

Poly(Vinyl Chloride) Doped by 2-(4-Isobutylphenyl)Propanoate Metal Complexes: Enhanced Resistance to UV Irradiation

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Abstract The photostabilization of poly(vinyl chloride) (PVC) films in the presence of 2-(4-isobutylphenyl) propanoate metal complexes (0.5 wt%) was investigated at room temperature under ultraviolet radiation ($\lambda = 320$ nm) for 300 h. The changes in various functional groups indices, viscosity average molecular weight and quantum yield of the chain scission of PVC films were monitored upon irradiation. The metal complexes used showed decreases in PVC films photodegradation. The quantum yield for the chain scission was measured exhibiting a range of 2.054×10^{-6} and 1.005×10^{-7} . The photostabilization of poly(vinyl chloride) in the presence of metal complexes was in the order $\text{ZnL}_2(\text{H}_2\text{O})_2 < \text{CdL}_2(\text{H}_2\text{O})_2 < \text{CuL}_2 < \text{SnL}_2(\text{H}_2\text{O})_2 < \text{NiL}_2(\text{H}_2\text{O})_2$. The metal complexes can act as hydrogen chloride scavengers, UV absorbers, peroxide decomposers and also as radical scavengers to enhance PVC photostability.

Keywords Poly(vinyl chloride) · Photostabilization · FTIR spectroscopy · Chain scission · Viscosity average molecular weight

1 Introduction

Poly(vinyl chloride), PVC, is a synthetic plastic that is produced at an industrial scale. PVC is the third most commonly produced synthetic polymer, coming after polyethylene and polypropylene [1]. There is an increasing market for the production of PVC due to low cost and its increased usage. Two types of PVC are common as flexible and rigid. Flexible PVC can be used in various applications as a rubber substitute. Rigid PVC can be used in building constructions. Rigid PVC can become softened by the addition of plasticizers [2]. PVC is a linear chain polymer with chlorine atoms that are randomly placed on the chain to provide an atactic polymer that prevents crystalline regions occurring normally. Therefore, PVC is hard and rigid material at room temperature [3]. PVC can be produced via free radical polymerization of vinyl chloride and/or treatment of acetylene with hydrogen chloride (HCl) [4].

Weathering of polymers involves physical, mechanical and chemical changes in their surface [5]. Solar UV radiation is the primary cause of weathering damage to PVC. Chromophores generally present in PVC absorb UV light and initiate its degradation at high temperatures and humidity environment in the presence of oxygen and air pollutants. Degradation of plastics can lead to physical changes in the surface such as the development of cracks and weakening of the material [6]. When exposed to natural weathering (e.g., sunlight), PVC deteriorates and becomes progressively discolored and brittle. Also, they begin to lose mechanical properties such as tensile strength, elasticity and impact resistance. Photodegradation of PVC could lead to the reduction in plasticizers and dehydrochlorination that are responsible for discoloration [7,8]. Therefore, PVC which is used for outdoor applications must be protected from light.

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Photostabilization of PVC can be achieved through the addition of UV stabilizers. Generally, such additives reduce photodegradation of PVC through various mechanisms. The most common additives act as UV absorbers, peroxide decomposers, excited state quenchers, hydrogen chloride (HCl) scavengers and/or free radical scavengers [9–17]. Hydroxybenzophenones and hydroxybenzotriazoles are the most common UV stabilizers for polymeric materials [8]. Some pigments can act as UV absorbers to prevent the harmful radiation penetrating the polymeric materials [18]. Metal complexes containing aromatics and heteroaromatics have been reported as effective peroxides decomposers [18–20].

Recently, we have successfully enhanced the photostabilization properties of polymeric films using metal complexes [21–23] as part of our ongoing research within the area of polymeric materials [25–28]. In this work, the enhancement of PVC photostability using metal complexes (ML₂) containing 2-(4-isobutylphenyl)propanoate, commercially available, as new photostabilizers is reported.

2 Experimental Section

2.1 Materials

2-(4-Isobutylphenyl)propanoate metal complexes (ML₂) were prepared according to the literature procedure [29]. The reaction of a mixture of 2:1 molar equivalents of a potassium salt of 2-(4-isobutylphenyl)propanoic acid and a number of divalent metal salts in ethanol for 30 min under reflux gave the corresponding ML₂ complexes (Table 1; Fig. 1) in 66.5–83.5 % yields. The structures of the produced ML₂ complexes were confirmed by various analytical and spectroscopic techniques and were consistent with those reported [29].

The absorption spectra in dimethylformamide (10^{−3} M; 25°C) for ML₂ complexes show absorption bands at 225–234 nm due to π – π^* transition of aromatic moiety. The CuL₂ and NiL₂ complexes show absorption bands (669 and

450 nm, respectively) due to $d-d$ electronic transitions [29]. Such absorption bands are due to $^2T_2 \rightarrow ^2E$ transition with a square geometry for the Cu complex [29,30] and $^3T_1(F) \rightarrow ^3T_1(P)$ and $^3T_1(F) \rightarrow ^3A_2(F)$ transitions with an octahedral geometry for the Ni complex [31,32]. The Zn, Cd and Sn complexes were diamagnetic with no $d-d$ electronic transition. Fourier transform infrared (FTIR) spectra for ML₂ complexes show absorption bands at 430–470 cm^{−1} (ν M–O), 1392–1399 cm^{−1} (ν COO[−] symmetrical) and 1542–1575 cm^{−1} (ν COO[−] antisymmetric). The NiL₂ and CuL₂ magnetic moment was 2.42 and 1.64 B.M. (Bohr Magnetons). Other ML₂ complexes show zero magnetic moment.

2.2 Films Preparation

The PVC films (40 μ m thickness) were prepared using the evaporation technique in tetrahydrofuran (THF) at room temperature for 24 h. The ML₂ complexes (0.5 % by weight) were added to PVC solution in THF (5 %) and measures were taken to ensure high optical quality and low turbidity. The solution was spread on a glass frame, and the solvent was allowed to evaporate overnight. The films produced after complete evaporation of THF were fixed using aluminum plate stands (Q-Panel Company, Homestead, FL, USA) [33].

2.3 Accelerated Testing Technique

Accelerated weather-meter QUV tester (Q-Panel Company, Homestead, FL, USA) was used to irradiate PVC films at a light absorption intensity of 7.75×10^{-7} ein dm^{−3} s^{−1}. The tester has two 40 watts fluorescent ultraviolet lamp (290–360 nm, $\lambda_{\max} = 320$ nm), one in each side [34].

2.4 Photodegradation Measuring Methods

2.4.1 PVC Films Photodegradation by FTIR Spectrophotometry

Photodegradation of PVC films was monitored by FTIR 8300 Shimadzu spectrophotometer (4000–400 cm^{−1}). The changes in absorption bands for several functional groups were recorded versus irradiation time as a way to measure the degree of photodegradation. For example, the bands appeared at 1724 (C=O), 1604 (C=C) and 3500 cm^{−1} (OH) were monitored [34]. The comparison between reference peak that appeared at 1328 cm^{−1} and those for three bands (base-line method) allow calculation of carbonyl (I_{CO}), polyene ($I_{C=C}$) and hydroxyl (I_{OH}) indices [34].

2.4.2 Determination of Viscosity Average Molecular Weight

The Mark–Houwink relation, Eq. (1), was used to calculate the PVC films average molecular weight (\bar{M}_V) in solution

Table 1 Structures of ligand (L) and metal complexes (ML₂)

Symbol	Name
L	Potassium 2-(4-isobutylphenyl)propanoate
ZnL ₂ (H ₂ O) ₂	<i>bis</i> [2-(4-Isobutylphenyl)propanoate] zinc(II) · 2 H ₂ O
CdL ₂ (H ₂ O) ₂	<i>bis</i> [2-(4-Isobutylphenyl)propanoate] cadmium(II) · 2 H ₂ O
SnL ₂ (H ₂ O) ₂	<i>bis</i> [2-(4-Isobutylphenyl)propanoate] tin(II) · 2 H ₂ O
NiL ₂ (H ₂ O) ₂	<i>bis</i> [2-(4-Isobutylphenyl)propanoate] nickel(II) · 2 H ₂ O
CuL ₂	<i>bis</i> [2-(4-Isobutylphenyl)propanoate] copper(II)

