

Weather-Induced Degradation Study of High Density Polyethylene Using the Photoprobe

Application Note

Polymer

Author:

Karen Sam

Abstract

This application note presents data on a rapid, automated polymer degradation study under ultraviolet (UV) light with the presence of oxygen at a controlled temperature.

Introduction

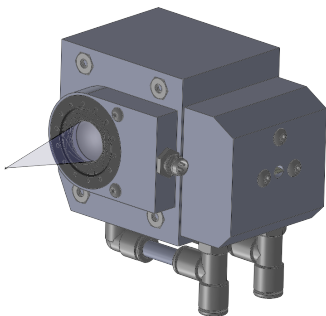
Three mechanisms of polymer degradation have been known as enzymatic, hydrolytic and oxidative¹. The oxidative degradation is caused by free radicals that are formed by the ultraviolet radiation from the sun at elevated temperature. These free radicals lead to bond cleavage in the polymer chains in the presence of oxygen. Traditional oxidative degradation study takes from hours to days to complete due to limited light intensity. CDS's novel Photoprobe is using free-space focusing technology and improves the light intensity to 800 mW/mm² within 260 – 400 nm irradiation wavelength, which reduces the time on weather-induced degradation study down to minutes.

Experiment Setup

A CDS 6200 Pyroprobe equipped with Drop-In-Sample Chamber (DISC) and Photoprobe was used, and an autosampler module was installed to automate the sequence. A High Density Polyethylene (HDPE) sample of 120 µg was irradiated in the DISC with the presence of air as reactant gas at elevated temperature. The volatiles generated from the photo-reaction were trapped on the analytical trap, and then desorbed to the GC/MS. Evolved gas analysis was also performed on the original and irradiated HDPE to observe how it had changed. A DISC quartz tube was used as the sample vessel.

Weathering method

DISC:	60°C	GC/MS	
UV irradiation:	30min	Column:	5% phenyl (30m x 0.25mm)
Reactant Gas:	Air 25mL/min	Carrier:	Helium, 20:1 split
Trap Rest:	40°C	Column Flow:	1.25mL/min
Trap Final:	300°C 3 min	Injector:	320°C
Trap Sorbent:	Tenax	Oven:	40°C for 2 minutes
Interface:	300°C		12°C/min to 320°C
Valve Oven:	350°C	Mass Range:	35-600amu
Transfer Line:	375°C		



EGA method

DISC Initial:	100°C	GC/MS	
DISC Final:	800°C	Column:	none: fused silica 1m
DISC Ramp:	100°C per min	Carrier:	Helium, 80:1 split
Interface:	300°C	Column Flow:	1.25mL/min
Valve Oven:	300°C	Injector:	300°C
		Oven:	Isothermal 300°C
		Mass Range:	35-600amu

Results and Discussions

HDPE under UV irradiation in an air atmosphere at a 60°C set-point produced triplicate peaks associated with random scission of the polymer backbone. Small amounts of aldehydes and alcohols are also identified, as shown in Figure 1.

Near UV light has enough energy to break most common chemical bonds, such as the C-C bonds in the HDPE chain. Once this occurs, free radicals are formed, which can form hydroperoxides (R-O-O·) when oxygen from the atmosphere, is added to the free radical. This radical grabs a hydrogen to form a hydroperoxide (R-O-O-H), which can decompose to form an alkoxy radical (R-O·). The alkoxy radical can stabilize by forming a double bond with beta scission, creating an aldehyde (R=O), or by abstracting a hydrogen to form an alcohol (R-OH)².

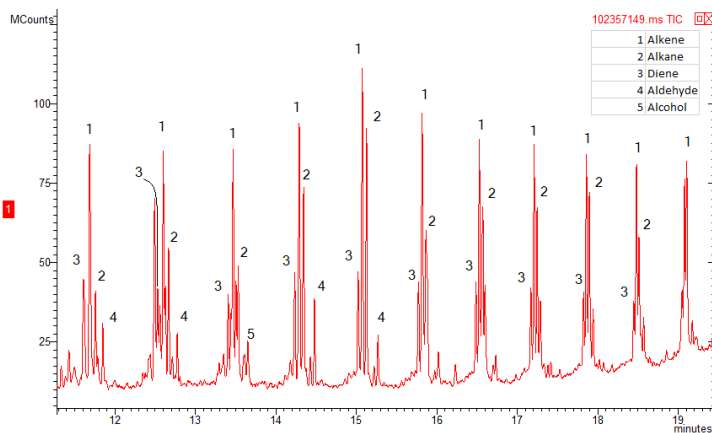


Figure 1. Photo Oxidative Degradation Products of HDPE.

Besides the traditional pyrolysis study, a 7-minute Evolved Gas Analysis (EGA) run was also completed to demonstrate a fast screening technique to differentiate the material that has been degraded by extended exposure to sun light. Figure 2 shows overlay of EGA runs between photo-oxidated HDPE and unaltered HDPE. A peak shift of 7°C was observed.

Conclusions

In addition to analytical pyrolysis, the Photoprobe, the newest addition to the Pyroprobe, can perform online weathering studies with hours of time saved in the UV irradiation step.

References:

1. Ojeda, Telmo. "Polymers and the Environment." *Polymer Science* 23 (2013).
2. Rånby, Bengt. "Photodegradation and Photo-oxidation of Synthetic Polymers." *Journal of Analytical and Applied Pyrolysis* 15(1989):237-247.

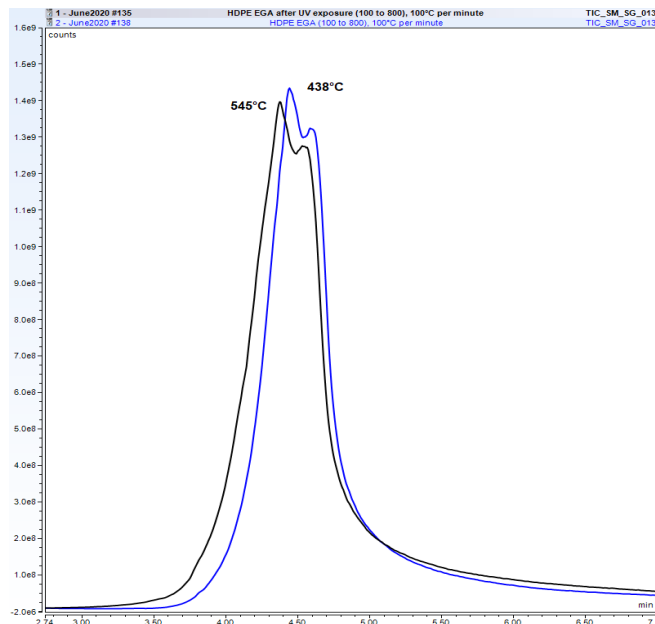


Figure 2. EGA overlay of HDPE (blue), and irradiated HDPE (black).