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Monitoring the Photodegradation of PVC Thin Films Containing Schiff Base Using FTIR Spectroscopy

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Abstract

Metal complexes of Cu(II), Cd(II), Zn(II), Ni(II) and Sn(II) containing Schiff base derivative (L) as a ligand (ML_2) utilized as additives to avoid PVC films photodegradation during UV irradiation (λ_{max}= 313 at a light intensity = 7.75×10^{-7} einstein dm^{-3} sec^{-1}). Irradiation of PVC films with UV light due to changes in infrared spectra.

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Introduction

Organic polymers (mainly synthetic plastics) are widely utilized in different industrial areas,[1] such as marine industries, civil engineering materials automotive fields, aerospace composites, and protective coatings,[2,3] and the needs for these materials are increasing. The high polymers now occupy second place behind steel in the scale of most important materials groups.[4] PVC has individual mechanical and physical properties and is almost used as a thermoplastic material.[5] It has several outdoor usage, fundamentally in construction materials.[6,7] PVC polymeric materials come next to polyolefins in global production and consumption terms;[8] however, due to its inherent brittleness and thermal instability, the plasticizers utilized and heat stabilizers are fundamental for PVC.[9] There are two kinds of PVC rigid and flexible. The flexible PVC utilized in several usages as a rubber substitute. While, rigid PVC utilized in building

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constructions.[10] The main problems associated with utilize of polymers, is their photodegradation.[11] All materials are subjected to weathering.[12] The polymer degradation occurrence recognized by its effects on the appearance and properties. The common effects are embrittlement, discoloration, tackiness, loss of surface gloss, and crazing or chalking of surface.[13] Polyolefins, poly(vinyl chloride) (PVC), polystyrene (PS), aliphatic and aromatic polyamides, polyurethanes, diene rubbers, and polymeric coatings, have an outdoor lifetime of less than a year when compounded without any photostabilizer added.[14] When exposed to natural weathering, PVC deteriorates and becomes increasingly colored and brittle, with a steady decrease in mechanical properties such as tensile strength, elasticity, and impact resistance.[15] The main factors influencing on PVC degradation products include oxygen, humidity, light, mechanical stress, aggressive media, and ionizing radiation; all are accelerated by increasing temperature. The degradation leads to changes in basic properties as a result of simultaneous chemical and physical processes, causing changes in chemical composition and structure.[16] Dehydrochlorination data can be used to follow changes in the stability of rigid PVC during outdoor exposure.[17] To inhibit or reduce the photodegradation, inorganic and organic UV absorbers, as well as stabilizers have been utilized.[18,19] Polymer photostabilization continues to be a rapidly advancing area of scientific and technological interest. When the polymer contains a stabilizer, the rate of oxidation is reduced. Stabilizers reduce but do not completely inhibit the oxidation. Any consideration of polymer stabilization has to take in account some basic.[20] This paper, utilizing a simple procedure to synthesis different divalent metal complexes containing Schiff base and study their PVC photostabilization efficiency.

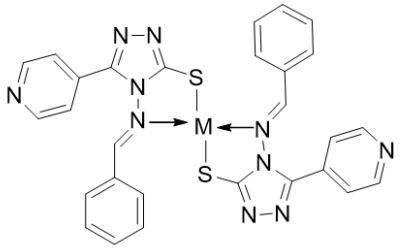
Experimental

Synthesis of Metal Complexes

The complexes $Cu(L)_2$, $Cd(L)_2$, $Zn(L)_2$, $Ni(L)_2$ and $Sn(L)_2$ (Figure 1) were synthesized as reported.[24]

Films Preparation

In chloroform solvent, PVC was dissolved with metals complexes to form PVC films.[21,22]



M= Cu(II); Cd(II); Sn(II); Zn(II) or Ni(II)

Fig. 1: Structure of $M(L)_2$

Photodegradation Rate of Polymeric Films by FTIR Spectrophotometry

The photodegradation degree of polymeric films was monitored with FTIR spectra. The bands appearance in 1772 and 1724 cm^{-1}, is refer to carbonyl groups formation. At different times of irradiation the photodegradation progress was studied by changes in carbonyl peak intensity; this called the "band index method",[23] as:

$$Is=As/Ar \quad ...(1)$$

Results and Discussion

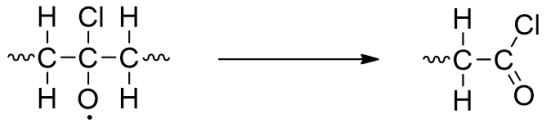
Metal complexes of Cu(II), Cd(II), Zn(II), Ni(II) and Sn(II) with Schiff base ligand (L), were used to enhance the PVC photostabilization. The PVC films have been irradiated with wavelength light, λ=313 nm led to changes in their IR spectra. (Figure 2) explain the photodegradation mechanism of PVC in presence of oxygen.[24]

The PVC photo-oxidation can be described by the sequence below:[25-27]

- The photolytic formation of polyenic series with growing of conjugation lengths by multistep photochemical excitations. It started by chromophoric defects excitation with α-chlorinated dienes structure.

The band at 1770 cm^{-1} can be attributed to the formation of acid chloride. This acid chloride is formed by β-scission of the alkoxy radical with scission of the macromolecular chain. This product is

then substituted in the b position by a chlorine atom and corresponds to the structure:[33]



- The photo-oxidation started by Cl* created over with polyenic series and produces to create the following products: α,α'-dichloroketones, acid chlorides and β-chlorocarboxylic acid.
- PVC cross-linking by association of in-chain macroradicals.

Polymer degradation may cause by heat, light, radiation (radiodegradation), mechanical action, or by algae, bacteria (biodegradation).[28] UV radiation hurtful to polymers, a phenomenon recognized as photodegradation is started which affects the mechanical, chemical and physical properties of the polymers.[29-31]

With a view to investigate additives photochemical activity for PVC photostabilization, the polyene, hydroxyl and carbonyl indices were detected upon irradiation time by IR spectrophotometry. The polyene, hydroxyl and carbonyl groups absorption was utilized to follow up the polymer degradation extent upon irradiation.[32]

The presence of $Cu(L)_2$, $Cd(L)_2$, $Zn(L)_2$, $Ni(L)_2$ and $Sn(L)_2$ show minimize the growth rate of indices against irradiation time upon consideration to PVC (blank). These additives worked as PVC photostabilizers. However, from the growth rate of polyene, hydroxyl and carbonyl indices, the Ni(II) complex is the most active photostabilizer, followed by Sn(II), Zn(II), Cd(II) and Cu(II) complexes, as shown in Figures 3, 4 and 5.

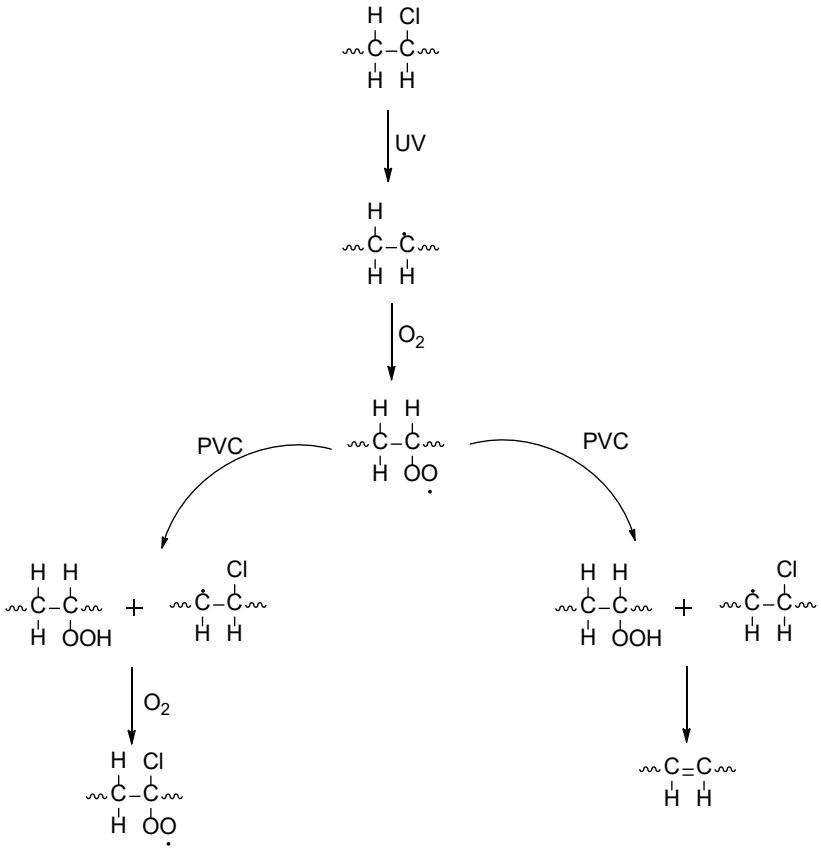


Fig. 2: The general process for PVC photodegradation

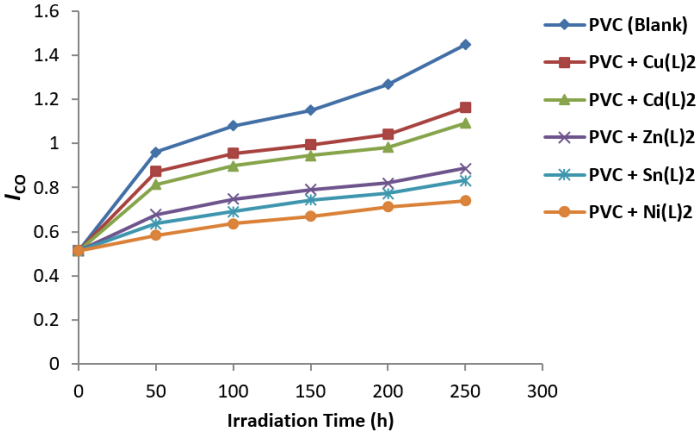


Fig. 3: Change in I_{CO} of PVC upon irradiation

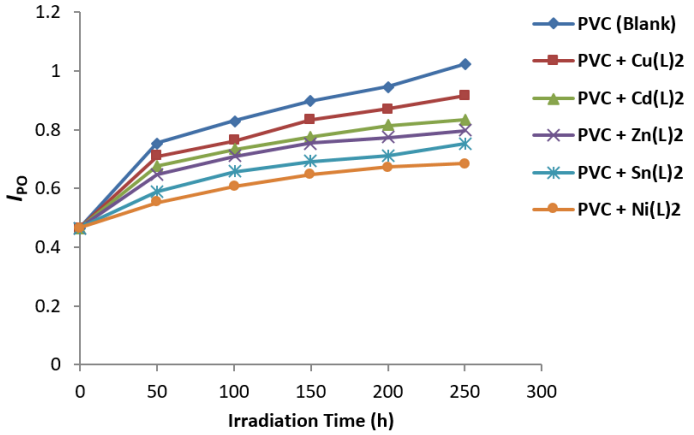


Fig. 4: Changes in I_{PO} of PVC upon irradiation

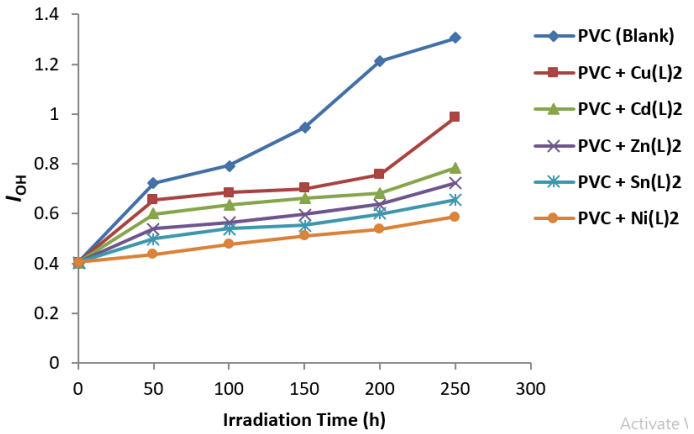


Fig. 5: Changes in I_{OH} of PVC upon irradiation

Conclusion

The PVC films photostabilization which containing Schiff base derivatives have been investigated. The additives act as effective PVC photostabilizers. According to reduction in indices, the additives take the following arrangement in photostabilization:

$$NiL_2 < SnL_2 < ZnL_2 < CdL_2 < CuL_2$$

Increasing activity

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