



Analysis of Artificially Weathered PET and a Separate PET Hydrolysis Evaluation Using the 4300 Handheld FTIR

Application Note

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Introduction

Elucidating chemical changes in carbon fiber composites prior to physical degradation has been effectively demonstrated using handheld FTIR analyzers [1]. This application note shows that a handheld infrared spectrometer is equally effective at measuring early onset chemical changes in environmentally stressed PET polymer, which precede cracking and other physical degradation processes. This is an important issue in applications where polymers (as well as other materials such as paints and coatings) are exposed to environmental conditions varying from climatic conditions that depend on their geographic locale to complete submersion, as in the case of marine paints. The commercial availability of handheld FTIR spectrometers affords the capability of nondestructively measuring areas of large polymer sheets, as well as other coatings.

A wide variety of polymer types are used in the photovoltaic industry as encapsulants, substrates, backsheets, adhesives, sealants, packaging, cabling, fasteners, frames, and junction boxes. PET is one of the most widely used commodity thermoplastics, and is frequently employed for the frames and junction boxes used to fit photovoltaic cells to buildings. In recent years, formulated PET has been considered for use in photovoltaic devices to replace other more expensive backsheet materials such as glass, PEN, or PVF. This requires that in-service PET has the correct additive(s) incorporated to enhance the weather resistance of the base polymer and thereby meet the expected lifetime of the solar panel.



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The polymer materials used in solar cells are exposed to a host of environmental and weather related stresses including light, temperature, moisture, and electric fields. This exposure initially leads to subtle chemical changes on the polymer surface. As the environmental stress continues, chemical and compositional changes become more severe, and there is deeper and more prevalent damage. At some point, the severity of the degradation leads to stress cracking, mass loss, and physical shrinkage of the material (Figure 1). Additive chemicals mixed in the base polymer can help delay these changes, but the wrong additive may have no effect, or worse, actually speed up the degradation.

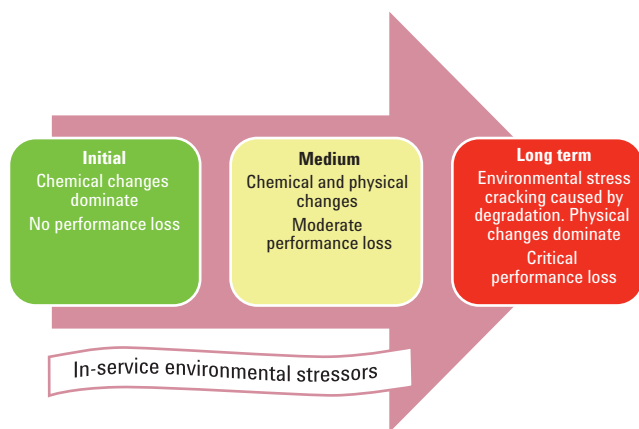


Figure 1. The common degradation pathway of polymers is shown, an arrow indicates increasing time/dosage.

An Agilent 4300 Handheld FTIR was used to measure chemical changes in PET polymer samples. The spectral data measured the effects of weathering in a controlled weatherometer (WOM) chamber, and separately, the effects of hydrolysis on fully submerged polymer samples. The spectroscopic changes were monitored as a function of time to elucidate the chemical changes related to each stress environment. The onset of these chemical changes provided an excellent benchmark performance for additive-free PET film. Subsequent proprietary formulations can be examined to gauge the effectiveness of degradation-resistant additives, compared to the benchmarked PET results, as well as a function of the additives costs. The conditions used to stress these films were selected to provide spectral results from incipient changes, that is, in the initial-medium range where the physical changes are less dominant and not visibly observable. The complexity of the chemical changes suit the use of multivariate based models, which were created and implemented into the Agilent 4300 Microlab PC Software and combined with conditional reporting. Traditional univariate analysis was

performed but correlated worse, as it could not account for the number and complexity of the changes.

Infrared spectroscopy for monitoring environmentally induced changes in polymers

There are major advantages in applying a rapid, nondestructive method to detect and analyze the onset of environment related stressors:

- Enables the selection of optimized additive formulations to the base polymer.

Determining the early onset of chemical changes reduces the cost of testing programs by rapidly eliminating those formulations likely to fail or not reach the expected performance criteria. Using the infrared analyzer, in combination with an accelerated environmental chamber, enables more rapid decisions to optimize the additive formulation. Handheld FTIR, which does not require the excision of a sample for lab analysis, means that the test protocol does not need to be disturbed for analysis, and the analysis can be carried out on-site, in actual weathering field locations.

- Enables nondestructive on-site analysis of in-service products containing polymers (for example, solar panels and so forth).

Extensive knowledge of the spectroscopic changes in polymers as a function of environmental stresses is gained during the development phase, leading to the selection of the proper additive formulation. This information provides maintenance and upkeep personnel a powerful nondestructive testing method capable of determining the condition of installed systems with respect to these stressors.

Method and Instrumentation

Mitsubishi Hostaphan RNK 50 poly (ethylene terephthalate) 50- μ m films were used in this project. This specific PET product has no extra performance additives, and the films were aged for 0, 5, and 10 days in an Atlas XLS+ xenon arc lamp WOM. The films were aged at 700 watts/m² irradiance with filter set A. This filter alters the chamber's xenon arc lamp to mimic the distribution of spectral frequencies in sunlight. The temperature of the chamber was set to 40 °C, the minimum achievable without external cooling apparatus. This light intensity was roughly equivalent to the power of the sun at the equator. The weathering chamber was set to constantly irradiate at this calibrated energy onto the thin PET films. Therefore, there was no night/day or radiant/irradiance cycling that results in only moderate rates of accelerated degradation.

A 4300 Handheld FTIR (Figure 2), equipped with either a diamond ATR or an external reflectance interface, was used to measure the 50- μm PET films. The weathered surface of the films (top, that is, facing the xenon lamp) and the lesser-exposed bottom surface of the films were both analyzed by FTIR. All FTIR spectra were collected at 4 cm^{-1} resolution, and consisted of 64 co-added interferograms resulting in a spectral acquisition time of ~ 35 seconds. The measured spectral range was 4,000–650 cm^{-1} . Films were placed flat to the bottom plate at the same horizontal plane as the irradiance calibration standard.



Figure 2. Agilent 4300 Handheld FTIR with diamond ATR and external reflectance sample interfaces used for measurement of PET. Sample interfaces are instantly interchangeable with no realignment necessary.

For the accelerated hydrolysis experiments, PET samples were refluxed in distilled water over a period of 0 to 14 days while fully submerged in water. The samples were measured *ex-situ* after drying, using the 4300 Handheld FTIR equipped with a spherical diamond ATR interface. The spectra were recorded at 4 cm^{-1} resolution, 64 co-added interferograms, and a spectral range of 4,000–650 cm^{-1} .

Results and Discussion

Simulated weathering of PET using a weatherometer

As expected, the infrared spectra of the top face of the thin film surface exhibited the greatest level of change, and only very slight differences were observed on the bottom side of the PET thin films. Since the PET material is free of additives, the light, heat, and moisture present in the chamber induces chemical and physical changes in the industry-standard base polymer. Results from infrared measurements of these samples were useful as a control benchmark. The results from similar measurements of PET, with additive formulations, can be compared to determine the best-in-class formulations.

The spectra of the top-side exposed films exhibit oxidation absorbance at 1,773 cm^{-1} and 1,690 cm^{-1} , consistent with typical oxidation products of hydrocarbons (Figure 3). The ISO 10640:2011(E) [2] standard also notes these same absorbance frequencies to measure the critical photoproducts in PET or polybutylene terephthalate (PBT). The 1,773 cm^{-1} band is typically assigned to the formation of peresters (R-C(=O)-O-O-R), however, other oxidation products may also give rise to this band. The strong oxidation band at 1,690 cm^{-1} is consistent with an aromatic carboxylic acid functional group, such as benzoic or terephthalic acids, which are common reaction products from photo-initialized hydrolysis. The broader absorbance observed in the 1,450–1,150 cm^{-1} region is also consistent with OH deformation and C-O stretch absorbance from carboxylic acid groups. In addition to the above specific vibrational changes, some general indicators of aging such as band broadening and baseline shifting were observed.

After 10 days of exposure, some oxidative damage was observed on the bottom side of the film. The photo-degradation of PET forms two types of radicals; an alkoxy type radical and a hydroxyl radical. The latter is highly mobile [3] and can diffuse through the polymer matrix from the top side to the bottom face of the film. This may be one possible source of the degradation measured on the bottom sides of the exposed films; secondary reflected light or thermal oxidation may also contribute to the degradation observed on the bottom surface.

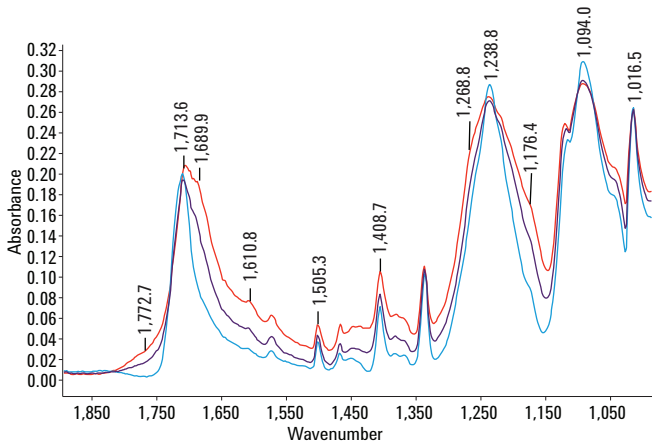


Figure 3. ATR spectra of weathered PET at 0 days (blue), 5 days (purple), and 10 days (red) of WOM chamber exposure.

Multiple discrete spectra from the top surface of the PET films were used to create a partial least squares (PLS) calibration for oxidative PET degradation. PLS calibrations are used to create multivariate correlations and allow multiple IR regions in the spectra to be used to build a calibration model. The PLS calibration (Figure 4) employed a gap 2nd derivative (nine points smoothing) and multiplicative scatter correction (MSC) preprocessing. The calibration with five factors (latent variables) resulted in a correlation coefficient of $R^2 = 0.9871$. This correlation coefficient is somewhat lower than a traditional FTIR calibration with a single analyte in a uniform polymer matrix, in which one might expect an R^2 of >0.99 . However, polymer oxidation is a complex mechanism with both chemical and physical variables which hinder direct polymer analysis correlations such as those described in this application note. The ISO 10640:2011 [2] (Section 3, 4 and annex A) standard describes the variables inherent in photo ageing measurements of polymers.

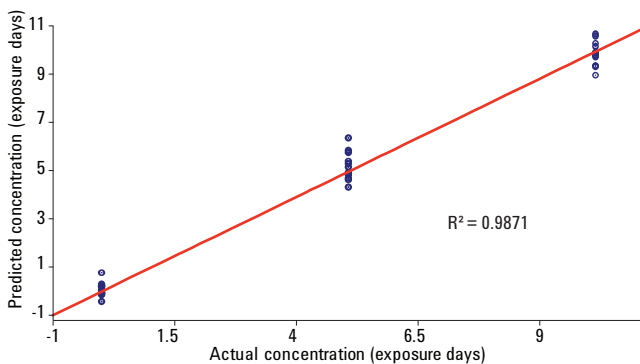


Figure 4. PLS actual versus predicted calibration plot for 0, 5, and 10 days of WOM-exposed PET (top side). This PLS calibration model uses mean centering, 2nd derivative (9 points), MSC, and 5 factors.

Spectra from the bottom side of the PET films were tested against this calibration. The results indicate little or no oxidative damage in the 0 and 5-day exposure coupons, but the bottom surface spectra of the 10-day exposure coupons exhibit oxidative exposure equivalent to 1 day of top surface exposure. Since the bottom side of the PET film spectra are not used in the PLS model, their results can be used to validate the models performance. The degree of damage in the bottom side of an exposed polymer film, relative to the damage on the exposed side, is a useful measurement for ascertaining the optimum film thickness with regard to weather-resistance.

The external reflectance (ER) infrared data also provide a similar performing correlation with amount of exposure. The ER PLS calibration model indicates an $R^2 = 0.987$ with two factors, using mean centering and gap 2nd derivative (5 points) for the preprocessing. Either sample measurement technique can be used to correlate the weathering damage of PET. The ATR spectra are more convenient to interpret and evaluate since they are more frequently described in literature, and more often contained in spectral libraries. The penetration depth of ATR is typically 2–3 μm , yielding results that are particularly surface-sensitive and ideally suited to monitor and evaluate chemical changes at or near the surface. The ER interface allows very easy sampling and minimal contact with the PET sample, but the spectra are less familiar in appearance (Figure 5) and cannot be analyzed with an ATR library or data set. ER spectra contain primarily first-surface reflected IR light, specular reflectance, and some degree of diffusely reflected IR light. The rougher the surface, the more diffuse reflectance will occur and, thus, a higher depth of penetration. Since highly photo-damaged polymers develop a rough surface, the ER measurement may have an advantage in this condition.

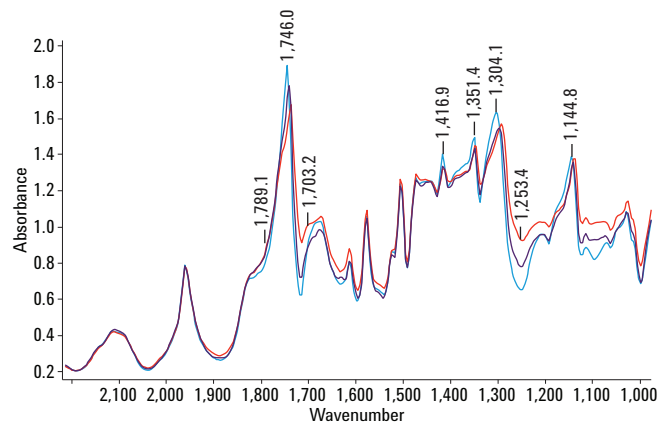


Figure 5. External reflectance (ER) infrared spectra of WOM-exposed PET: 0 days (blue), 5 days (maroon), 10 days (red).

The PLS calibration models can be incorporated into the 4300 MicroLab Software to predict the equivalent weathering of an unknown sample. The exposed PET sample shown in Figure 6 indicates a high degree of oxidation, equivalent to 10 days of accelerated WOM exposure. The software also evaluates the Mahalanobis distance, as a secondary check, to gauge whether the sample spectrum is appropriate for the model. High values indicate the sample is different from the calibration set.

Marginal (yellow) and critical (red) thresholds are set in the method to provide actionable limits for unknown damaged samples. The Mahalanobis distance (M-distance) field in Figure 6 indicates the sample is matching or fits the calibration set, within an acceptable range. Samples with M-distances greater than six are considered statistically different from the calibration set. Samples that are not PET will also be flagged with high M-distance warnings. Comparison of the PET data from these experiments to those of levels of polymer oxidation from natural and artificial aging in the literature [4], indicate that 1 day of WOM exposure in nonstabilized PET is approximately equivalent to 2 years of ambient weather exposure in fully stabilized PET. This calculation is based on the conditions expected in a photovoltaic cell application, and takes into account the indirect exposure to sunlight.

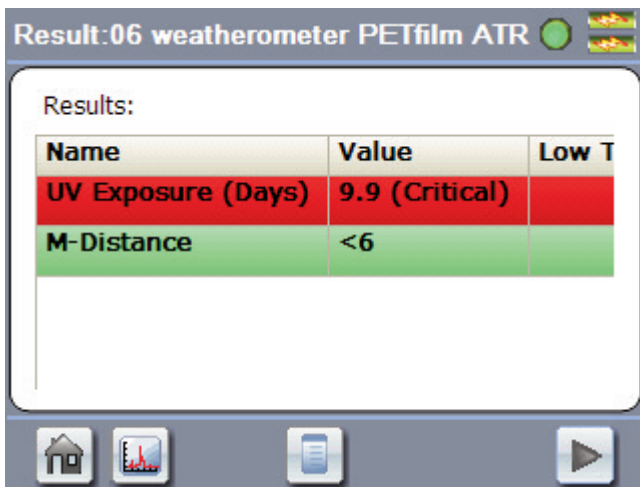


Figure 6. Results from this sample of PET indicate a significant degree of oxidation and alerts the user through a color coded (red) warning. The level for the warning, red critical value, can be tailored to suit.

Hydrolysis of PET

The backsheets of solar panels are typically exposed to above-ambient temperatures, which are especially higher in tropical climates. The following experiment was designed to mimic these conditions and provide information regarding the effectiveness of antihydrolysis additives in PET, without photo-induced events.

PET samples, having been immersed in refluxing distilled water for 0, 3, 7, 10, and 14 days to accelerate hydrolysis, were measured with the 4300 Handheld FTIR equipped with the spherical diamond ATR sample interface. The differences in spectral features of PET exposed to these conditions are weaker, less visible, and mainly involve changes in the aromatic ring vibration bands. This is consistent with published research indicating hydroxyl free radical reactions as the sole source of chemical change in the samples. This polymer system was exposed to two major stressors; temperature, the boiling point of water, along with full submersion of the PET samples. The full sample submersion virtually removes any photo-degradation or oxygen-based changes, as oxygen and light are excluded from the experiment. PLS regression was used to correlate the spectra with the time-based degree of hydrolysis (Figure 7). The model used 2nd derivative (12 points) and standard normal variate (SNV) preprocessing to produce an acceptable grouping of replicates, resulting in a correlation coefficient of $R^2 = 0.9131$. Only two PLS factors were necessary to produce the best performing calibration with the ATR data. Some of the samples became brittle, making sampling more difficult. However, the method and calibration was sufficient to categorize the hydrolysis into low (0–3 days), medium (3–7 days), and high (> 7 days) ranges.

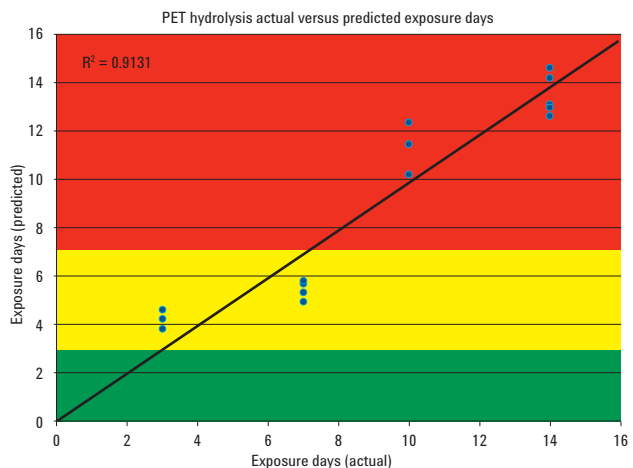
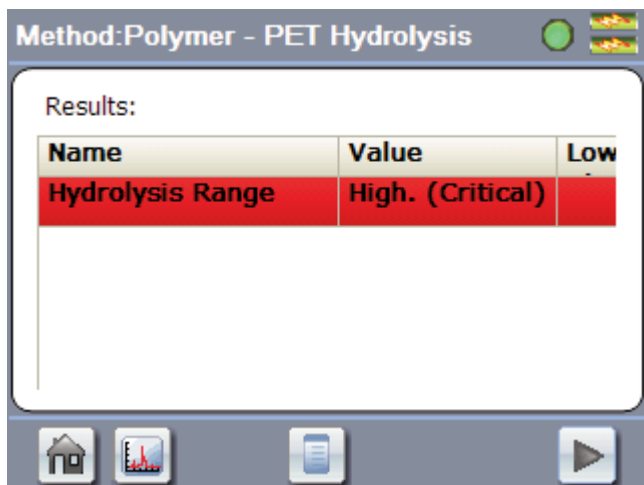


Figure 7. The ATR 4300 PLS actual versus predicted calibration plot for 0, 3, 7, 10, and 14 days of hydrolysis-exposed PET.

These hydrolysis ranges can be incorporated in the Microlab PC software using the conditional reporting feature, and used to report an appropriate text message depending on the model's prediction (Figure 8).



The screenshot shows a software window titled "Method: Polymer - PET Hydrolysis". Inside the window, there is a "Results:" section containing a table with three columns: "Name", "Value", and "Low". The "Name" column contains "Hydrolysis Range", the "Value" column contains "High. (Critical)", and the "Low" column is empty. The entire table is highlighted in red, indicating a critical warning. At the bottom of the window, there are icons for home, a graph, a document, and a play button.

Name	Value	Low
Hydrolysis Range	High. (Critical)	

Figure 8. This PET sample indicates a critical level of hydrolysis. The method shown is incorporated in the Agilent 4300 MicroLab Software and warns the user through a color-coded message. The level can be chosen and changed by the user.

Conclusions

We have shown that a handheld FTIR analyzer, the Agilent 4300 Handheld FTIR spectrometer, can rapidly elucidate early changes in PET polymer after exposure to simulated constant irradiance sunlight, 40 °C temperatures, and air. The PET film that had been exposed in the weatherometer exhibited predominantly chemical changes, with the actual weight and physical dimensions of the sample remaining unchanged. A separate hydrolysis experiment enabled the chemical changes in submerged samples to be modeled in isolation of the oxidative or photo-degradative events.

The 4300 Handheld FTIR can rapidly determine the equivalent aging time of PET formulations with regard to hydrolysis and photo-degradation. This enables more efficient determination of additive effectiveness in less time. The system can alert the user if the polymeric material is exhibiting signs of significant change through color-coded warnings.

The information from these testing protocols results in a new nondestructive, on-site method for measuring the aging of polymers used in solar panels, or in other industrial applications. The ruggedness, performance, and ease-of-use of the 4300 Handheld FTIR system maximizes the value of the technology for field use, and represents a new means for on-site determination of deleterious changes in a wide range of organic-based materials. This capability is especially applicable to on-site testing in weathering fields, where samples are aged in real time, under actual ambient conditions.

Acknowledgments

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References

1. F. Higgins, "Non-Destructive Evaluation of Composite Thermal Damage with Agilent's New Handheld 4300 FTIR" March 2, 2014 Retrieved from <http://www.chem.agilent.com/Library/applications/5991-4037EN.pdf>
2. ISO 10640:2011(E), Plastics – Methodology for assessing polymer photoageing by FTIR and UV/Visible spectroscopy, Section 4.2, Table 1 – Critical photoproducts and modified properties.
3. S. Junkichi, "Radical Migration as an elementary process in degradation", *Pure & Appl. Chem.*, Vol. **55**, No. 10, pp. 1595-1601, 1983.
4. W.J. Brennan, S.J. Sheperd, "Developments in weatherable Polyester Films For Photovoltaic Applications" DuPont Teijin Films, http://www1.eere.energy.gov/solar/pdfs/pvmrw2011_p62_csi_brennan.pdf

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