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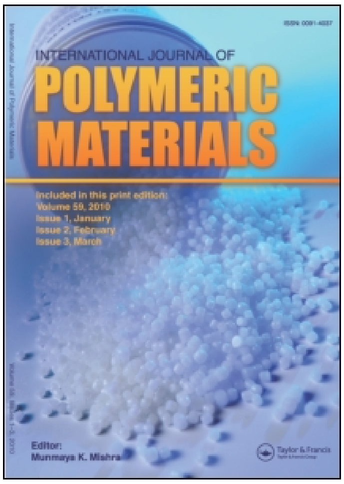

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Effects on Impact and Tensile Behavior of Transparent Polymer Materials by the Addition of Anti-Biofouling Agents

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Effects on Impact and Tensile Behavior of Transparent Polymer Materials by the Addition of Anti-Biofouling Agents

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This paper reports the effects on both the impact and tensile behavior, impact resistance, modulus, strain at break, and peak load for a series of polymers with anti-biofouling agents added. The materials include PMMA, bisphenol-A polycarbonate, and a co-polyterephthalate derived from 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 1,3-propanediol (CBDO). The anti-biofouling agents studied were the algaecides Irgarol 1051 and Diuron. The anti-biofouling agents were not simply used as a coating but were compounded into pelletized material and then compression molded into test plaques. The results show that PMMA is the only polymeric material studied that does not show a decrease in impact resistance with an increasing quantity of the anti-biofouling agent. With respect to modulus, strain at break, and peak load, both PMMA and CBDO showed little dependence on the amount or type of anti-biofouling additive.

Keywords: anti-biofouling, CBDO, impact resistance

INTRODUCTION

Solar panels and bio-optical sensors play a significant and growing role in a number of applications that are of importance to many

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organizations. Many of these instruments (solar panels, spectrophotometers) require a high transmission of radiation (UV, visible, and infrared light) into the device for it to work properly. Typically, these devices have a coverglass affixed over the active part of the device to protect the sensor or panel from harsh ambient conditions. A problem that presently exists with both sensors and solar panels is biological fouling of the coverglasses on these instruments. Over time in an ocean environment, any number of both plants and animals (algae, seaweed, barnacles, tube worms) will attach themselves to the coverglass, ultimately obscuring the glass and rendering the instrument useless. As such, an anti-fouling mechanism is needed for these instruments that is inexpensive, long-lasting, and environmentally friendly.

Two things must be considered when examining optical coverglass materials. These include the optical behavior of the material, percent transmission, UV stability, and the mechanical properties. Polymers such as bisphenol-A polycarbonate (PC) provide excellent impact resistance [1] but do suffer from poor resistance to UV [2] with extended exposure. On the other hand, materials such as poly(methylmethacrylate) (PMMA) display excellent UV stability [3] but suffer in that their impact resistance is significantly lower than that of PC. Over the years there has been a moderate industrial interest in a co-polyterephthalate composed of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) and 1,3-propanediol (PDO) (Figure 1) [4–8]. While this material has sparked moderate interest from industry, it has only recently been examined from the academic side. This material displays enhanced UV stability [9], when compared to PC, as well as enhanced impact resistance [10], when compared to both PC and PMMA. This material is a co-polyterephthalate synthesized using 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) and 1,3-propanediol (PDO) (Figure 1). Notched Izod impact values for the CBDO-PDO co-polyterephthalate have been reported as high as 1070 J/m [9], depending on the percent incorporation of the monomers, and ballistic testing shows the material to be as much as 35% better than PC.

The problem of developing an anti-biofouling optical coverglass material is further complicated because a small molecule additive must be compounded into the material. Polymers such as polycarbonate

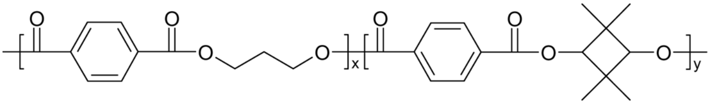

FIGURE 1 CBDO-PDO co-polyterephthalate.

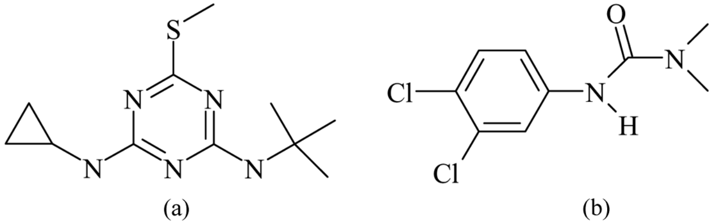

FIGURE 2 Structure of Irgarol® 1051 (a) and Diuron (b).

are notorious for showing a decrease in mechanical properties with the introduction of additives [11]. This diminution of mechanical properties is typically less of a problem in vinyl systems such as PMMA, and in many cases an increase in the mechanical properties is observed [12]. Recent studies reported for the CBDO-PDO co-polyterephthalate show that the addition of additives, in this case organoclay nanoparticles, contributes to an increase in stiffness and elongation at break [13]. There is a reduction in impact resistance, but that corresponds to the amount of additive utilized.

This study will address the effects on both the impact and tensile behavior of the addition of two anti-biofouling algaecides, N-(tert-butyl)-N′-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine (Irgarol® 1051) and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron) (Figure 2), to three optically transparent polymeric materials: PMMA, PC, and the CBDO-PDO co-polyterephthalate. The effects on the materials' impact and tensile properties will be discussed. The effects on the materials' optical properties will be reported in a subsequent paper.

EXPERIMENTAL

Chemicals

Both the PMMA and polycarbonate were purchased in resin form from TDL Plastics (Corpus Christi, Texas). The polycarbonate utilized was Wonderlite® PC-110 while the PMMA utilized was a Continental Acrylics CA-1000. The CBDO used was donated by Eastman Chemical Company and has a *cis/trans* ratio of 46/54 with a M_w of 55,000. Two anti fouling agents were examined. The first was Irgarol® 1051 (Figure 2). The Irgarol® 1051 was donated by Ciba Chemical Company. The second anti biofouling agent was Diuron (Figure 2). The Diuron was purchased from Sigma-Aldrich Chemical Company. All chemicals were used as received after thorough drying.

Characterization

The concentration of the additives in each polymer sample was verified using the Beer-Lambert Law relationship (Equation (1)):

$$A = \alpha \, l \, c \tag{1}$$

where A is absorbance, α is the absorption coefficient (L/mol cm), l is the cell path length (cm), and c is the solution concentration (mol/L). UV spectroscopy was carried out utilizing an Ocean Optics S2000 UV-Visible spectrometer with 600 grooves/mm and a blaze wavelength of 300 nm. A deuterium light source was used for the ultraviolet absorption studies. A series of calibration curves was constructed resulting in absorption coefficients of 17086 L/mol cm for Diuron at 254 nm with $R^2 = 0.9987$ and 8697 L/mol cm for Irgarol at 251 nm with $R^2 = 0.9946$.

Several compounded sample pellets were dissolved in CH_2Cl_2 for testing. The targeted values for the compounded Irgarol® 1051 samples were 0.25 and 0.5% by weight of Irgarol to polymer while the targeted values for the Diuron compounds were 2 and 4% by weight. The UV concentration studies resulted in actual Irgarol weight fractions of 0.39 and 0.70 and actual Diuron weight fractions of 2.10 and 4.23.

Thermogravimetric analysis (TGA) was obtained using a TA Instruments Q50 TGA. Scans were performed using 5–10 mg samples at a rate of 20°C per min from ambient to 800°C. Decomposition temperatures are reported as the value at which the sample displays a 10% loss in mass.

Differential scanning calorimetry (DSC) was conducted using a TA Instruments Q200 DSC. Scans were obtained using 5 mg samples at a heating/cooling rate of 10°C per min. All scans were conducted under an inert atmosphere. Reported data was collected on the first cooling and second heating cycles.

Modulus data was collected using a MTS/Sintech Model 1D Tensile Tester equipped with a Pentium data station. Samples were standardized and tested according to ASTM D628.

Impact resistance was obtained using a Gardner Impact Tester. This system is a "dart style" tester which utilizes a hammer of specific mass dropped from a calibrated distance. For this study a 227 g hammer was used for the PMMA samples while a 3632 g hammer was used for the PC and CBDO. Plaques utilized for this test were 2.5 cm × 2.5 cm × 0.16 cm.

Processing

The polymer resin was dried using a Napco E series vacuum oven equipped with a Welch 1402 mechanical vacuum pump. The polymer resins were dried for 48 h at 70°C under vacuum. Processing of the polymer resins with the anti-biofouling agents was accomplished using a HAAKE Rheodrive 500 connected to a HAAKE Rheomax CTW 100 twin screw extruder. PMMA was processed using a temperature range of 108–210°C, PC was processed using a temperature range of 180–200°C, and the CBDO was processed using a temperature range from 150–165°C. Each of the three polymers examined was compounded with 100% and 50% of the manufacturers' suggested quantity of anti-biofouling agent while performing a 2-factorial designed experiment. For the Irgarol® 1051, the manufacturers' suggested incorporation is 0.5% (w/w) and for the Diuron, the suggested percent incorporation is 4% (w/w). The premix formulations were compounded by dry blending the individual components and melt-mixing them in the HAAKE twin screw extruder. The extruder was fitted with a monofilament die head, and upon extrusion the compounded polymers were pulled through a water trough cooled using dry ice and then finally into a Haake PP1 Postex Pelletizer. The pelletized compounded polymer resin was then dried at 70°C for 24 h under vacuum.

Test plaques were made using compression molding on a Carver Laboratory Press. Sample plaques were formed using aluminum plates and aluminum molds with dimensions of 18 cm × 18 cm × 0.16 cm. The press was preheated to the predetermined temperature suitable for molding of the polymer composites. The molding temperature for PMMA and polycarbonate was determined to be 204°C, while the molding temperature for CBDO was 163°C. The aluminum molds were sprayed with Universal II mold release to prevent the compound from adhering to the molds. To form the plaques, 60 g of composite resin was placed into the heated mold and left for 5 min. The top mold plate was then placed on the mold and the press was raised to close the mold. The closed mold was allowed to equilibrate for 5 min, after which pressure was slowly increased until a pressure of 1.38×10^8 Pa was reached. The mold was then removed from the press and allowed to cool. The polymer plaque was removed from the mold and then cut and shaped to the measurements specified by the particular test to be performed.

RESULTS AND DISCUSSION

TGA and DSC studies show that all materials examined are amorphous. Additionally, no effect on the thermal decomposition temperature of the materials was observed with the introduction of the additives. The measured T_d for the PMMA was 315°C, the CBDO-PDO co-polyterephthalate was 370°C, and the PC was 415°C.

Several mechanical tests were performed in order to evaluate the effect of adding the anti-biofouling agents to the optical plastics. Impact resistance was evaluated using dart impact studies. Both the CBDO co-polyterephthalate and the bisphenol-A polycarbonate were evaluated using the standard 3632 g hammer, while the PMMA samples were evaluated using a 227 g hammer. The results from impact testing are shown in Table 1.

The data show that bisphenol-A polycarbonate and, to a lesser extent, the CBDO co-polyterephthalate display a decrease in impact strength with increasing anti-biofouling additive. The polycarbonate shows a large decrease with the introduction of the Diuron. What is not clear is whether this is due specifically to the Diuron or simply the amount of additive being introduced. Bisphenol-A polycarbonate is notorious for being sensitive to additives and as much as 4 wt% of the Diuron was used. As discussed earlier, the incorporated weight percentages for both Diuron and Irgarol® 1051 were based on the manufacturers' suggested incorporation values and a 2-factorial designed experiment that was run concurrently. In this study, the Diuron was incorporated at 2.1 and 4.2 wt% while the Irgarol® 1051 was incorporated at 0.39 and 0.70 wt%.

With respect to the PMMA samples, there is, statistically, no difference in the impact resistance of the neat PMMA samples when compared to the PMMA samples compounded with the anti-biofouling agents.

TABLE 1 Impact Resistance

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	5.00
2% Diuron	4.45	6.67	4.45	4.45	N/A	5.00
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	2.22	4.45	4.45	N/A	3.34
% Diuron	4.45	4.45	4.45	6.67	N/A	5.00

In addition to the impact values, DMA was run to obtain tensile data, peak load, peak stress, percent strain at break, and modulus. The values are shown in Table 2 and reflect the neat, 0.39 and 0.70% Irgarol® 1051, and neat, 2.1 and 4.2% Diuron for all three polymer samples.

Impact resistance for the neat samples is in good agreement with published values. The CBDO-PDO co-polyterephthalates displayed a 6% higher impact resistance when compared to bisphenol-A polycarbonate. Earlier reports [10], which utilized injection molding rather than compression molding, show that the CBDO-PDO co-polyterephthalates are capable of up to a 35% increase in impact resistance over bisphenol-A polycarbonate. We attribute this difference to the use of compression molding rather than injection molding.

The PMMA shows no difference in impact resistance with either of the anti-biofouling agents at any loading. This result is not unexpected; PMMA has a good reputation of accepting and handling additives without loss of thermal or mechanical properties [14]. With respect to the tensile properties the PMMA displays only a moderate decrease in peak load, peak stress, percent strain at break, and modulus. In most cases, the 0.39% loading of Irgarol® actually increases the properties. This increase is most likely due to the reinforcement effects of the additives as has been shown with other PMMA additives in other studies [15–16]. The general findings show that at low loadings the mechanical properties are increased. This finding is attributed to the additive acting to stiffen regions of the amorphous polymer and create regions which are self-supporting—similar to the behavior of semi-crystalline materials. At higher loadings, the additives simply limit the polymer chain motion to the point that the material becomes more brittle and a loss of mechanical reinforcement is observed.

The CBDO-PDO co-polyterephthalate does display an almost linear decrease in impact resistance with increasing additive. The overall impact resistance falls 34% with the addition of 4.2 wt% Diuron; but at 641 J/m, this value is still high enough to qualify as a high-impact resistance material. As with the PMMA, this is not unexpected; the CBDO-PDO co-polyterephthalate has been reported to display a loss in impact resistance with increased additive loading [13]. Other work has been carried out using organo-clay nanoparticles as the additives, and the reasons reported are that the clay particles are tactoidal in nature and therefore act to stiffen the material at low loadings; however, with increased percent loadings, the nanoparticles impart brittleness to the polymer system.

TABLE 2 Mechanical Values

Material			Peak load (N)	Peak stress (N/mm^2)	% Strain at break	Modulus (N/mm^2)
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% 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**
CBDO	Neat	Run 1	1566	14	101.5	443
		Run 2	1568	14	N/A	440
		Run 3	1522	13	172.9	432
		Average	**1552**	**13.7**	**137.2**	**439**
	.25% Irgarol	Run 1	1652	16	171.5	512
		Run 2	1684	16	145.4	525
		Run 3	1710	16	159.1	516
		Average	**1682**	**16**	**158.7**	**517**

(*Continued*)

TABLE 2 Continued

Material			Peak load (N)	Peak stress (N/mm^2)	% Strain at break	Modulus (N/mm^2)
	.50% Irgarol	Run 1	1739	15	83.4	486
		Run 2	1745	16	N/A	497
		Run 3	1656	15	154.8	488
		Average	**1713**	**15.3**	**119.1**	**490**
	2% Diuron	Run 1	1836	16	131	479
		Run 2	1768	16	152	511
		Run 3	1793	16	102	515
		Average	**1799**	**16**	**128**	**501**
	4% Diuron	Run 1	1795	16	163	506
		Run 2	1784	16	64	485
		Run 3	1792	16	136	500
		Average	**1790**	**16**	**121**	**497**
Bis A-PC	Neat	Run 1	2532	358	10.3	7174
		Run 2	2446	366	11.1	7218
		Run 3	2474	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	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	109	1.4	8475
		Run 2	813	89	1.1	8351
		Run 3	1124	117	1.7	7288
		Average	**984**	**105**	**1.4**	**8038**
	4% Diuron	Run 1	709	72	0.9	8052
		Run 2	524	59	0.7	8977
		Run 3	1254	130	1.8	7850
		Average	**829**	**87**	**1.1**	**8293**

The effects on the tensile properties of the CBDO-PDO co-polyterephthalate with increasing anti-biofouling additive are unlike the other samples investigated. For all tensile values examined, peak load, peak stress, percent strain at break, and modulus, the values showed an increase with the lower loading of each additive and then a subsequent decrease at higher loadings of each additive. Work reported using organo-clay nanocomposites of the CBDO-PDO co-polyterephthalate showed this same trend [13]. The material showed an increase in tensile values with up to 10 wt% loading of the organo-clay particles. This increase in tensile values was attributed to orientation effects created not only by injection molding but also the large aspect ratio of the organo-clay particles. That does not seem to fit the model here in that the additives used in this study are small organic molecules and not large aspect ratio organo-silicates. More likely, the explanation is related to the self-orientation of the polymer chains themselves. For flexible polymers, such as PMMA, injection molding imparts more order than compression molding. But for polymers that contain rigid units connected by flexible units, such as the CBDO-PDO co-polyterephthalate, there is an intrinsic amount of ordering which occurs with any processing; whether it be compression or injection molding. This ordering is likely the cause of the increase in tensile properties.

The bisphenol-A polycarbonate shows the most dramatic effects with increasing additive. The neat PC samples have an average impact resistance of 916 J/m. The samples with 0.39 and 0.70% Irgarol® added fall to 783 and 700 J/m, respectively. With the incorporation of the Diuron, the impact resistance falls to values lower than those reported for the PMMA samples. This dramatic decrease in the observed impact resistance is most commonly associated with a decrease in the motion of the phenylene units of the bisphenol-A group [17]. The introduction of small organic molecules which contain polar functionality limits the allowed rotation of the phenylene units via electrostatic interactions.

CONCLUSIONS

For the PC samples, all tensile properties, except modulus, display a decrease with increasing percent additive. As discussed above, the increase in stiffness of the material is best explained by examining the decrease in phenylene unit rotation [17]. The decrease in polymer chain (specifically the phenylene units) rotation will without doubt add to the stiffness of the material.

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