Poly(vinyl chloride) reinforced Schiff base as an eco-friendly alternative to conventional PVC

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Abstract

A new Schiff base (L) was synthesized and confirmed by ¹HNMR, FTIR spectroscopy. The modified PVC with new Schiff base (L) was synthesized to produce a homogenous blend (PVC-L). A homogenous blend (PVC-L) added to copper chloride to produce PVC-L-Cu(II). The PVC films had been irradiated with an ultraviolet light for long period and confirmed by FTIR spectroscopy, weight loss and surface morphology was investigated by scanning electron microscopy.

Keywords PVC · Schiff base · UV-radiation · Modification · Films · Honeycomb-like

1 Introduction

The surface is modified by surface grafting method, without changing in the bulk properties. Mostly, the effect found for surface parameters may be detected both by the bulk polymer radical chemical modifications and modification influenced accurately at surface level, without modifying the structure and the bulk polymer properties. Surface graft polymerization used to modify the surfaces of membrane, using various surface activation methods included UV-irradiation [1], treatment of plasma [2], ozone [3], and chemical initiator [4] which can performed by either living graft polymerization or free radical graft polymerization. The direct modification onto the surface of polymer produces pore sizes change and may result to develop the polymeric membrane performance [5]. Graft copolymerization includes the reaction of already formed homopolymer or copolymer with fresh monomers [6] which are covalently bonded within polymeric chains, and thus conventional polymerization ways can be used. These techniques involve chemical, radiation, photochemical, and plasma-induced ways [7, 8]. Graft polymerization is also used in PVC modification to improve the performance of the polymer derivate and to exploit their application area

[5]. The aim of this work, modification of PVC and a Schiff base containing heterocyclic aromatic ring with Copper(II), after irradiation using UV for a long period. In addition, the Schiff base improved PVC photostability upon photo-degradation. Weight loss and surface morphology of PVC films were affected by transition metal. These heterocyclic aromatic units are connected to PVC chains as pending groups will greatly improve PVC photostability.

2 Materials and methods

2.1 Instrumentation

A record of FTIR spectra was conducted using Jasco FTIR-4200 spectrometer (Tokyo, Japan) (KBr disc). QUV Acceleration weather-meter tester (by Q-Band company, USA) was deployed to study the morphology changes of the PVC films prepared samples. This morphology investigation was performed utilizing Inspect S50 microscope (by FEI company, Czech Republic) while EDX patterns were examined by Bruker XFlash 6/10 (Japan).

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3 Materials

The entire chemicals used in this work were of highest purity available and they used without further purification. Ethyl cyanoacetate (98%), 1-naphthaldehyde (98%), hydrazine hydrate (86%), methanol (99%), ethanol absolute (99.9%) and carbon disulfide (99%), were provided by Sigma-Aldrich, USA. Polyvinyl chloride (PVC) was provided by Hanwha (KM-31, Seoul, Korea).

3.1 Synthesis (E)-2-(5-mercapto-4-((naphthalene-1-ylmethylene)amino)-4H-1,2,4-triazol-3-yl)acetonitrile

A mixture of (0.0006 mol, 0.1 g) 2-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl)acetonitrile were synthesized as previously reported [9], and 1-naphthaldehyde (0.0006 mol) in ethanol (10 mL) containing glacial acetic acid was refluxed for 4–6 h. After cooling, an orange solid appeared which was collected by filtration and recrystallized from ethanol to give Schiff base as a final sample.

3.2 Preparation of PVC-ligand films

0.25 g PVC and 0.05 g Schiff base in tetrahydrofuran (THF) solvent were mixed and refluxed for 3 h. The prepared PVC solution was casted onto cleaned glass plate and the films have been generated by implementing the evaporation method at 25 °C. Digital vernier was used to maintain 40 µm as a thickness for PVC-L films.

3.3 Preparation of PVC-ligand-Cu(II) complex films

0.3 g of synthesized modified polymer (PVC-L) and 0.05 g of copper chloride were dissolved in 5 mL of THF. The mixture was refluxed for 3 h in order to form the complex PVC-L-Cu(II) by evaporation technique for 24 h at room temperature.

3.4 UV light exposure

The achieved samples of PVC films mention above were exposed to UV light generated from QUV tester

(313 nm as λ_{max} , while light intensity was set to be 6.43×10^{-9} ein dm⁻³ s⁻¹) for 300 h as irradiation testing.

4 Results and discussion

Schiff base was synthesized as shown in Scheme 1. Reaction of 2-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl)acetonitrile and 1-naphthaldehyde in boiling ethanol containing acetic acid as a catalyst for 4–6 h gave Schiff base (Scheme 1) with melting point range (190–191) °C in 59% yield.

The structure of Schiff base was confirmed by FTIR spectroscopy. The FTIR spectra of Schiff base shows the presence of intense absorption bands at 1578 cm⁻¹ can be attributed to the CH=N bond, also indicate disappearance of (C=O) and NH₂ groups absorptions. The FTIR spectra of Schiff base shows (C–H) aromatic, (C–H) aliphatic, C=C and C–S absorptions at 3108, (2872–2984), 1508 and 773, respectively.

¹H-NMR spectroscopy was used to record the proton nuclear magnetic resonance (¹H-NMR; 300 MHz) spectra for 4 in DMSO-*d*₆, it showed signals at (3.75) ppm for CH₂, signals at (7.91–8.11) for 6H of two phenyl group, (8.21) ppm for CH=N, and (10.18) ppm for SH. Recently, scientists ought to modify PVC, via creation aromatic and heterocyclic moieties thru reaction of halogen displacement. Generally thought, the displacement of facial chlorine from PVC introduces the potential of anchoring of ligands simplicity to PVC matrix and the immobilized transition metal complexes [10]. Figure 1 confirmed the changed in the polymeric film. Coordination of the ligand by SH with PVC chains.

The SN² is the mechanism for the preparation of the modified PVC by aromatic and heterocyclic moieties in case of introducing of halogen as displacement agent. The photodegradation degree of polymeric films was monitored by FTIR spectra in the range (4000–400) cm⁻¹. The FTIR spectra of modified PVC-L film show (C–H) stretching of –CH₂– at 2885 cm⁻¹, (C–Cl) stretching at 630 cm⁻¹, stretching vibration of (CH=N) at 1687 cm⁻¹ and (C–H) bending of –CH₂– at 1385 cm⁻¹. The FTIR spectra of PVC-L-Cu(II) show (C–H) stretching of –CH₂– at 2937 cm⁻¹, (C–Cl)

Scheme 1 Synthesis of Schiff base

Fig. 1 Suggested geometrics of PVC-L-Cu(II)

stretching at 697 cm^{-1} , stretching vibration of ($\text{CH}=\text{N}$) at 1687 cm^{-1} and ($\text{C}-\text{H}$) bending of $-\text{CH}_2-$ at 1437 cm^{-1} .

The most common oxygenated products are aldehydes, chloroketones, chlorocarboxylic acids, and acid chlorides. The carbonyl-containing fragments usually can be detected using FTIR pattern upon irradiation. Therefore, PVC films were exposed for UV light irradiation for different time periods and the FTIR spectra were subsequently recorded. The FTIR spectra for PVC (blank) before under three conditions (Indeed beside the original sample): (0 h) and after irradiation (100, 200, and 300 h) are shown in Fig. 2. It clearly shows that the intensity of the peak at 1722 cm^{-1} corresponding to carbonyl group ($\text{C}=\text{O}$) vibration became apparent upon irradiation, and its intensity increased as the irradiation time increased. PVC films blended with Cu(II) chelates suggests the increase of photostabilization [10].

The intensity of the $\text{C}=\text{O}$ group in the FTIR spectra was monitored upon irradiation which has been compared to a standard peak of 1328 cm^{-1} that corresponds with $\text{C}-\text{H}$ bond in the CH_2 units of PVC. Films blended with

Cu(II) chelate acts as photostabilizer. As Fig. 3 shows $I_{\text{C}=\text{O}}$ changes occurred for PVC films due to irradiation exposure. Carbonyl index ($I_{\text{C}=\text{O}}$) was used to identify PVC films photo-oxidation degree using below formula:

$$I_{\text{C}=\text{O}} = A_{\text{C}=\text{O}}/A_{\text{Ref.}}$$

where $A_{\text{C}=\text{O}}$ is the carbonyl group peak area, and $A_{\text{Ref.}}$ is the $\text{C}-\text{C}$ bonds peak area corresponding (1328 cm^{-1}).

Accelerated degradation of PVC and the mechanism of occurred degradation under wavelength 313 nm irradiation light have been carefully studied. This study shows if degradation can take place under accelerated sunlight, this method will become an excellent one for the degradation of waste plastics, which is mainly required for green chemistry.

The PVC films were weighted during irradiation process. The measurements were performed every 50 h till reach to 300 h after removing them from the climatic chamber, using an analytical balance. The presented data proves the weight loss for blank PVC film was higher in compared to

Fig. 2 The changes in FTIR spectra of PVC-L-Cu(II) film after UV irradiation exposure

Fig. 3 The changes in $I_{C=O}$ of PVC films during irradiation exposure

PVC films blended with Cu(II) which exhibit least weight loss, as displayed in Fig. 4.

The SEM examines the effect of UV irradiation on the surface morphology of PVC films [11]. Chemical modification on PVC films can be done through chlorine atom nucleophilic substitution reaction inside certain kind of solution which works as giver, as have been reported by other scientists. The surface morphology of PVC films were examined using SEM, the results were shown in Fig. 5. UV light has been supplied on both of PVC (blank) film and PVC-L-Cu(II) films for irradiation with an ($\lambda_{max}=313$ nm) for 300 h. SEM images provided the necessary information about particle shape and size which expressed that the for the non-irradiated PVC (blank) had smooth and neat surfaces with a high degree of homogeneity [12, 13].

Fig. 4 Changes in the weight loss percent in PVC films during irradiation exposure

For PVC-L contains Copper(II) chloride film after UV irradiation for 300 h, the results shown that fabrication of porous PVC material is due to the cross-linking and evolution of hydrogen chloride and other volatile products.

The SEM images of PVC films revealed forming of honeycomb-like morphology which we can conclude safely this roughness at the film surface is due to the interaction/coordination happened between the PVC-Schiff base blend and Cu(II) ion as a consequence of pass-linking. The images designate that the PVC mixture changed into well suited with identical matrix [14]. Obviously, for each Schiff base and $CuCl_2$ had been often distributed inside the chains of the PVC sample. However, numbers of round pores were noticed on the surface probable as a result of

Fig. 5 SEM images for PVC-L-Cu(II) film after irradiation process: **a** 200 μm scale of 500 $\times$; **b** 100 μm scale of 1000 $\times$; **c** 50 μm scale of 2000 $\times$

the accelerated evaporation of tetrahydrofuran which has been introduced to the process of the film production as a solvent. Knowing the different or variation in what is known as deriving forces during the phase separation, the pore size turned into varying [15]. Meanwhile, PVC and Cu(II) Schiff morphology has changed to the hexagonal profile. High stability of the treated PVC samples was achieved as effect of that hexagonal shape and

the Cu^{2+} ion which might act as transmit stabilizers [16]. Porous shape was endorsed to Cu^{2+} ions coordination and incorporation on the sample surface and more within the polymer matrix. Commonly, high surface area comes as consequence of the porous nature existence on the film surface with decreasing of crystalline size [17]. It has cited by number of researcher that the shape of the honeycomb is strongly depending number of factors such as solvent

Fig. 6 EDX for PVC-L-Cu(II) film

type, polymer facet-chain period and the polymer concentration [17]. The SEM topography has been intensively analyzed to study the impact of UV light exposure on the PVC film samples as an effective tool and diagnose the particles size the their shapes [18, 19]. The EDX technique is sufficient technique to detect the elemental composition of polymeric materials [12], Fig. 6 shows that the PVC-L-Cu(II) film exhibits appearance of new band that related to the Cu(II).

5 Conclusion

In summary, we investigated a simple method for the preparation of modified poly(vinyl chloride). A Schiff base containing the 1,2,4-triazole moiety was synthesized and used to modify the polymer. PVC film blended with Cu(II) chelates was irradiated with UV light to observe a number of honeycomb-like on the surface. The PVC-L-Cu(II) was found to be the most effective in photostabilization process.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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