IR Optical Properties of ZnS/ZnSe-Modified High-Density Polyethylene

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ABSTRACT: The goal of this work was to find practical materials for infrared motion sensors that are more selective for IR radiation of human origin. Motion sensors used for security purposes can be vulnerable to false alarms. Along with sensitivity to infrared radiation produced by human intruders, they also sense white radiation from a number of common environmental sources. One material used for sensor optics is high-density polyethylene (HDPE). Since pigments alter the IR absorption properties of materials, the focus of the research was to produce pigmented HDPE and to determine the optical and mechanical characteristics of the resulting materials. Different pigments added to HDPE produced varying results. One pigment, a mixture of zinc sulfide and zinc selenide, performed well in eliminating white radiation, while attenuating the IR transmittance minimally. Accelerated weathering by exposure to high-intensity ultraviolet radiation gave information on the usefulness of the pigmented plastics for actual sensor installations. Accelerated weathering of clear HDPE and plastic pigmented with ZnS/ZnSe produced a negligible loss. Impact testing for assessment of the embrittlement of the aged plastics showed that the clear HDPE and the ZnS/ZnSe pigmented polymer failed only at high impact and long simulated aging times. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2727–2732, 1997

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INTRODUCTION

Many false alarm sources for infrared security sensors exist in the visible and near-infrared (400 nm to 3 μm) portion of the electromagnetic spectrum. Some sources of radiation in this wavelength range are headlight beams and reflected sunlight. High-density polyethylene is used widely in a variety of consumer products including infrared lenses in security sensors. Even though IR transmittance through this material is lower than through semiconductor or zinc selinide optics, other factors outweigh this shortcoming.[1–3] Attractive properties exhibited by HDPE for sensor optics are transmission in the IR range, low cost, and compatibility with mass production techniques, such as injection molding. Also, with plastic optics, the engineer can design alignment keys and installation features directly into the part. The goal of this research was to modify HDPE to improve its selectivity in distinguishing radiation of human origin from environmental sources. The main thrust of this research was to alter the optical properties of HDPE by adding pigments in processing. This method is attractive because of simplicity in processing and low cost.

Historically, chalcogenides and aluminum oxide have all been additives in infrared transmit-

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Table I Short and Long Wavelength Cutoff Values for Potential Pigments

Material	Short Wavelength Cutoff (μm)	Long Wavelength Cutoff (μm)
Al_2O_3	0.24	4.0
ZnS	0.9	13
ZnSe	1.0	20

ting materials.[4] Zinc oxide, although not considered an infrared material, is widely used as a white pigment in plastic infrared lenses and windows. Of the materials possible for use in pigmenting HDPE, four were selected because of their transmission range in the pure state or past use of the material in plastic optics, as is the case for ZnO. Table I shows the ranges of transmission for the three other additives chosen.

The lower edge of transmission of a material depends on its energy gap. When photons impinge on a material, electron emission occurs. If the excited electrons have sufficient energy, they can cross the gap. A large energy gap means that only higher-energy photons will be absorbed; therefore, materials with large energy gaps transmit into the ultraviolet range. A low-energy gap allows only absorption of lower-energy photons, producing a short wavelength cutoff in the visible and infrared regions.

Interatomic bond strength and the molecular mass of a material determine the long wavelength cutoff. Molecules in a material vibrate in response to an applied electromagnetic field. Peak absorption occurs when the frequency of the field matches the resonant frequency of the molecule. Because materials with weak bonds and large molecular mass have lower resonant frequencies, they are good infrared transmitters. Other practical considerations in selecting pigments are that the pigment must mix evenly in high-density polyethylene and that pigment addition must not compromise the polymer's mechanical properties, which include shrink rate and impact strength. Color is an important attribute for customer satisfaction.[5] Experience indicates that sensor customers prefer a white or off-white color in the lenses. Between the long and short wavelength cutoff points, the material will refract light.

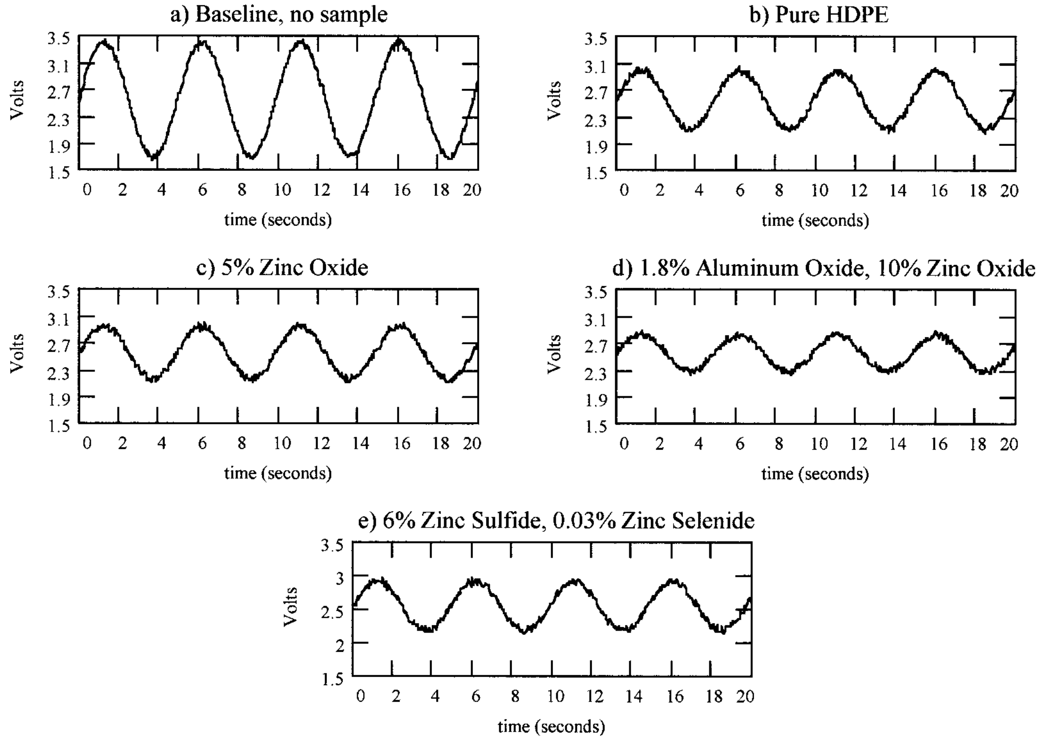
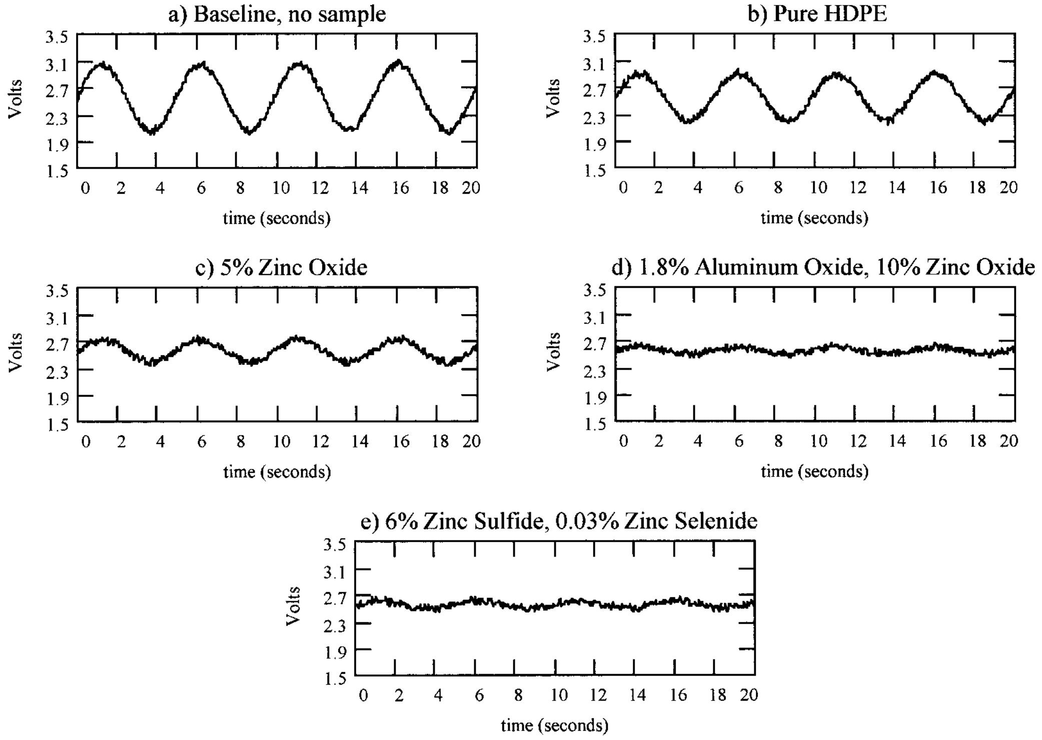


Figure 1 (a) Signal from the sensor with no sample placed in the radiation path. (b–e) Signals when samples with different pigments were placed between the sensor and blackbody.


a) Baseline, no sample

b) Pure HDPE

c) 5% Zinc Oxide

d) 1.8% Aluminum Oxide, 10% Zinc Oxide

e) 6% Zinc Sulfide, 0.03% Zinc Selenide

Figure 2 (a) Signal from the sensor with no sample placed in the radiation path. (b–e) Signals when samples with different pigments were placed between the sensor and white light source.

PROCEDURE, RESULTS, AND DISCUSSION

This study required us to produce many different samples. We prepared the initial samples in the laboratory. This reduced the cost of the study and the response time incurred by contracting a plastic extruder to do the work. This procedure consisted of the following fabrication steps: melting the HDPE polymer to a temperature 20–30% higher than its melting point, 130°C, adding powdered pigments and using an electric mixer to produce a homogeneous mixture, pouring the mixture into thin strips, and finally cutting the material into small pellets. Each 1.5–2.5 kg batch of pellets produced by the above processes was then injection-molded into flat strips and lenses.

We used our optical test procedure, described below, to identify the preliminary samples that were most likely to produce the results that we were looking for. After a sample showed promising results, we contracted a plastic compounding company to produce a larger sample using a twin-screw extruder with a processing temperature of 245°C. This temperature is similar to the temperature used in the injection-molding process.

To measure selectivity for mid-IR transmission, a blackbody and a white light source were used for determination of the amounts of IR and white radiation transmission. A C&K Systems XJ-440 passive infrared sensor measured the relative transmittance of the sample polymers. The instrument consisted of a Heimann Li958 pyroelectric device, supporting circuitry, and the sample lens under test. The sensor was not cooled or set up in a nitrogen atmosphere. The test used the conditions that the sensor and lens would experience in the field.

Baseline (100% transmittance) measurement for each batch of samples was the peak-to-peak voltage difference in the output signal with no sample in the radiation path. To obtain the material's percent transmittance, we inserted the sample into the radiation path and measured the output signal. We performed this test using the black body and white light source to determine the infrared and white light transmittances.

The blackbody had an aperture diameter of 25 mm and a cavity depth of 100 mm. The temperature was 38°C, average human body temperature. A mechanical chopper with a frequency of 0.25 Hz and a duty cycle of 50% modulated the energy from the blackbody.

Table II Transmittance of Pigmented Polymers

Additive	Percent Transmittance IR	Percent Transmittance White Light
None (pure HDPE)	0.53	0.69
ZnO	0.49	0.31
ZnS/ZnSe	0.36	0.08
Al_2O_3/ZnO	0.36	0.08

White light transmittance measurements were obtained in a similar manner. The light source was a halogen head lamp. The beam had a vertical spread of 9.5° and a horizontal spread of 31°. The lamp was positioned to obtain an intensity of 750 lx at the surface of the sensor. Power was cycled to the lamp at 0.25 Hz with a 50% duty cycle. To simulate the instrumental configuration in a security sensor, two sheets of plate glass approximately 6 mm thick were installed between the polymer sample and the radiation source. The glass prevents mid- and far-IR from reaching the sensor and simulates an actual installation, since most sensors are installed inside buildings. We used the glass plates only in the white light portion of the test. Testing using this setup is commonly used in the security industry and is referred to as the white light immunity test.[6]

A xenon arc lamp giving an intensity of 20 mW/cm^2 was used to accelerate UV radiation aging process in the polymers. The visible radiation emitted from the lamp occurs at discreet wavelengths in the range of about 450–800 nm. Brittleness of the aged polymers was determined using the Underwriter's Laboratories (UL) mechanical impact test.[7] In this test, a 68 g steel ball was dropped from two different heights to produce impacts of 5 and 10 J.

Aluminum oxide (Al_2O_3), zinc oxide (ZnO), zinc sulfide (ZnS), and zinc selenide (ZnSe) singly or in combination with each other produced varying results when added to HDPE. Zinc oxide (5% by weight) addition produced an off-white polymer, while pure zinc selenide (1% by weight) gave the plastic a dark bronze color, eliminating its practicality for this application. Further testing revealed that 0.02–0.06 wt % zinc selenide used in combination with zinc sulfide produced a variety of off-white shades.

We did not use master batches in the blending process. Our strategy was to control the mixture by closely controlling the formula. We produced a purchase specification based on the results of this study. Besides the grade of HDPE, this specifica-

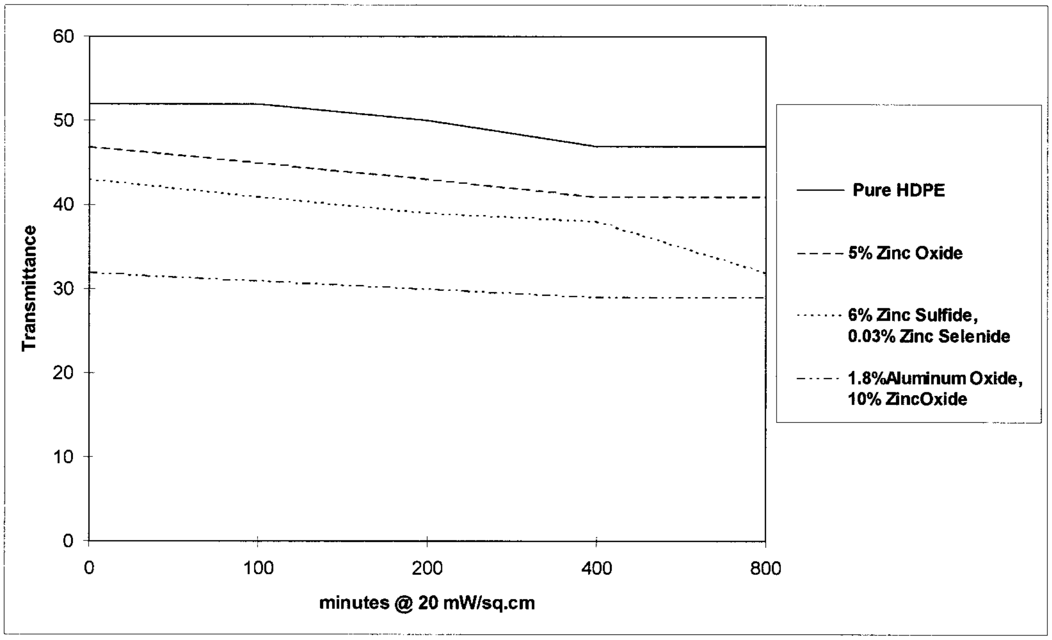


Figure 3 Transmittance of the undoped HDPE polymer and three pigmented samples, showing changes in transmittance with exposure to a xenon arc lamp of intensity 20 mW/square cm.

Table III Impact Results for Accelerated Aging Conditions

Aging Time (min)	Impact (J)	Pure HDPE	ZnO	ZnS/ZnSe	Al_2O_3/ZnO
0	6	Pass	Pass	Pass	Pass
	10	Pass	Pass	Pass	Pass
100	6	Pass	Pass	Pass	Pass
	10	Pass	Pass	Pass	Pass
200	6	Pass	Pass	Pass	Pass
	10	Pass	Pass	Pass	Fail
400	6	Pass	Pass	Pass	Pass
	10	Fail	Fail	Fail	Fail
800	6	Pass	Pass	Fail	Fail
	10	Fail	Fail	Fail	Fail

tion controls the particle size and purity of the powdered additives. Our first consideration was the repeatability of the optical performance. Repeatability of the color was a secondary consideration. To date, over 500,000 lenses have been produced with the compounds created from this study. We have not experienced any color-related problems.

Figures 1 and 2 show the peak-to-peak voltages obtained for the base line, pure HDPE, and three pigmented samples. To obtain the baseline, we positioned the passive infrared sensor in front of the blackbody and measured the signal produced by the sensor. This was a relative measurement only because the sensor is designed as a commercial motion sensor and its output is not calibrated to a scale of radiometric units. To obtain transmittances, we placed flat molded pieces of the sample material in the radiation path between the sensor and light source and repeated our measurements. These samples were flat sheets with a thickness of 0.6 mm and a surface finish of 2 μm. This type of sample represents a typical lens or window used in an infrared motion sensor.

In Figure 1, the baseline signal had an amplitude of 3.5 V, peak-to-peak. For the sample molded from pure HDPE, the signal dropped to 1.85 V, indicating a total transmittance of 0.53. Reflections at both surfaces contribute to some of the signal loss. The index of refraction for HDPE is 1.54 and Fresnel's equations predict a reflective signal loss of 0.0903. We removed the reflective loss from our raw data to obtain the material transmittances for each sample. Table II lists the results for each sample.

Figure 2 displays the measurements taken with the white light source and the passive infrared sensor. We positioned the sensor and white light source as described in the experimental procedure. We obtained the baseline and performed the measurements according to the procedure described above. For example, the baseline was 1.1 V peak-to-peak and the measurement for pure HDPE was 0.76 V. This indicates a total white light transmittance of 0.69. After removing the reflective losses, the material transmittance was 0.77. Table II lists the remaining results.

The data show that the white light transmittance of HDPE decreased as we added the powdered pigments to the plastic. According to the data in Table II, zinc oxide reduced white light transmittance from 0.77 to 0.40. The zinc sulfide and aluminum oxide blends further reduced white light transmittance to 0.17. Pigments also caused small to moderate decreases in infrared transmittance. Infrared transmittance ranged from 0.62 for pure HDPE to 0.42 for the aluminum oxide blend.

From the data, we selected the zinc sulfide–zinc selenide blend. This blend included 6% ZnS by mass, small amounts of ZnSe, UV stabilizers, and a process stabilizer. We found that by varying the quantity of ZnSe between 0.01 and 0.04% we could produce various shades of off-white, while maintaining good infrared transmittance and white light immunity.

Photodegradation is responsible for aging the material. Exposure to sunlight and some artificial light sources can damage the material's optical and mechanical properties. UV radiation from these sources can break down the chemical bonds in the polymer. Photodegradation can cause the material to crack, change color, become brittle, and lose its optical transmittance. To prevent photodegradation, we included a small amount of a hindered amine UV stabilizer in the mixture. This type of UV stabilizer works by reacting with free radicals that are formed when UV light begins to break apart the polymer's chemical bonds. We tested the material to verify that the loss of its transmittance is not significant over the lifetime of the product. We measured the optical properties of the material by exposing it to a xenon arc lamp and making transmittance measurements at specific intervals.

Estimates for UV irradiance in office installations were 0.2 μW/cm^2 for typical conditions and 1.8 μW/cm^2 for the worst case.[4] Typically, a sensor is installed facing away from windows and other lights. For such a scenario, the irradiance comes from indoor lighting. The worst case is for a sensor near a southward facing window. No qualified installer will place a sensor directly facing sunlight, due to potential false alarms, but for our test purposes, this represents a worst-case scenario. Sunlight is the main source of UV radiation in this case. Figure 3 shows the IR transmittance vs. time for polymers aged at accelerated rate (20 mW/cm^2).

At long exposure times, the ZnS/ZnSe pigmented sample showed a decrease in transmittance of about 10% between 600 and 800 min. Using the estimates above for irradiance, the loss is negligible over the 10 year product life. To test how the impact strength of the plastic responded to accelerated aging, we used a standard test specified by Underwriter's Laboratories. In this test, steel balls weighing 330 g were dropped onto the installed lenses from heights of 0.75 m and 1.5 m to produce impacts of 5 and 10 J. Impact results for the aged pigmented polymer are shown in Table III. The material failed with the 10 J impact at accelerated aging times of 400 h or greater. At low impact, 800 h of accelerated aging was required to make the material fail. No change in the optical properties with aging was noted except at long aging times. Typical problems in molding processes, such as excess shrinkage, uneven thickness, and failure to release from the mold, were not observed for the molded products.

SUMMARY AND CONCLUSIONS

Addition of ZnS/ZnSe pigment to high-density polyethylene altered its selectivity for human radiation sensing. In addition, the pigment did not alter the mechanical, materials processing, or aesthetic properties necessary for the application. Other compounds tested produced undesirable color, attenuated IR too much, or did not eliminate white light transmission. Pigment addition type and amount were empirical in this research, so there are many opportunities to explore different formulations and determine the scientific basis for the optical properties of pigmented plastics. Possibilities exist for tailoring IR transmission materials by adding different combinations of chalcogenides. The great advantage of using pigment suspended in polymer for IR materials is in the cost, but other factors, such as toughness or other physical properties, could also be an improvement over ceramic optics.

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