



## Textural, surface and chemical properties of polyvinyl chloride particles degraded in a simulated environment

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### ABSTRACT

Virgin polyvinyl chloride (PVC) particles were exposed to heat, ultraviolet B (UVB) and solar radiation either in artificial seawater or in air for different periods of time. The surface and chemical properties of fresh and degraded particle surfaces were determined via image analysis using scanning electron micrographs, a Brunauer-Emmett-Teller (BET) specific surface area analyzer and infrared spectroscopy. Thermal and UVB degradation resulted in unique PVC morphologies. In addition, the increased presences of functional groups were evident as dehydrochlorination and oxidation during the degradation process, which altered the chemical properties of PVC. In contrast, under solar exposure with or without seawater, unevenness to the surface was noted that seems to originate from degradation of the PVC surface; in addition, no new functional groups were found. This suggests that the chemical properties of PVC are stable over extended periods in the marine environment.

### 1. Introduction

Polyvinyl chloride (PVC) is a synthetic resin made by polymerization of vinyl chloride monomer (VCM), developed in 1926 by Waldo Semon and the B.F. Goodrich Company. This material is the third-most widely-produced plastic in the world, after polyethylene and polypropylene, with 37.3 million tons consumed globally in 2014 and estimated to reach 50.27 million tons by 2020 (Business Wire, 2016). PVC plays an important role in our daily lives as it composes many objects of daily use in building, transport, packaging, and electrical/electronic and healthcare applications. It is estimated that global demand for PVC will rise by about 3.2% per year through to 2021 (Ceresana, 2014). Many PVC products end up as *plastic marine debris*, derived not only from land-based sources, including (1) storm water discharge, (2) combined sewer overflows, (3) littering, (4) solid waste disposal and landfills, and (5) industrial activities, but also from ocean-based sources, including (1) commercial fishing, (2) recreational boating, (3) merchant, military and research vessel activity, and (4) offshore oil and gas extraction and exploration (Allsopp et al., 2006; Auta et al., 2017). Marine litter might be on a beach, in a saltwater wetland or other marine environment for hundreds of years and suffer from fragmentation, photo degradation, thermal degradation, biodegradation and

other processes (Baulch and Perry, 2014; Syakti et al., 2017; ter Halle et al., 2017).

Marine habitats and their biota are affected by micro-plastics, which are defined as plastic particles smaller than 5 mm and are spread rapidly in geographical terms (Ivar do Sul and Costa, 2014; Leslie et al., 2017). The impact of plastic pollution via animal ingestion and entanglement ranges through marine fauna from zooplankton to organisms at higher trophic levels (Besseling et al., 2017; Connors et al., 2017; Hermesen et al., 2017; Hirai et al., 2011; Long et al., 2017; Rist et al., 2017; Sharma and Chatterjee, 2017; Steer et al., 2017). Organisms that ingest micro-plastics may not only suffer physical harm, such as internal abrasion and blockage, but they are also exposed to chemical additives in plastics, which are often persistent, bioaccumulative, and toxic chemicals that adsorb and concentrate on plastic in the water column (Baulch and Perry, 2014; Fossi et al., 2017; Massos and Turner, 2017).

Teuten et al. (Teuten et al., 2009) suggested that sorption and desorption are essential in governing the distribution, persistence, and ecological impact of hydrophobic anthropogenic contaminants in terrestrial and aquatic systems. In addition, he pointed out that the extent and rate of hydrophobic organic contaminant (HOC) sorption and desorption are influenced by factors including the properties of the

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sorbent (i.e., sorbent organic matter) and sorbate (i.e., HOC), dissolved organic compounds in the aqueous phase, pH and temperature (Teuten et al., 2009). The sorption distribution coefficient of phenanthrene onto virgin PVC has been found to be as high as  $1650 \text{ L kg}^{-1}$ , though salinity was found to have insignificant effect on the time required to reach equilibrium (Bakir et al., 2014; Teuten et al., 2007). Furthermore, surface properties such as surface functional groups, surface topography, zero point charge, and color change of eroded PVC collected from the coastal environment show evidence of transformations during degradation. Surface alterations that arise during degradation might partially explain the interactions between plastics, microbes, and pollutants (Fisner et al., 2017; Fotopoulou and Karapanagioti, 2015; Rummel et al., 2017). However, earlier work used polymer samples that were collected directly from coastal environments and compared with virgin plastic pellets. It is thus impossible to ascertain what degradation processes the samples have undergone.

The primary objective of this research is to investigate alteration in morphologies and functional groups of PVC particles exposed to heat, UVB, and solar radiation in simulated terrestrial and aquatic environment for different periods of time as well as the possible mechanisms of PVC degradation.

## 2. Materials and methods

### 2.1. Materials

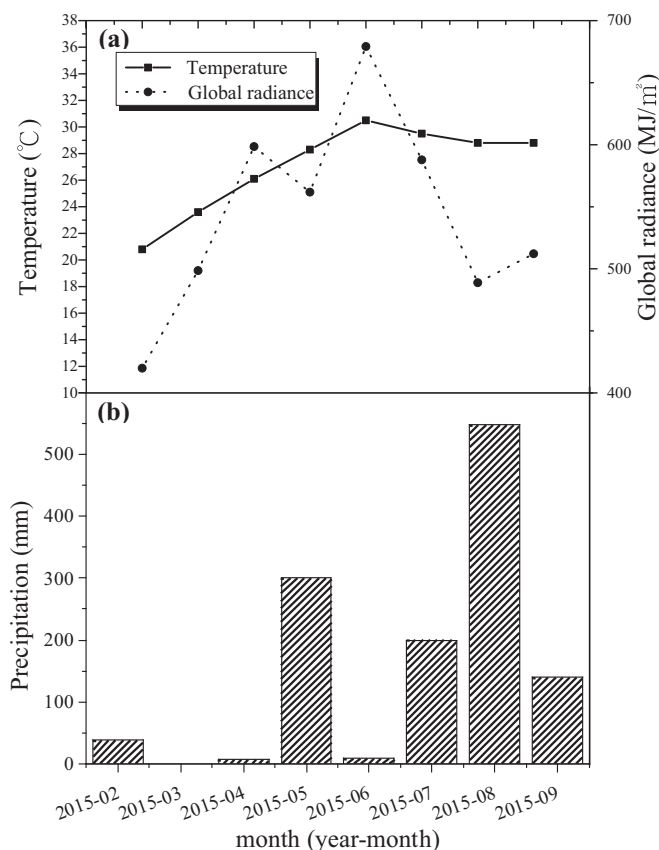
The virgin PVC (PVC-V, brand name S-65) used in this study was supplied by Formosa Plastics Corporation, Republic of China and has a density of  $1.391 \text{ g cm}^{-3}$ , a melting point of  $212^\circ\text{C}$ , glass transition temperature ( $T_g$ )  $82\text{--}85^\circ\text{C}$ , and thermal decomposition temperature of  $150\text{--}170^\circ\text{C}$ . The PVC has good plasticizer absorption and good heat stability. It is intended for soft applications such as flexible films and other flexible articles. It is also suitable for cable and wire applications. The shape of PVC particles we used in this study is an oval pellet with a diameter of approximately  $100 \mu\text{m}$ . The color of these particles is white, but not transparent. Table 1 shows the sample code name, degradation method, time and site used in this study. PVC products could be found on the land, at the beach, in the saltwater wetlands, or on the seabed. In this study, we set PVC-Su to simulate PVC products degraded in the land, PVC-SWSu to simulate PVC products degraded on a beach or in wetlands, and PVC-SW to simulate PVC products degraded on the seabed without solar radiation. In order to compare the aforementioned degradation characteristics of PVC in the simulated environment from photo-degradation or thermal-oxidative, we used PVC-U and PVC-SWU.

Temperatures were quite high as those measured directly on the ground, especially on dark beach sand, may exceed air temperatures by  $30$  to  $50^\circ\text{C}$  (Mildrexler et al., 2011), and the theoretical maximum possible ground surface temperature has been estimated to be between  $90$  and  $100^\circ\text{C}$  for dry, darkish soils of low thermal conductivity (Garratt, 1992). Furthermore, the highest natural ground surface temperature,  $93.9^\circ\text{C}$ , ever recorded was at Furnace Creek Ranch on 15 July 1972 (Kubecka, 2001). Therefore, thermal degradation of PVC particles was studied at  $50^\circ\text{C}$  and  $100^\circ\text{C}$  for 12 and 4 months, respectively,

**Table 1**

Sample code name, degradation method, time and site.

Sample code name	Photo degradation	Thermal degradation	Artificial seawater	Degradation time (days)	Degradation site
PVC-V	Without	Without	Without	210	In the laboratory
PVC-Su	Solar radiation	Without	Without	210	On the roof top
PVC-SWSu	Solar radiation	Without	With	210	On the roof top
PVC-SW	Without	Without	With	210	In the laboratory
PVC-O50	Without	$50^\circ\text{C}$	Without	360	In the laboratory
PVC-O100	Without	$100^\circ\text{C}$	Without	120	In the laboratory
PVC-SWU	UVB radiation	Without	With	210	In the laboratory
PVC-U	UVB radiation	Without	Without	210	In the laboratory



**Fig. 1.** (a) Monthly average temperature and monthly cumulative global radiance and (b) monthly rainfall for Kaohsiung City, Taiwan for 2015.

under forced convective air circulating inside an oven to increase the speed of degradation. These two sets of samples are denoted PVC-O50 and PVC-O100. During the thermal degradation experiments, the particles were samples two times (at 270 and 360 days) at  $50^\circ\text{C}$  while five times (at 9, 25, 45, 83, and 120 days) for  $100^\circ\text{C}$ . Ultraviolet B (UVB) radiation from a high-pressure mercury lamp (type Sankyo Denki G8T5E Japan) was used to degrade PVC under irradiation in air for 7 months. This degraded PVC is denoted PVC-U. Degradation characteristics were studied by drawing four samples (at 15, 60, 133, and 210 days) during the UVB degradation experiment. In parallel, another set of samples was dipped into artificial seawater in a tank with or without UVB irradiation, with depth maintained at 2 to 3.5 cm by adding deionized (DI) water continuously at all times to compensate for evaporation over the 7 month exposure. These degraded samples were termed PVC-SWU and PVC-SW. In both sample sets, each of the samples was placed at a distance of 15 cm from the light source, and the temperature around the tank was maintained at  $25 \pm 2^\circ\text{C}$  via external ventilation. To study the degradation characteristics of PVC-SWU, we drew samples at 30, 60, 133, and 210 days (7 months) during this

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