postex Pelletizer. (Booth 2008) The pellets were dried at 70°C for 24hrs under vacuum.

In order to manufacture test plaques, compression molding on a Carver Laboratory Press was implemented. Using plates and molds of aluminum, which had the dimensions of 18cm x 18cm x 0.16cm, the sample plaques were created. (Booth 2008) For both PMMA and polycarbonate, the molding temperature was found to be 204°C. For CBDO, the molding temperature was 163°C. In order to ensure that the polymer did not stick to the mold, Universal II mold release was used. In order to form plaques, 60g of compounded resin was transferred to the mold. The compounded resin was uniformly packed to insure even distribution of heat and equilibration. The molds were heated for five minutes, without the top plate of the mold. After five minutes, a slight amount of pressure was applied to the mold until the mold and resin equilibrate. Over a period of five minutes pressure was applied gradually until a total pressure of 1.38x10<sup>8</sup> Pa was reached.

The mold was then pulled off the press and allowed to cool. The compounded was removed and it was prepared in accordance to the standards and specifications of each test. For optical testing the plaques were polished to remove surface haze resulting from the manufacturing process.

## **Chapter III**

#### **Results and Discussion: Mechanical Properties Testing**

The TGA and DSC were used to confirm that all the polymers studied were amorphous. After comparing the thermal degradation ( $T_d$ ) of treated polymers and neat sample no difference could be found. The  $T_d$  measured for PMMA was 315°C, the CBDO was 370°C, and the PC was 415°C. DMA testing was conducted in order to obtain the tensile modulus, peak load, and the percentage strain at the break. These values are tabulated in (table 1). Impact resistance for all neat samples coincides with existing published data. The CBDO-PDO shows a higher percentage of impact resistance as compared to that of Bisphenol-A polycarbonate. The higher impact resistance percentage value is six percent. Existing literature shows CBDO-PDO the potential of a 35 percent increase in impact resistance over Bisphenol-A polycarbonate (Booth 2008), however, these reports used injection molding instead of compression molding. We account for this difference because it is well known that injection molding increases the amount of orientation in a polymer over compression molding.

The impact resistance values for PMMA show no difference with any amount of anti-biofouling agents loading.

This property is well known; previous studies have shown PMMA's ability to accept and handle additives without decreasing thermal or mechanical properties. Most of the values show 0.39 percent loading of Irgarol actually increases these tensile properties. We suspect that this increase is because of the reinforcement effects of the additives, which has been shown in previous studies. In general, the data show that PMMA, with small percent incorporations of additives improve the mechanical properties.

	Material		Peak	Peak stress	% Strain	Modulus 2
			load (N)	(N = mm)	at break	(N = mm)
PMMA						
	Neat	Run 1	1170	708	4.2	21348
	:	Run 2	1557	956	5.9	23142
		Run 3	1338	788	5.5	19728
		Average	1355	817	5.2	21406
	.25%	v				(
	Irgarol	Run 1	1366	1150	6.4	27080
		Run 2	1069	781	4.1	23379
		Run 3	1328	1001	5.5	26454
		Average	1255	977	5.3	25637
	.50%					
	Irgarol	Run 1	1019	520	3.0	19857
	:	Run 2	1542	619	5.8	14918
		Run 3	1260	596	4.1	18091
		Average	1273	578	4.3	17622
	2%					
	Diuron	Run 1	1200	978	4.4	26938
		Run 2	1287	769	4.9	20006
		Run 3	1457	847	5.6	19793
		Average	1315	865	5.0	22246
	4%					
	Diuron	Run 1	927	546	3.6	17575
		Run 2	1255	1023	5.5	25991
		Run 3	1144	665	3.9	20020
		Average	1109	745	4.3	21195

## Table 1: Test Results of PMMA Mechanical Values

V.

	Material		Peak load (N)	Peak stress $(N = mm^2)$	% Strain at break	$Modulus (N = mm^{2})$
CBDO						·
	Neat	Run 1	1566	14	101.5	486
		Run 2	1568	14	N/A	497
		Run 3	1522	13	172.9	488
		Average	1552	13.7	137.2	490
	.25%					
	Irgarol	Run 1	1652	16	171.5	479
		Run 2	1684	16	145.4	511
		Run 3	1710	16	159.1	515
		Average	1682	16	158.7	501
	.50%					
	Irgarol	Run 1	1739	15	83.4	506
		Run 2	1745	16	N/A	485
		Run 3	1656	15	154.8	500
		Average	1713	15.3	119.1	<b>497</b>
	2%	r				·
	Diuron	Run 1	1836	16	131.0	7174
		Run 2	1768	16	152.0	7218
		Run 3	1793	16	102.0	7140
		Average	1799	16	128.0	7177
	4%					
	Diuron	Run 1	1795	16	163.0	6479
		Run 2	1784	16	64.0	6792
		Run 3	1792	16	136.0	4478
			1790	16	121.0	5916

# Table 2: Test Results of CBDO Mechanical Values

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			Peak	Peak stress	% Strain	Modulus
	Material		load (N)	$(N = mm^2)$	at break	$(N = mm^2)$
Bis A-P	°C					
	Neat	Run 1	2532	358	10.3	7174
		Run 2	2446	366	11.1	7218
		Run 3	2574	350	10.3	7140
		Average	2484	358	10.6	7177
	.25%				·	
	Irgarol	Run 1	2861	269	6.3	6479
		Run 2	1946	199	3.4	6792
		Run 3	2105	112	206.0	4478
		Average	2304	193	4.1	5916
	.50%				,,	
	Irgarol	Run 1	2300	353	13.1	4051
		Run 2	2192	310	5.1	8700
		Run 3	2609	362	8.9	8366
		Average	2367	342	9.0	7029
	2% Diuron	Run 1	1014	100	1 /	8475
	270 Diulon	Run 2	813	89	1.7	8351
		Run 3	1124	117	1.1	7288
			984	105	1.7	8038
	4% Diuron	Run 1	709	72	0.9	8052
		Run 2	524	, 2 50	0.7	8052
		Run 2	1254	130	1.8	7850
		Average	<b>829</b>	<b>87</b>	1.0 1.1	8293

## Table 3: Test Results of Bis A-PC Mechanical Values

Material	Plaque 1 (J/m)	Plaque 2 (J/m)	Plaque 3 (J/m)	Plaque 4 (J/m)	Plaque 5 (J/m)	Average (J/m)
PMMA	× .					
Neat	4.45	4.45	4.45	4.45	4.45	4.45
.25% Irgarol	4.45	4.45	4.45	4.45	4.45	4.45
.50% Irgarol	4.45	4.45	6.67	4.45	N/A	5
2% Diuron	4.45	6.67	4.45	4.45	N/A	5
4% Diuron	4.45	4.45	4.45	2.22	N/A	3.89
CBDO						
Neat	1031	961	996	961	925	975
.25% Irgarol	890	961	925	925	925	925
.50% Irgarol	890	818	854	890	N/A	863
2% Diuron	854	747	818	854	N/A	818
4% Diuron	818	712	605	427	N/A	641
Bis A-PC						
Neat	925	890	925	925	N/A	916
.25% Irgarol	712	783	854	N/A	N/A	783
.50% Irgarol	783	712	605	N/A	N/A	700
2% Diuron	2.22	2.2	4.45	4.45	N/A	3.34
4% Diuron	4.45	4.45	4.45	6.67	N/A	5

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# Table 4: Results from Impact Resistance Testing

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We credit this property to the effect the additive displays on the amorphous polymer by creating self supporting regions and stiffening regions which is what would be expected from a semi crystalline material. At high percent incorporations the additives hinder the polymer chain where the material displays a loss of mechanical properties and becomes brittle.

The CBDO-PDO data demonstrate a decrease on impact resistance with the increase in additive. However, even when the impact resistance drops 34 percent, this value is sufficient enough to be considered as a high impact resistant material. In previous reports CBDO-PDO revealed a drop in impact resistance with increasing the additive. These studies demonstrate that the additives used were organoclay nanoparticles and these studies credit the tactoidal behavior of the clay particles; by stiffening the material at low percent incorporations and with higher percent incorporations the nanoparticles contributes to the increased the brittleness of the polymer material.

The effect of the mechanical properties of the CBDO-PDO with increasing amounts of anti-biofouling agents are worth further investigation. The mechanical values examined: peak load, peak stress, percent strain at break, and modulus, the values revealed a rise with the decreased percentage loadings of additive and a significant decrease when the percentage loadings of each additives went higher. The previous studies conducted with organoclay nano composites of CBDO-PDO showed the same trend. (Booth 2008) It should be noted that the composite material revealed higher

mechanical values, when the loading was 10 percent for the organoclay particles. The increase in the mechanical properties was because of the orientation effects by injection molding and organoclay particle's large aspect ratio. This study employed smaller organic molecules without the large aspect ratio. Consequently, this explanation is not compatible with the results found in this study. The self orientation of the polymer chains is the most likely explanation for this difference. For flexible chain polymers such as PMMA, injection molding imparts more order to the polymer system then compression molding. (Booth 2008) Polymers which have the connection between rigid and flexible units such as CBDO-PDO, an intrinsic amount of ordering exist when processed by any method compression or injection molding. Consequently, this ordering is responsible for increasing the mechanical properties.

The bisphenol-A polycarbonate displays the most spectacular outcomes with increasing amounts of additives. The added impact resistance of the neat samples is 916 J/m. the specimens with 0.39 and 0.70 % Irgarol®1051 fall to 783 and 700 J/m. The values for impact resistance fall dramatically below those values reported for the PMMA samples when diuron is incorporated. The severe reduction in impact resistance is normally connected with the decrease of motion of the phenylene units of the bisphenol A-PC group. When small organic molecules that contain polar functionalities are introduced they limit the permissible rotary motion of the phenylene units by means of electrostatic interactions. (Werle 2005)

#### **Results and Discussion: Optical Properties Testing**

Optical testing was conducted in order to determine the efficiency and the effectiveness of the anti-biofouling agents. The data collected in these studies show minor degradation of the visual and optical attributes of all the polymers studied with the addition of the anti-biofouling agents.

Polycarbonate samples retained the highest percent transmission with the addition of antifouling agent. Only a 3% or less reduction in percent transmission was observed in all polymer samples over the course of study. When reviewing the data for PC and PMMA with Irgarol®1051 incorporated, the percent loss of transmission decreased as the percent of Irgarol®1051 increased. With respect to UV studies conducted on the polymer samples, all polymers displayed a loss in the percent transmission with an increasing amount of additive, with the exception of PC with Irgarol®1051. The polycarbonate with Irgarol®1051displayed less percent transmission loss then the untreated polymer sample. Leach rate studies were also conducted where polymer samples were placed into containers of 100 ml of deionized water and allowed to set for an extended period of time. At the time when the last tests were conducted the samples had been sitting for 687 days. Aliquots of the deionized water were then examined by UV-visible spectroscopy for the presence of Irgarol®1051. A series of calibration curves resulted in the Beer-Lambert relationship of Irgarol®1051 moles per liter. After examining the data from the leach rate test, no detectable levels of Irgarol®1051 were found. These findings give a leach rate of less than 1.8 ng. More concentrated leach rate tests were also conducted. In this test, a large amount of the 0.3 percent Irgarol®1051/PMMA pellets were placed into 100ml of deionized water. After soaking for 79 days, no evidence of the Irgarol®1051 leaching into the deionized water was detected. These results show that Irgarol®1051/PMMA would have a minimum impact on the environment as anti-biofouling polymers.

			%	
		Transmission	Transmission	% Loss of
	Sample	at 600 nm (%)	after Algae	Transmission
CBDO	Neat	89.4	85.8	4.01
	0.25% Irgarol	86.8	80.8	6.85
	0.5% Irgarol	86.7	81.2	6.35
	2% Diuron	84.5	75.6	10.59
	4% Diuron	81.5	73.4	9.89
PMMA	Neat	92.2	84.7	7.74
	0.25%Irgarol	90.3	86.4	4.25
	0.5% Irgarol	90.9	86.9	4.36
	2% Diuron	90.3	83.6	7.39
×	4% Diuron	89.7	84.6	5.7
Bis A	Neat	89.3	88.2	1.2
	0.25% Irgarol	90.1	89.3	0.94
	0.5% Irgarol	90.4	88.8	1.78
	2% Diuron	90.3	88	2.55
	4% Diuron	89.5	87.4	2.4

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 Table 5: Average Optical Transmission Values for Algaecide Impregnated Samples

 after Algae Exposure

			%	
		Transmission	Transmission	% Loss of
	Sample	at 600 nm (%)	after Algae	Transmission
CBDO	Neat	90.4	88.1	2.57
	0.25% Irgarol	90.1	87.1	3.29
	0.5% Irgarol	90.3	86.4	4.37
	2% Diuron	88.54	84.7	4.33
	4% Diuron	86.74	81.3	6.29
PMMA	Neat	88.6	87.9	0.78
	0.25%Irgarol	90.9	89.7	1.67
	0.5% Irgarol	91.0	89.1	2.10
	2% Diuron	90.4	84.4	5.97
	4% Diuron	90.2	82.6	7.40
Bis A	Neat	90.9	88.8	2.23
	0.25% Irgarol	90.8	89.7	1.24
i	0.5% Irgarol	90.2	89.0	1.27
	2% Diuron	N/A	N/A	N/A
	4% Diuron	N/A	N/A	N/A

Table 6: Average Optical Transmission	Values for	Algaecide	Impregnated	Samples
after UV Exposure				

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### **Chapter IV**

### Conclusions

After reviewing the results from the UV studies (Table 5); the data show all test plaques demonstrated a percent transmission loss as the amount of additive increased, excluding bis A-PC with Irgarol®1051. These plaques displayed the same percent loss and the untreated (neat) plaque.

Leach rate studies were also conducted on a series of 1 cm<sup>2</sup> test plaques of 0.5% Irgarol®1051 in PMMA in 100ml of deionized water and soaked for an extended period of time. For the tests results reported in Figure 6, the samples had been soaking for 687 days. Sample aliquots of solution were examined by UV-Visible spectroscopy. After establishing a series of calibration curves using the Beer-Lambert Law relationship of Irgarol®1051 concentration (moles/liter) to absorbance (A); we concluded, A=8697.2 moles/liter and the R<sup>2</sup>=0.9946.

With respect to optical properties, and after reviewing the results from the percent transmission studies the materials with Irgarol®1051 incorporated display the best performance after being submerged for six months. The test plaques with Diuron incorporated display a greater loss in transmission with both minimal and maximum

amounts added. When comparing the difference between the values, plaques with Irgarol®1051 posses the best retained properties. The submerged materials with Irgarol®1051 incorporated into to matrix displayed the best resistance to biofouling. The data show clear evidence that Irgarol®1051 is the best choice as an anti-fouling agent for addition into the polymer matrices studied in this work.

Diuron treated samples displayed a considerable loss in percent transmission and some results could not be obtained because of the condition of the sample. The bis A-PC/Irgarol®1051samples displayed less percent transmission loss than the neat material. This can be attributed the Irgarol®1051absorbing the UV rays and this translates to less UV transmission by the bis A-PC itself. However as the amount of Irgarol®1051 incorporated increased from 0.25% to 0.5%, so too, did the loss in percent transmission. All other sample observed displayed the anticipated results of a decrease in percent transmission as UV exposure increased. The PMMA/Irgarol®1051 combination results yielded the best overall retained optical properties and anti-biofouling protection.

The mechanical test results showed all bis A-PC samples displayed a decrease of tensile properties, as additive increased. All bis A-PC mechanical properties decreased except for modulus. This is attributed to an increase in stiffness and brittleness because of the decrease in the phenylene unit rotation. (Werle 2005) (Hansen 1992) (Plummer 1995)

The mechanical results for CBDO show almost a linear decrease of properties with increasing amounts of additive. The combination of CBDO and 0.5% Irgarol®1051 display the best retained mechanical properties with respect to the neat and biofouling protection. (Table 2) Only percent strain at break test results, displayed a decrease in values when compared to the neat material. All other test results display an increase in mechanical properties. (Table 2) All combinations of CBDO and anti-fouling agent displayed a decrease in impact resistance. (Table 4) The combination of 0.25% CBDO/Irgarol®1051 demonstrated higher impact resistance than neat bis A-PC. (Table4)

The PMMA/Irgarol®1051 sample demonstrated an increase in all mechanical properties with regards to biofouling protection. Past studies have demonstrated PMMA's ability to incorporate additives and still retain its desired properties.

For applications where a protective coverglass is needed to protect against biofouling, our tests show the combination of PMMA/Irgarol®1051 is the material for this application. If a protective coverglass in needed for high impact resistance and biofouling protection the combination of CBDO/Irgarol®1051 is the material for this application.

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### VITA

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