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Effect of titanium dioxide on chemical and molecular changes in PVC sidings during QUV accelerated weathering

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ABSTRACT

Titanium dioxide (TiO_2) is the most essential additive in polyvinyl chloride (PVC) matrixes used for outdoor applications. In this study, we primarily investigate the effect of TiO_2 on the chemical and molecular changes in PVC sidings during QUV accelerated weathering. The results of this study show that carbonyl and polyene groups were generated on the surface of all of the specimens after 480 h of accelerated weathering but that loading TiO_2 into PVC successfully inhibited the increase in the number of these oxidative groups over the entire exposure period compared to PVC without TiO_2. In addition, a significant decrease in the number average molecular weight (M_n) and the formation of an insoluble gel were observed for PVC without TiO_2 after accelerated weathering. However, the time required for the M_n to decline increased with the amount of TiO_2 that was loaded into the PVC matrix, and no insoluble gel was observed during weathering. Furthermore, the crystallinity of PVC without TiO_2 increased noticeably after 1920 h of accelerated weathering, whereas no significant change was observed in the crystallinity of PVC with TiO_2. These results demonstrate that simultaneous chain scission and crosslinking reactions occurred in PVC without TiO_2, whereas only chain scission occurred in PVC containing TiO_2. In addition, the chain scission of PVC without TiO_2 was initiated earlier than for PVC with TiO_2, producing shorter and more mobile chains that underwent secondary crystallization. Accordingly, TiO_2 acted as a UV absorber and a radiation screener such that the probability of chain scission was reduced for TiO_2-loaded PVC sidings.

1. Introduction

In 2011, 32.3 million tons of polyvinyl chloride (PVC) were used worldwide. PVC usage is predicted to reach approximately 49.53 million tons in 2020, corresponding to an annual average growth rate of 4.9% [1]. However, PVC use in Asia accounts for over half of the PVC products used worldwide [2]. After the addition of appropriate stabilizers, PVC can be applied in various fields, such as automobiles, aviation, civil construction and home and electronic appliances, etc. This polymer is an indispensable material for supporting our lifestyle and industrial infrastructure. In recent years, sustainable building construction has been the primary concern in the fields of civil engineering and architecture to maintain a sustainable society and protect the global environment. Therefore, appropriate building materials must be selected that are durable, recyclable and have low CO_2 emissions in consideration of the entire life cycle. In addition, the low cost and good weatherability of PVC products make this polymer very suitable for use in exterior applications in construction, such as windows, cladding structures and sidings, which are primarily used in North America. In particular, PVC use in exterior siding in new single-family houses accounted for approximately 36% of total PVC use in the USA in 2010 [3]. However, such PVC sidings suffer from degradation by various natural weathering factors, e.g., UV, heat and moisture.

However, PVC exterior materials used in practice contain additives such as calcium/zinc stearates, organotin mercaptide and inorganic UV absorbers that directly protect the material from degradation. TiO_2 is an inorganic UV absorber that is often used in PVC materials to prevent reaction with UV, humidity and oxygen by reducing the diffusion of electrons and positive holes to the reaction surface. Therefore, the surface becomes photo-oxidative and prone to photo-catalytic degradation because of the production of free radicals that accelerate degradation [4]. Many studies have

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investigated the changes in the chemical and physical properties [5–8] and photo-oxidation mechanisms [6,9–14] of PVC films with and without additives under artificial weathering. Unfortunately, limited information is available on the physicochemical properties of PVC sidings with or without TiO_2 under QUV accelerated weathering. Thus, the aim of this work is to determine the effects of TiO_2 on the weathering properties of PVC sidings and to investigate physicochemical changes, including in chemical functional groups, the molecular weight distribution (MWD), the crystallinity and color changes, as a function of the exposure time.

2. Materials and methods

2.1. Materials

Compression-molded 0.5-mm thick PVC specimens (Kane Vinyl S1001) were supplied by Kaneka Co. (Japan). The PVC matrix contained additives that were similar to those used in outdoor applications of PVC sidings. The formulations used in the specimen are summarized in Table 1. These additives, which included acrylic polymer (Kane Ace PA-20, Kaneka, Japan), paraffin wax (Luvax-1266, Nippon Seiro, Japan), organotin mercaptide (TM-181 FS, Dow Chemical, USA) and fatty acid soap (calcium stearate and zinc stearate), are used as a processing aid, a lubricant, a thermal stabilizer and a HCl quencher, respectively. In addition, TiO_2 (R-105, DuPont, USA) is used as an inorganic pigment. In this study, the content of all of the additives was kept constant, except for TiO_2, which was added at contents of 0, 5 and 10 phr.

2.2. Accelerated weathering test

Accelerated weathering was conducted in a QUV tester using fluorescent lamps UVA-340 (Q-Lab, USA). The varying spectral energy distribution provided the best possible simulation of sunlight over the critical short wavelength region from 365 nm to the solar cutoff of 295 nm. The irradiance of the peak emission was 0.68 W/m^2 at 340 nm. This wavelength is significant in the accelerated degradation of PVC because PVC only absorbs irradiation from 310 to 370 nm [15]. The test cycle in this study consisted of 8 h of UV exposure at 50 ± 3 °C and 4 h in the dark with condensation at the same temperature. A complete test lasted 1920 h (80 days). All weathered specimens were air-dried in ambient conditions for 24 h before measuring various properties.

2.3. ATR-FTIR spectral measurements

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the PVC specimens were recorded using a Spectrum 100 FTIR spectrometer (PerkineElmer, UK) equipped with a MIRacle ATR accessory (Pike Technologies, USA). The spectra were collected by co-adding 32 scans at a resolution of 4 cm^{-1} over a 650 to 4000 cm^{-1} range.

Table 1
Specimen formulations in this study.

Ingredient	Chemical formula	Content (phr)		
		PVC(T_0)	PVC(T_5)	PVC(T_{10})
PVC matrix	$(CH_2CHCl)_n$	100	100	100
Acrylic polymer	$(CH_2CCH_3COOCH_3)_n$	0.7	0.7	0.7
Paraffin wax	C_nH_{2n+2} (n = 18–48)	0.5	0.5	0.5
Organotin mercaptide	$R'_nSn(SCH_2COOR'')_{4-n}$	0.6	0.6	0.6
Fatty acid soap	$Ca(RCOO)_2$, $Zn(RCOO)_2$	1.5	1.5	1.5
Titanium dioxide	TiO_2	0	5	10

2.4. Gel permeation chromatography (GPC)

The number average molecular weight (M_n), the weight average molecular weight (M_w) and the MWD of the PVC specimens were measured using a GPC, which was equipped with a PU-2080 pump (Jasco, Japan), a RI-2031 refractive index detector (Jasco, Japan) and 10E3A/10E4A columns (Phenogel, USA). Tetrahydrofuran (THF) was used as the isocratic mobile phase at a flow rate of 1 mL/min. A series of polystyrene calibration standards was used to calculate M_n and M_w. Before sample injection, the specimens were dissolved in THF and then filtered through a 0.2-μm hydrophilic polypropylene (GHP) membrane to remove insoluble particles.

2.5. Gel content analysis

For determination of gel content, the weathered specimens were cut into pieces and immersed in THF for 24 h. In order to wash a gel completely free of soluble PVC, three extractions by the repeated centrifugation and decantation of a gel with fresh THF was used. The weight of the gel is determined after removal of THF by evaporation.

2.6. Differential scanning calorimetry (DSC) thermal analysis

The thermal properties of the PVC specimens were measured using a DSC-7 (PerkineElmer, UK). The samples (ca. 1 mg) were encapsulated in aluminum pans and heated from room temperature to 260 °C at a heating rate of 20 °C/min under a nitrogen flow (20 mL/min). The PVC crystallinity (X) was obtained as a function of the weathering time using the following expression: $X\,(\%) = \Delta H_{m(t)}/[\Delta H_m^0 \times W_p] \times 100$, where $\Delta H_{m(t)}$ denotes the melting enthalpy for the specimen at the weathering time t, ΔH_m^0 denotes the melting enthalpy of 100% crystalline PVC, and W_p denotes the weight percentage of the PVC in the samples. The ΔH_m^0 value has been estimated to range between 40 and 181 J/g [16]. In this study, we tool ΔH_m^0 to equal 176 J/g, which is the value obtained for fully crystalline PVC, as measured by TA instruments [17].

2.7. Surface color

The CIE $L^*a^*b^*$ color system on surface color of specimens after accelerated weathering were measured by a spectrophotometer (Minolta CM-3600d, Japan) under a D_{65} light source. Therein, L^* is the value on the white/black axis, a^* is the value on the red/green axis, b^* is the value on the yellow/blue axis and ΔE^* is the color difference ($\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$).

2.8. Statistical analysis

All of the results were expressed in the form of a mean ± SD. The significance of difference was calculated using Scheffe's test, and P values < 0.05 were considered to be significant.

3. Results and discussion

3.1. FTIR analysis

FTIR-ATR was used to determine the changes in the functional groups on the surface of the specimens during accelerated weathering. The characteristic absorption bands of the PVC sidings were determined by separately measuring the components of the specimen, including the PVC matrix and each additive, before weathering. As expected, no absorption peak was found over the 1450–1750 cm^{-1} range in the PVC matrix spectrum [18]. In contrast, the fatty acid soaps (Ca/Zn stearates) exhibited significant