



Effects of Weathering on the Properties of Vinyl Siding

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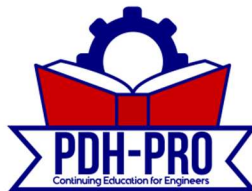
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1. Introduction

1.1. Vinyl siding and research objectives

According to the Energy Information Agency (EIA) of the United States Department of Energy, the average U.S. household commits nearly half (52 %) of its total energy consumption to heating and cooling [1]. Thus, improving home insulation can have a measurable impact on overall U.S. energy demand. In 2021, the International Energy Conservation Code (IECC) mandated the inclusion of exterior continuous insulation for walls across much of the United States - specifically in IECC climate zone 4 and above - when following the prescriptive compliance option in residential buildings [2]. IECC has also introduced similar requirements for commercial buildings [2]. Exterior insulation can include highly flammable foam materials like polystyrene foams [3, 4]. Non-combustible exterior insulation materials like mineral wool offer an alternative, albeit at a higher cost. When exposed to an ignition source, polystyrene and polyurethane foams, and, to a lesser extent, polyisocyanurate foams can catch fire and accelerate flame spread throughout the entire structure [5]. The importance of this vulnerability is expected to grow in the future, driven by the rapid increase in both the severity and frequency of wildland-urban interface (WUI) fires [6]. This issue is particularly notable in the Northeast and Midwest regions of the U.S., where vinyl siding is the predominant exterior material for residential buildings, and the 2021 IECC mandates the use of exterior insulation when following the prescriptive compliance option [2, 7].

Vinyl siding is a cladding material for exterior walls. It is primarily composed of unplasticized polyvinyl chloride (U-PVC). It was introduced into the U.S. market in the late 1950s, gradually replacing wood, aluminum, or fiber-cement clapboard. Vinyl siding manufacturing involves the co-extrusion of two layers: (1) the substrate layer, which is based on a low-cost U-PVC compound, and (2) the “weatherable capstock,” a thin outer layer enriched in titanium dioxide (TiO_2), which is composed of either U-PVC, poly(methyl methacrylate) (PMMA), acrylonitrile styrene acrylate (ASA) or blends of these materials. Additional additives are incorporated into U-PVC compounds used for substrates or capstocks to aid in processing and shaping, lower costs, and achieve specific final characteristics such as weather resistance, fire performance, color, aesthetics, and mechanical properties. In the case of insulated vinyl siding, a layer of foam insulation (usually expanded polystyrene or polyisocyanurate) is included beneath the vinyl shell.

Vinyl siding typically exhibits a low flammability thanks to the properties of its main component, polyvinyl chloride (PVC). PVC is an inherently flame retarded polymer with a favorable combination of ease of extinguishment, low heat release rate, ignitability, and flame spread rate [5, 8, 9]. While PVC is a low-cost commodity polymer akin to polyethylene, polypropylene, and polystyrene, it possesses a significantly lower flammability. For comparison, the fire growth capacity (a fundamental property measured by ASTM D7309 that correlates with a material’s flammability [10, 11]) is $1078 \text{ J}/(\text{g} \cdot \text{K})$ for polyethylene, $836 \text{ J}/(\text{g} \cdot \text{K})$ for polypropylene and $88 \text{ J}/(\text{g} \cdot \text{K})$ for PVC [12].

In this study, the effects of weathering were investigated on (1) commercial vinyl siding with an ASA capstock sourced from the U.S. and (2) vinyl siding formulations developed explicitly for this research (R&DFs), wherein additives such as light and thermal stabilizers, impact modifiers, titanium dioxide (TiO_2) and fillers were systematically adjusted. Specimens from both groups were exposed to natural and accelerated weathering to evaluate the effect of these additives during weathering. Following weathering exposure, samples were retrieved for extensive characterization as appearance (color/gloss) measurements, Fourier Transform Infrared Spectroscopy (FTIR), laser scanning confocal microscopy (LSCM), scanning electron microscopy (SEM), and mechanical testing. These analyses aimed to monitor the polymer degradation rate and the overall deterioration of siding performance.

The fire performance of U-PVC compounds was assessed by Microscale Combustion Calorimetry (MCC), according to ASTM D7309 method A [10], and a modified cone calorimeter test - ASTM E3367 [13].

MCC was used to measure the heat release rate of each U-PVC formulation by pyrolyzing specimens in nitrogen and then oxidizing the pyrolyzates in a combustion chamber at 900 °C [12, 14, 15]. While MCC does not match any specific fire test scenario and does not consider extrinsic factors (like heat irradiance, ventilation, shape, size, and density of the specimen), it measures intrinsic material properties (i.e., properties depending solely on the chemical structure of the material) relevant to flammability. Despite its limitations, MCC has effectively predicted a material's likelihood to meet fire test requirements. For instance, the fire growth capacity (FGC) measured in MCC has been used to predict the outcome of tests like UL 94 V and 14 CFR 25 [11, 12].

As previously noted, vinyl siding is expected to exhibit low flammability. Yet, its effectiveness as a fire barrier requires further validation, and it may be compromised by factors such as embrittlement and cracking in weathered samples. ASTM E3367 is a recent test developed to assess the combustion behavior of layered assemblies, such as those found in upholstered furniture [16, 17]. Herein, this test was used to evaluate the ability of vinyl siding to shield a flammable substrate, such as polystyrene foam, by acting as a protective barrier.

1.2. Weathering of acrylic-based polymers

PMMA and ASA-based capstock are commonly used as protective layers due to their optical clarity, absence of color, and ease of application. Typically, they contain at least 10 % by mass of TiO_2 , which shields the polymer matrix from UV-induced degradation. PMMA and ASA weathering have been extensively discussed elsewhere [18-20]. Briefly, the TiO_2 -rich polymers primarily degrade via photo-degradation in areas where oxygen is depleted, and TiO_2 initiates photo-oxidation in regions where oxygen is available. Both processes lead to chain scission in the polymer backbone, resulting in decreased mechanical properties, color alteration, and gloss reduction.

1.3. Thermal degradation and weathering of PVC

When exposed to heat, PVC undergoes thermal degradation. This degradation involves sequentially eliminating hydrogen chloride (HCl) from allylic chlorine and forming polyene sequences. This process, catalyzed by HCl and Lewis acids, operates through an ionic mechanism [21]. Allylic chlorine is also the target of photochemical reactions during weathering.

Extensive studies by various authors, mainly in the 1980s and 1990s, have detailed the weathering of PVC [22-28]. Weathering of U-PVC is a complex phenomenon that involves photo-degradation, photo-oxidation, photo-catalyzed oxidation, photobleaching, thermal degradation, and other chemical reactions. Weathering of PVC results from photon-induced reactions on the material's surface. These reactions, with or without oxygen and water, lead to mechanical and aesthetic issues such as loss of mechanical properties, yellowing, and chalking. Dark-colored U-PVC articles, reaching temperatures over 70 °C, may undergo simultaneous light-induced and thermal degradation.

During the weathering of PVC compounds, chemical reactions on the surface lead to the formation of three layers [25, 26]. The first is the oxidized layer, where photo- and photo-catalyzed oxidation are the dominant reactions; its thickness depends on TiO_2 concentration, grade, and oxygen diffusion. The second is a colored layer with a high molar extinction coefficient, containing polyene sequences (generated by photo-degradation) and condensation products. The third one is the undegraded core, whose degradation is prevented by the protective action of the second layer.

Because U-PVC is transparent at wavelengths below 250 nm, the initiation of these processes is likely caused by chromophores present in the resins or generated during product manufacturing. These chromophores absorb UV radiation, leading to the degradation and alteration of the chemical structure of the U-PVC compound over time, which can result in changes in color, strength, and other properties. Hydroperoxides and ketones are typical chromophores found in U-PVC. When exposed to light irradiation, they generate radicals through a Norrish type I reaction [22].

Polyene sequences can be formed during the PVC resin synthesis or the U-PVC compound processing. Due to their high extinction coefficient, polyenes rapidly become the main absorbing chromophores. Only polyene sequences containing more than four units interact significantly with sunlight. Sunlight reaching the Earth's surface is filtered by the atmosphere, and wavelengths shorter than 290 nm are mostly absorbed. Consequently, sunlight does not affect polyene sequences with four or fewer units. In comparison, those with more than four units absorb light in the range of wavelengths that penetrate the atmosphere, contributing to the photochemical degradation and weathering of PVC materials [21] [29]. The interaction between light and polyene generates an excited singlet state of polyene, which deactivates via both radiative and non-radiative pathways. In one of the non-radiative pathways, a chlorine

radical is released. Cl from allylic chlorine leads to the formation of polyene sequences, HCl, crosslinking, and chain scission products, as previously described [22].

This pathway rapidly releases Cl before oxygen can quench the excited singlet polyene, a process known as photo-degradation. Importantly, photo-degradation can occur both in the presence and absence of oxygen. However, the second radical formed from deactivating the excited singlet polyene has a longer lifetime, allowing it to react with oxygen. This initiates a series of reactions responsible for the photooxidation of the matrix, including chain scission and the formation of carbonyl and carboxyl groups. The prevalence of photo-degradation occurs in areas where oxygen is limited, such as beneath the surface. Conversely, photo-oxidation prevails in regions near the surface where oxygen can readily diffuse, facilitating reactions with the radicals generated by the excited singlet polyene [25].

Common additives found in the U-PVC compound can further complicate the weathering pattern. For example, titanium dioxide (TiO_2) is a standard pigment and light stabilizer for outdoor PVC items. TiO_2 grades for PVC are surface-treated with SiO_2 , Al_2O_3 , and zirconium to reduce their photocatalytic activity. In this way, their unique ability to adsorb most UV light impedes a deeper penetration of the photons and protects the bulk matrix from degradation. Even with a coating, TiO_2 retains enough residual photocatalytic activity to facilitate surface oxidation, leading to bleaching and chalking, particularly in the presence of water [30]. Experimental results indicate that direct contact with water, such as from condensation or rain, leads to more severe degradation than conditions with high air humidity.

Furthermore, fillers commonly used in PVC articles can influence the degradation and chalking of weathered PVC items. For example, calcium carbonate reacts with HCl and yields calcium dichloride, which, being hydrophilic and water-soluble, increases oxygen concentration in the matrix, thus promoting photo- and photo-catalyzed oxidation. Photo-catalyzed oxidation, photo-oxidation, photo- and thermal-degradation, and chemical reactions leading to the formation of water-soluble and hydrophilic molecules are responsible for the surface disintegration of the polymeric matrix in outdoor applications. As a result, free particles of TiO_2 and other fillers are released, and microcracks or holes become visible on the surface as faded and chalked areas. Eventually, the disintegration of the polymeric shell matrix exposes the U-PVC substrate to light and oxygen. Polyene sequences are oxidized through photobleaching (which leads to shorter polyene sequences), and photo- or photo-catalyzed oxidation perpetuates the erosion process deeper into the material.

1.4. Polymer decomposition and combustion

As a thin layer, the PMMA or ASA capstock assumes a secondary role in fire performance compared to the U-PVC substrate. The initial stage of the thermal decomposition in PVC occurs between 220 °C and 350 °C, where HCl is released in the gas phase - leaving polyene sequences, their condensation products, and unsubstituted aromatic hydrocarbons in the gas phase. In the subsequent stage, above 450 °C, primarily aliphatic hydrocarbons are released, and a

carbonaceous char is formed from the condensation products of polyene sequences. The decomposition pathway and release of flammable pyrolyzates are further complicated by additives in PVC compounds. Detailed information on the decomposition and combustion of PVC-based formulations is available elsewhere [31-34].

2. Materials and Methods

2.1. Materials, formulations, and sample preparation

A commercial insulated vinyl siding was purchased in the U.S. The siding complies with ASTM D7793, which defines requirements for thermal insulation, warp and shrinkage resistance, impact strength, appearance, thermal distortion resistance, flame spread, and wind-load resistance [35]. The vinyl shell consists of rich TiO₂ ASA capstock and U-PVC substrate, while the insulation material is expanded foamed polystyrene (EPS).

R&DFs were also prepared (Table 1). Table 1 shows the type, trade name, manufacturer, CAS #, and mass of raw material required to prepare 100 g of a given R&DF.

Table 1. Type, trade name, manufacturer, CAS#, and mass of raw material required to prepare a given R&DF.

Raw Materials	Trade name	Manufacturer	CAS #	A ref [g]	C [g]	F [g]	H [g]
PVC	PVC 264GC	Inovyn, UK	09002-86-2	85	85	85	85
PVC	PVC S5745	Inovyn, UK	09002-86-2	15	15	15	15
CaCO ₃ coated	VALTOCHIM	Umbria Filler, Italy	00471-34-1	15	15	15	30
Acrylic impact modifier	KANE ACE FM 50	Kaneka, Belgium		2.5	2.5	7.5	7.5
Chlorinated polyethylene	CPE 6135	R.G. chem, Italy	64754-90-1	2.5	2.5	-	-
Processing aids	REAMOD P 220	Reagens, Italy	-	0.5	0.5	0.5	0.5
TiO ₂	TRONOX CR 826	Tronox, U.S.	1317-80-2	1.0	7.5	7.5	7.5
Tin stabilizer	REA. TIN. OR 860	Reagens, Italy	68109-88-6	2.5	-	-	-
Calcium stearate	ARESTAB CA	Reagens, Italy	1592-23-0	1.0	-	-	-
Polyethylene wax	REALUBE PO	Reagens, Italy	9002-88-4	0.5	-	-	-
Internal lubricant	REALUBE SD	Reagens, Italy	90193-76-3	0.6	0	0	0
Calcium zinc stabilizer	RPK B-AV/2140	Reagens, Italy	-	-	4.0	4.0	4.0

In the U.S. market, the U-PVC substrate formulations are usually stabilized with di alkyl tin mercapto alcohol esters (also known as alkyltin “reverse esters”), dosed at (0.4 to 0.8) % by mass. This class of stabilizer is not registered in the European Union (EU) and, therefore, is not used in this research. Instead, an alkyl tin carboxylate stabilizer, dioctyl bis-(ethyl maleate), CAS number 68109-88-6, was utilized.

The blends of Table 1 were prepared in a turbo mixer (model RV/10/20/FV, Plas Mec) with a maximum processing temperature of 105 °C. The dry blends were cooled to room temperature and calendered at 180 °C for 3 min to form polymer sheets. The sheets were hot pressed at



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