



RESEARCH ARTICLE

ANALYSIS, PHOTO DEGRADATION, THERMAL DEGRADATION AND REUSE OF PVC FLEX SHEETS COLLECTED FROM ARIYALUR DISTRICT, TAMIL NADU, INDIA

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ABSTRACT

Now a days, PVC flex sheets (Banners) are used for almost all kinds of advertisements or information. These low cost and durable materials are flexible and almost unaffected by sunlight, heat and rain. They have been used for political popularity, public and private advertisement, religious festivals, family functions etc., These banners are mostly thrown away as landfills which cause environmental pollution. The present work deals with the physico-chemical analysis, photo degradation, thermal degradation and biodegradation of waste /used PVC flex materials collected from Sendurai, Ariyalur and Udayarpalayam Taluks in Ariyalur District, Tamil Nadu. Also, a few utility articles like flower vase, bag etc. were made from the used PVC flex sheets.

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INTRODUCTION

Polyvinyl chloride (PVC) is the second most produced and used plastic (polyethylene being the first). Its use is widespread and diverse, ranging from everyday products to highly specialized applications. The building and construction sector (piping, guttering, window profiles and wall plates) makes the broadest use of PVC (Yoshioka *et al.*, 2008; Folarin, 2008; Simon, 1992). Other important applications are flooring and wall coverings, electrical cables, packaging, cars (bumpers, interiors), furniture coverings, tubes and medical applications (blood bags) (Chaochanahaikul *et al.*, 2013; Deng and Tang, 2010; Stark and Matuana, 2004). Polymer degradation is mainly caused by chemical bond scission reactions in macromolecules. It is useful to subdivide this broad field according to its various modes of initiation (Matuana *et al.*, 2001; Abubakar *et al.*, 2005; Chaochanahaikul and Sombatsompop, 2011; Filson *et al.*, 2009). These comprise:

- Chemical degradation
- Thermal degradation

- Mechanical degradation
- Photo degradation
- Degradation by high-energy radiation
- Biodegradation

Photodegradation

Most commercial polymers undergo chemical reactions upon exposure to the ultraviolet light, since they have chromophoric groups capable of absorbing UV light. This fact is important because the spectrum of the sunlight passing the earth atmosphere contains a portion of UV light. Therefore, photoreactions are usually induced when organic polymers are subjected to outdoor exposures. In general, photoreactions in commercial polymers are harmful: they cause embrittlement and color changes. Since the large-scale production of organic polymers, the producers have invested on the prevention of photo degradation. In this respect, photolytic reactions of special importance are UV light initiated oxidative chain reactions. Apart from deterioration effects, the field of photo degradation comprises beneficial aspects also. A typical example is the utilization of readily degradable polymers as positively acting resists for the production of solid-state electronic microstructures.

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It is appropriate to emphasize here two important aspects:

- (i) The specific interaction of light with organic compounds and
- (ii) The randomness of photochemical reactions in polymer.

Light absorption in a molecule consists of a specific interaction of a certain chromophoric group with a photon of given energy. The remainder of the molecule remains unaffected during the absorption activity. If a polymer chain is supposed to be ruptured at a certain position on irradiation, this goal can be achieved by synthetically introducing an appropriate chromophore at that place in the polymer backbone. The second aspect, referred to above, derives from the fact that light is absorbed statistically by the chromophores in a system. All that we know is the probability for the absorption of a certain photon by a certain chromophore. There is an equal probability of absorption of a photon by the chromophore in the polymeric matrix. Therefore, chemical reactions occurring subsequent to light absorption can be initiated at any place at the backbone of the polymer (Martin *et al.*, 2013; Worsley *et al.*, 1995; Robinson *et al.*, 2004; Worsley and Searle, 2002).

Thermaldegradation

The low thermal stability of PVC is considered as one of the most serious industrial problems. The degradation of PVC has been widely studied since 1940. Most of the early research works have been focused on the dehydrochlorination reactions to improve the thermal stability of PVC. The overall experimental results have led to the discovery of new heat stabilizers. In further research works the kinetics of thermal degradation and decomposition products have been studied. Today, the thermal degradation mechanism of PVC is established. The main process involved in thermal degradation

of PVC is known to be dehydrochlorination (Owen, 1984; Braun and Bazdadea, 1986). The onset temperature of PVC dehydrochlorination is around 100°C which due to the formation of long conjugated double bonds or polyene sequences a process of discoloration develops. The rate of this process becomes even more rapid in presence of oxygen and HCl, which results in formation of carbonyl groups, as reaction catalyst which auto catalyzes accelerating reactions. In order to process PVC with minimum extent of thermal degradation, a number of chemical combinations, such as lead compounds, organotin compounds and those of other metals can be used as stabilizers. In addition to the above heat stabilizers, incorporation of polyethylene into PVC compounds has been reported to prevent PVC degradation (Kim, 2001; Patil and Bagde, 2012).

Biodegradation

Biodegradation generally allows for cheaper final disposal of plastic waste through composting and returns the polymer into the natural carbon cycle. By definition, biodegradable polymers are those that are degraded into carbon dioxide, water, and biomass as a result of the action of living organisms or enzymes (Shah *et al.*, 2009; Tomita *et al.*, 2004; Nahar *et al.*, 2011; Saeki *et al.*, 2003). The rate of degradation and polymer crystallinity are important factors affecting the biodegradability, with degradation taking place preferentially in the polymer amorphous domains. It is important to mix (blend) the polymers to obtain a matrix with good mechanical properties and which is suitable for disposal in the environment. Some of the factors that affect the biodegradation process are the nature of the polymer, the interactions among the blend's components; its crystallinity; and environmental conditions (light, temperature, O₂ concentrations; and humidity) (Shina *et al.*, 2002; Premraj and Mukesh, 2005).

Study Area



Fig.1A. Tamil Nadu Map

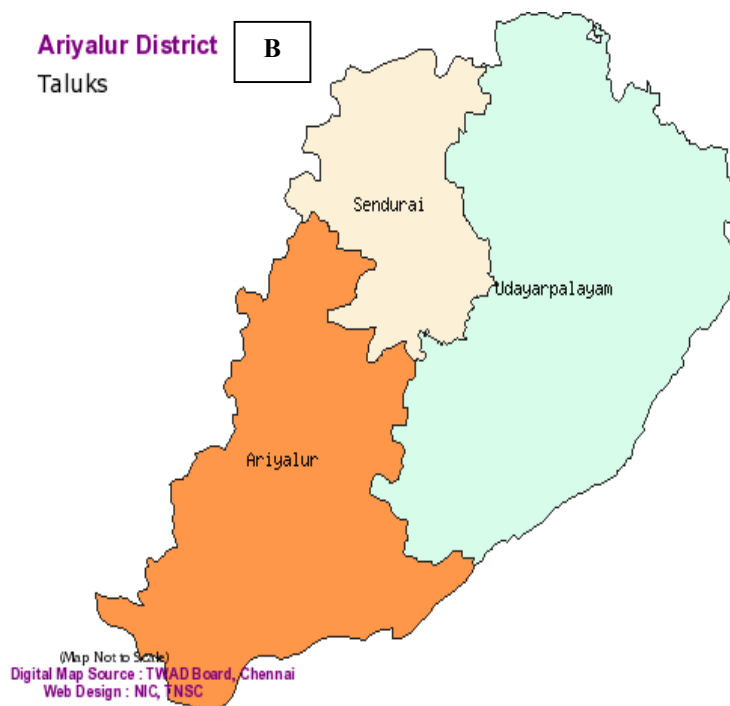


Fig.1B. Ariyalur District Map

Experimental

The used / waste PVC flex samples were collected from various places of Ariyalur, Sendurai and Udayarpalayam Taluks in Ariyalur District during January 2016, washed with water and dried. The sheets were cut in to small pieces and used for physical and chemical analyses. The sheets were subjected to photo degradation using a Multi Lamp Photo reactor (Fig.2A). The degradation was studied using different wave lengths of UV lamp by varying irradiation time; thermal degradation of the samples was carried out at different temperatures and different time intervals using a muffle furnace (Fig.2B). Biodegradation study was carried out by burying the PVC flex samples in the soil at about one foot depth and kept under the dry and moist conditions for 2,4 and 6 months. The samples, before and after the degradation processes were analyzed by SEM and IR spectroscopic technique. Also, attempts were made to make a few utility articles using the waste PVC flex sheets.

Table 1. Physical/Chemical Properties of PVC flex materials

S.No.	Physical/Chemical Parameter	Inference
1	i.Colour	Colorless
	ii.Thickness	0.20mm
2	Solubility	
	i.H ₂ O	Insoluble
	ii.Ethanol	Insoluble
	iii.Methanol	Insoluble
	iv.Ether	Insoluble
	v.Benzene	Insoluble
	vi.DMF	Insoluble
	vii.Acetone	Slightly soluble
	viii.THF	Soluble
3	Elemental Analysis	
	i.Nitrogen test	Absent
	ii.Sulphur test	Absent
	ii.Halogen test	Cl Present
4	Test for Functional Groups	
	i.Acid	Absent
	ii.Phenol	Absent
	ii.Amine	Absent
	v.Ester	Present

RESULTS AND DISCUSSION

Physico- chemical analysis

The PVC flex materials were found to have the following physical and chemical properties (Table 1)

Degradation Studies

Photo degradation of PVC flex sheets was studied using UV light of wavelength 254 and 365 nm. with the Photo reactor. The experiment was carried out at different intervals of time (30 min, 60 min and 120 min) and the samples were collected after each time interval. Similarly thermal degradation of PVC flex sheets was carried out using a muffle furnace at 170°C and at different intervals of time (15min, 30 min and 60 min).



Fig. 2A. Multilamp Photo reactor



Fig.2B. Muffle furnace

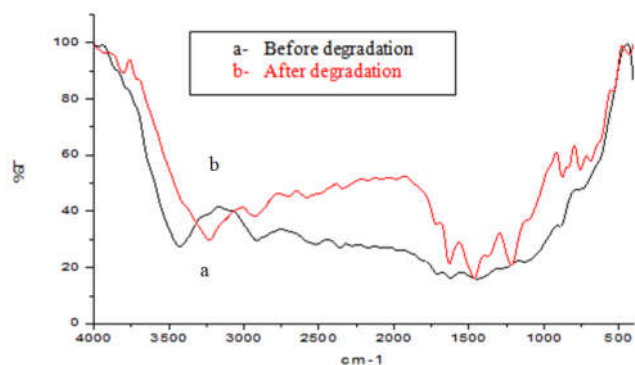


Fig.3. FT-IR Spectrum of raw sample of PVC flex on UV irradiation (254 nm for 60 min)

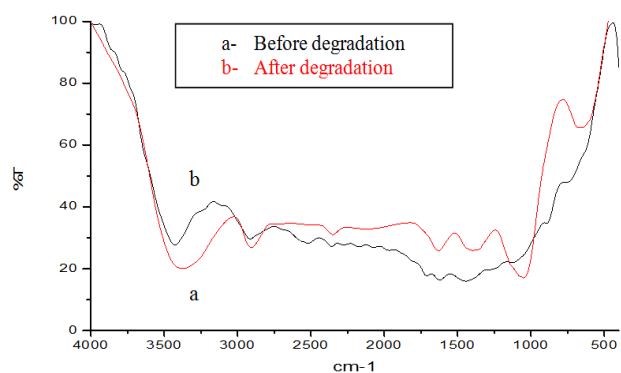


Fig.4. FT-IR Spectrum of raw sample of PVC flex on UV irradiation (365 nm for 60 min)

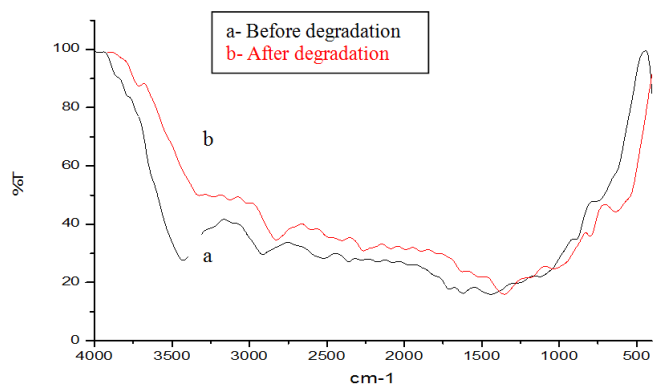


Fig.5. FT-IR Spectrum of raw sample of PVC flex on UV irradiation (254 nm for 120 min)

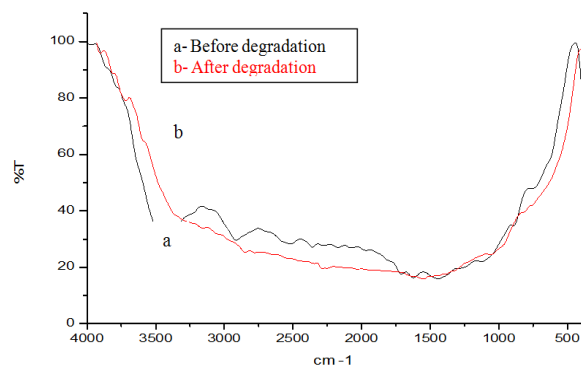
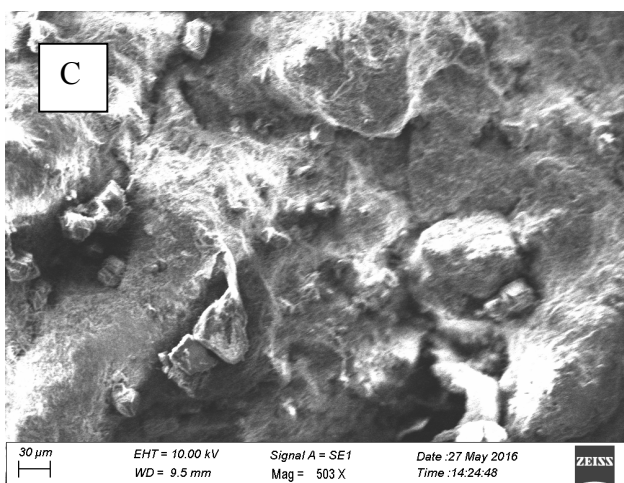
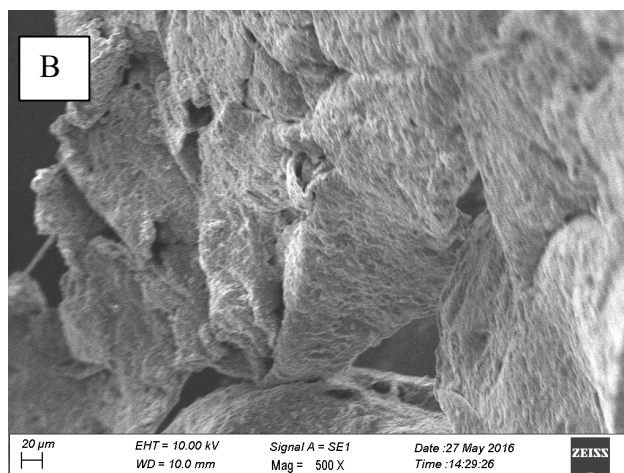
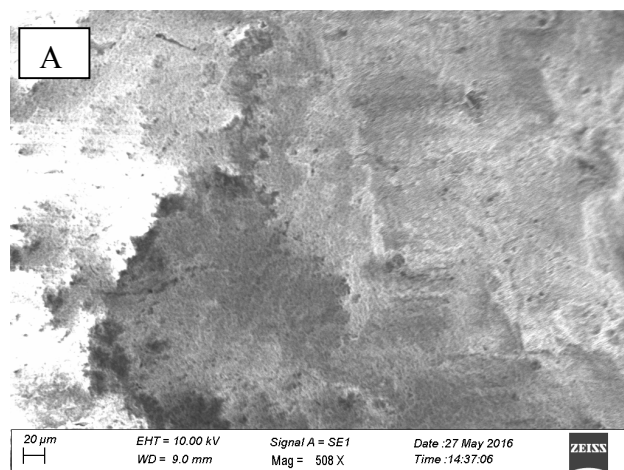


Fig.6. FT-IR Spectrum of the sample after Thermal degradation (170°C for 30 min)



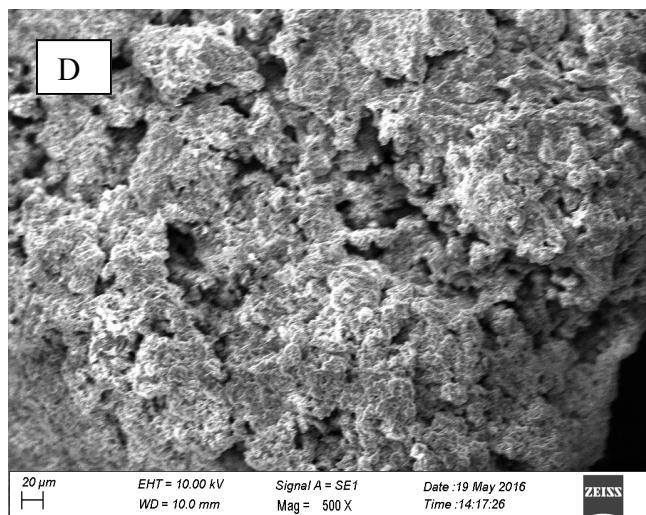


Fig.7. SEM images of the sample after degradation
 a) Before degradation b) Photodegradation (60 min)
 c) Photodegradation(120 min) d) Thermal degradation (30 min)

1590 cm^{-1} is observed in the spectra (Madhavan *et al.*, 2016). This is assigned to a carbon-carbon double bond structure is formed as a result of dehydrochlorination. The IR spectral data suggest that dehydrochlorination has taken place when photo degradation and thermal degradation processes were carried out on the PVC flex sheets. No change in the IR stretching frequencies was observed after the biodegradation process. Hence, it is concluded that the PVC flex materials are non biodegradable. In order to examine the surface morphology of the treated flex sheet SEM analysis was carried out at different magnification. The untreated flex sheet displayed a normal surface view but the treated sheets showed the appearance of numerous holes, cracks and change were observed. (Saeedi *et al.*, 2011) (Fig.7)

Reuse of waste PVC flex sheets (Wealth from Waste)

By using the waste PVC flex sheets, the following utility articles were made: flower vase, bag, purse and shelter sheet Fig.8.

Conclusions

The waste and used PVC flex sheets / banners were collected from different villages of Sendurai, Ariyalur and Udayarpalayam Taluks in Ariyalur District. The collected waste PVC flex materials were washed with water and analyzed for various physico- chemical parameters. The flex sheets were completely soluble in tetrahydrofuran (THF), slightly soluble in acetone and insoluble in other organic solvents. The elemental analysis revealed the presence of chlorine. The presence of ester group was found by functional group test. The change in FT-IR spectral data suggests dehydrochlorination has taken place after photo degradation and thermal degradation of PVC flex sheets. The waste PVC flex sheets were used to make a few utility articles like flower vase, bag etc.,

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Fig.8. Utility Articles made from used /waste PVC flex sheets

The FT-IR spectrum of raw PVC flex shows stretching frequency at 2915cm^{-1} due to $\nu(\text{C-H})$, small band at 713cm^{-1} due to $\nu(\text{C-Cl})$ and a sharp peak at 1431cm^{-1} due to $\nu(\text{C-C})$. A shift in $\nu(\text{C-H})$ and $\nu(\text{C-Cl})$ were observed after the photo degradation and thermal degradation processes (Fig 3 to Fig.6). In both these degradation a weak absorption band at

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