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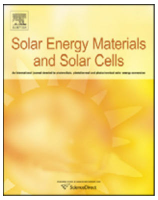

An investigation of the changes in poly(methyl methacrylate) specimens after exposure to ultra-violet light, heat, and humidity

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ABSTRACT

The degradation of poly(methyl methacrylate) (PMMA) exposed to ultra-violet (UV) light, heat, and humidity is examined using a variety of materials characterization techniques. Using contemporary material formulations, some of which are specifically marketed to the PV industry, techniques were identified that can readily discern material changes in PMMA degraded by artificial weathering. Separate PMMA formulations were categorized as “hazy” or “yellow”, based on their visual appearance after 18 cumulative months of indoor aging in an environmental chamber equipped with a xenon-arc lamp. The characteristics examined included: optical transmittance (and the corresponding yellowness index); surface roughness (examined via atomic force and scanning electron microscopy); surface chemistry (via X-ray photoelectron spectroscopy); elastic modulus and mechanical hardness (via nanoindentation); thermal decomposition (via thermogravimetric analysis); bulk chemistry (via nuclear magnetic resonance); molecular weight (via gel permeation chromatography); and optical fluorescence. The comparison between the most affected “hazy” and “yellow” specimens illustrates some of the ways these measurement techniques can be used to explore changes in application-critical characteristics and mechanisms involved in material degradation.

1. Introduction

Concentrating photovoltaic (CPV) systems use optical component(s) to focus the direct solar flux onto a relatively small photovoltaic (PV) cell [1]. The CPV approach uses higher efficiency cells and reduces cost by replacing large-area solar cells with less-expensive optical components. To realize a low levelized cost of electricity, the optical components must provide good performance over the desired service life of 25–30 years. Although the advancement of high-efficiency PV cells (such as multijunction III–V technology) has recently motivated interest in CPV, understanding related to the durability of the optical components remains limited.

Many of the recently proposed CPV systems use an optically refractive element, *i.e.*, Fresnel lens. This may consist of a monolithically constructed lens composed of poly(methyl methacrylate) (PMMA), a silicone on glass (SoG) laminated composite, or a PMMA on glass (PoG) laminated composite [2]. Factors including cost, weight, optical performance [3], and attachment of the lens affect the CPV module design and its subsequent cost. A strong motivation therefore exists for the selection of the appropriate type(s) of lens, suitable for extended outdoor deployment.

Recent studies of the durability of CPV lens technology include Refs. [4,5,6,7], and the subject has been reviewed in Ref. [2]. Relevant topics include the degradation of the component material(s), fracture, mechanical fatigue, delamination, physical aging (visco-elastic flow and shape change), solid erosion (abrasion and wear) of the field-exposed surface, soiling (the accumulation of airborne contamination), solarization (change in the optical performance based on the redox balance within glass), and chemical corrosion [2]. Material degradation may occur as the result of ultraviolet (UV) radiation, temperature, and moisture. Chemical corrosion may occur as the result of airborne species, including: acidic (or basic) rain, industrial chemicals, or ozone. Many of the studies in the literature focus on material specific issues, especially the optical performance.

The vast majority of the literature examines the lower-cost PMMA lens implementation, which has yet to be formally proven site sufficient. There is no SoG or PoG durability data available

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in the literature, recent publications have instead focused on evaluating the use of PMMA in CPV Fresnel lenses. PMMA formulations have continued to evolve, so it is unclear whether studies initiated more than 20 years ago will be predictive of the performance of today's PMMA. Additives including the UV absorbers (UVA), hindered amine light stabilizers (HALS), and antioxidants (AO) may all be different in contemporary PMMA.

The results of our previous PMMA study (reported after six months of cumulative indoor aging in the environmental chamber equipped with a xenon-arc lamp) [5] are as follows: The transmittance of all specimens [including unpatterned PMMA sheet, contemporary Fresnel lenses, and previously deployed ("veteran") lenses] was reduced with aging. Optical attenuation increased more significantly at the shorter wavelengths above the UV cut-off wavelength. In many specimens, the UV cut-off wavelength was increased with age, while a few specimens demonstrated a UV cut-off at shorter wavelengths. The effects of soiling (which could be reduced by cleaning) were found to be similar to those of degradation, where transmittance was reduced at shorter wavelengths. Change in optical performance could not be attributed to moisture absorption, which may specifically affect transmittance at the wavelengths of 1415, 1910, 2160, 2700, and 2955 nm (wavenumbers of 7067, 5244, 4630, 3708, and 3384 cm^{-1}, respectively) [8]. An asymptotic mass loss as great as 1.3% was attributed to the loss of the volatile by-products of degradation. The contact angle was reduced with age, with the contact angle for the veteran lenses being significantly lower than unstressed PMMA. Contact angle, however, was largely restored when the specimens were inadvertently cleaned at 6 months prior to measurement. Radial cracks were observed about the center of an injection molded lens stressed in a damp heat (85 °C/85% relative humidity) chamber. The surface roughness was significantly greater for veteran lenses, where features at the surface suggested the processes of solid erosion and scratching (from cleaning) in addition to embedded material. The largest features observed at the surface approached 4 μm in width and 400 nm in depth. Lastly, Fourier transform infrared (FTIR) spectroscopy did not readily distinguish between stressed and unstressed specimens, a result consistent with the damage mechanism of chain scission.

The goal of this study is to examine the characteristics and related characterization methods most relevant to degraded PMMA, using a variety of contemporary material formulations. The PMMA specimens were subjected to accelerated aging in a closed-loop-controlled environmental chamber. The specimens are examined here at 12 and 18 cumulative months of aging relative to their previously reported condition at 6 months [5]. As before, the optical transmittance and surface morphology are investigated. Characteristics not previously examined include: surface chemistry (examined using X-Ray photoelectron spectroscopy); mechanical modulus and hardness (examined using instrumented indentation); thermal degradation (examined using thermogravimetric analysis); bulk chemistry (examined using nuclear magnetic resonance); molecular weight (examined using gel permeation chromatography); and electronic structure (examined using fluorescence spectroscopy). The study examines performance characteristics essential to the CPV application in addition to characteristics that may be used to quantify the extent of damage or investigate the degradation mechanisms. The results for the indoor aging are compared to similar work in the literature, as well as to previous outdoor studies.

2. Experimental

2.1. Details of the specimens

The specimens examined include 11 varieties of stock (sheet) PMMA, one Fresnel lens with a linear focus, eight varieties of lenses with a spot focus, and five varieties of veteran spot-focus lenses. Five of the material specimens were marketed to the PV industry, Fig. 3. For specimens in sheet form, some type of post-processing is required for lens forming. Specifics of the manufacturing procedure for PMMA may affect its durability. For example, PMMA extruded from a monomer mixture is frequently pelletized (ground) for storage prior to further use, e.g., a second extrusion to the intended shape. Pelletizing may enable contamination (resulting in batch to batch variation), while the re-use of material establishes additional thermal history. Spurious chromophore content or time at temperature may subsequently limit lifetime in the field. The manufacturing process itself is another example, where cast PMMA typically has a greater molecular weight relative to extruded PMMA. The initial molecular weight may prove to correspond to field longevity.

In most cases, the optical measurements were averaged for three replicate specimens. One of the replicates was then taken for destructive characterizations after 12 months cumulative aging. A wide variety of stock specimens, including formulations not intended for outdoor use, was purposely chosen here to identify all possible failure modes. The veteran lenses included those fielded in an urban desert environment (Phoenix, AZ) on a tracker for 8, 22, and 27 years. Since the summary [5], two veteran specimens (deployed for 13 and 3 years in Phoenix) were added to the study. A PMMA specimen ("clinical grade", lacking formulation additives with minimal residual monomer, P/N ME303011, Goodfellow Corp.) was also characterized using certain methods. Except where noted, specimens were not cleaned prior to measurement.

2.2. Aging of the material specimens

Specimens were stressed in a Ci4000 Weather-Ometer (ATLAS Material Testing Technology LLC), operating at the chamber temperature of 60 °C and relative humidity (RH) of 60%, rendering a black-panel temperature of 85 ± 7 °C. (The local conditions for transparent polymeric specimens were previously verified at 70 °C and 38% RH, as facilitated by their optical absorptance). Specimens were placed on a carrousel that rotates about a xenon-arc lamp. An inner glass filter (Right Light, ATLAS Material Testing Technology LLC) was used to filter the lamp in conjunction with a coated infrared absorbing quartz outer glass filter so that the lamp closely replicates the AM1.5 spectrum, with the power level being controlled to 114 $\mathrm{W\,m^{-2}}$ for $300 \leq \lambda \leq 400$ nm, i.e., $2.5\times$ the AM1.5 global spectrum [9]. The Ci4000 therefore provides $\sim 8\times$ the raw UV daily dose, assuming a field UV dose of 6 $\mathrm{h\,d^{-1}}$ of the AM1.5 global spectrum. The site-specific acceleration factor for the degradation rate depends on the climate of the deployment location, being likely coupled to the factors of temperature and humidity. Specimens were stressed for the cumulative durations of 0, 1, 2, 4, 6, 12, and 18 months, where one month corresponds to 30 day. Subsequent examinations are intended to occur every 6 months.

2.3. Characterization of the stressed specimens

A variety of methods were used to study the indoor stressed PMMA specimens. Some of these methods are in addition to those used in previous characterization [5,8]. Based on the results after 12 months cumulative stress, two PMMA formulations were examined in detail using each technique.

2.3.1. Optical transmittance, mass loss, and surface energy characterization

Optical transmittance, mass, contact angle, and visual appearance were examined after each aging interval. Optical measurements were