Morphological, Color Impact and Spectroscopic Studies of New Schiff Base Derived From 1,2,4-Triazole Ring

A. A. Ahmed¹, M. H. Al-mashhadani¹, H. Hashim², D. S. Ahmed³, E. Yousif**¹
¹ Department of Chemistry, College of Science, Al-Nahrain University, P.O. Box: 64021, Baghdad, Iraq.
² Department of Physics, College of Science, Al-Nahrain University, P.O. Box: 64021, Baghdad, Iraq.
³ Department of Medical Instrumentation Engineering, Al-Mansour University College, P.O. Box: 64021, Baghdad, Iraq.

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1. Introduction

Nowadays, Heterocyclic moieties represent the most active part of the medications as antibacterial side [1, 2]. 1,2,4-triazole unit, among so many types of heterocyclic segments, can effect polarity, lipophilicity, and hydrogen bonding between molecules. It can also enhance the pharmacological, toxicological, pharmacokinetic, and physicochemical characteristics of the medications [3, 4]. Naturally, 1,2,4-Triazole derivative molecules are holding an active pharmacological series such as anticancer [5, 6], antiviral [7, 8], antitubercular [9, 10], antifungal [11, 12], antibacterial [13, 14] activities and photostabilizers series [15, 16]. Long time ago, plastic waste has been recognized as a threatening for the marine ecosystems. However, in the recent years, the concern regarding this issue started growing due to the increasing of plastic production rates almost a hundred times since the huge production has been started. The research estimates that around 10 million tons of plastic waste entered the marine environment for only one year [17]. Polystyrene (PS) is considered as one of the most important plastic due to its unique properties. It is very cheap, flexible, hard, light, clear, and can resist different types of solvents, acids and bases. It can also be synthesized in different forms such as solid or foam. All these exceptional properties make PS suitable for use in different applications such as wrapping, labeling, and various engineering needs [18, 19].

Plastic polymeric materials are used in many...
applications for example anticorrosive coatings for metals [20] and organic electronics applications [21] such as polymeric light emitting diode (PLED), transistors, sensors and solar cells. The photo-stability of plastic polymer can be enhanced by modifying the chemical structure of the polymer chain. Hence this primary approach is very rarely used because of mixing UV absorbers compounds and/or different types of amines as photo stabilizers have showed an excellent plastic protection [22]. Since long time, the organic UV stabilizers have been used to increase the polymer photo-stability, but these stabilizers themselves can be degrade and transfer within the polymer chains and they might cause safety problems if used in a high concentrations [23]. Many researchers have used different types of additive to stabilize the polystyrene materials against the photo degradations such as aromatic [24], heterocyclic [25], and organometallic [26] additives.

Herein is reported the synthesis and characterization of the derived novel Schiff bases and also their influence on the morphology and chemical structure of polystyrene films were studied.

2. Experiment

2.1. Materials and instrumentation
Chemicals, reagents, and solvents have been purchased from Sigma-Aldrich, Mercury, and Alfa-Aesar Companies and they were used without further purification. Jasco FT/IR-4200 spectrometer was utilized to record the FTIR (Fourier transform infrared) spectra. $^1$H NMR (proton nuclear magnetic resonance) spectra were recorded by using Varian Mercury-300 MHz spectrometer. EDX (energy dispersive X-ray spectroscopy) patterns were measured by using the Bruker XFlash® (Bruker, Tokyo, Japan) and finally Inspect S50 microscope was utilized to study the morphology of the prepared polystyrene and Schiff base porous films.

2.2. Synthesis of Schiff base

Compound (2) was synthesized by reacting compound (1) with ethyl 4-chloroacetate using ethanol as a solvent and potassium carbonate as a catalyst. The reaction mixture was refluxed for 3 h to yield compound (2) with reasonable 67% yield. While compound (3) was prepared by reacting compound (2) with hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) using the same solvent (ethanol) and left the mixture to stir at reflux for 3 h, to obtain product (3) with 60% yield [28]. Finally, compound 4 was synthesized via reacting (1.76 g, 5.0 mmol) of compound (3), with 2-hydroxy benzaldehyde. Ethanol was used as a solvent, and 0.2 mL of glacial acetic acid was added to the reaction mixture and refluxed for 4 h. The residue was filtrated and recrystallized from ethanol to produce the final pure target product compound (4) with 58% yield. Scheme 1 shows all the chemical structures in these reactions.

2.3. Films preparation

A mixture of PS (4 g) and Schiff base 4 (20 mg) in CHCl$_3$ solvent (80 mL) was stirred for half an hour at ambient temperature to obtain a homogenous film. The mixture was transferred to glass plate by using drop-casting technique. The films produced were dried for 2 days at room temperature. The polystyrene (PS), and (polystyrene: Schiff base) (99:1 w/w) films were with a thickness 40 µm.

2.4. Irradiation by UV ray

The prepared polystyrene films were exposed to UV light for 300 h at light intensity of $6.43 \times 10^{-6}$ einstein m$^{-3}$ s$^{-1}$, wavelength of 313 nm, and 25 °C. It was also used the QUV tester as an accelerated weather-meter.

3. Results and Discussion

Reaction of compound (3) and 2-hydroxy benzaldehyde, in ethanol as a solvent in the presence of acetic acid at reflux for 4 h, resulted in a crude product compound (4) as shown in scheme 1. The crude product was purified by recrystallization from ethanol resulting in a pure Schiff base compound (4) as brown crystals with 58% yield and the melting point in the range of 100-102 °C.

$^1$H-NMR and $^{13}$C-NMR spectroscopic techniques were utilized to identify the chemical structure of compound 4. Both $^1$H-NMR and $^{13}$C-NMR spectra showed all the characteristic peaks which are required to approve the chemical structure of compound 4. DMSO-$d_6$ was used as a deuterated solvent. $^1$H-NMR spectrum shows signals at aromatic region between 7.02 to 8.28 ppm which are related to the phenyl groups, and (9.26) ppm for CH = N. However, the $^{13}$C-NMR spectrum of 4 shows the overlap of various signals in the aromatic region such as 129.2, 131.1, 128.8, 127.5, 121.4 and 132.4 (CH$_3$); 154.3 and 146.0 (CH=N); 151.1 and 170.0 (C=O). The FTIR spectroscopy was used to identify the chemical structures of the Schiff base compound. The FTIR spectrum
demonstrated the existence of strong peaks at 3190, 3058, 2969, 1662, 1508, and 762 cm\(^{-1}\). These peaks showed the vibration of N-H, C-H (Ar), C-H (Aliph.), C=N, C=C, and C-S, respectively for Schiff base (compound 4).

In this work we used the Schiff base containing 1,2,4-triazole segment (compound 4) as a photo-stabilizer for polystyrene films. We used the Schiff base compound (dimercapto-thiadiazole) as photo-stabilizers for polymethylmethacrylate (PMMA) films and it showed an excellent efficiency to reduce the photo degradation of the polymer backbone [29]. Emad et al. has also used 2-thioacetic acid benzothiazol complexes as stabilizers of polystyrene and it showed good outcomes [30]. In this work, we used pure organic materials (compound 4) as a photo-stabilizers of polystyrene films. Figure 1 is a schematic diagram which shows the irradiation of the polymeric film containing the photo-stabilizer under sun light and how the light energy transfer to the heat without affecting the polymeric structure of the film. A spot size of 50 nm was utilized for the EDX (energy dispersive X-ray spectroscopy) measurements and the 3-D resolution of the EDX was calculated by the interaction volume size of the electron beams with the polymer films and was expected to be approx. [27]. There are two main reasons for measuring the EDX patterns. The first one is to analyze the major elements in the polymeric films, and the other one is to investigate the homogeneity of the polymer films. By comparing Figures 2 and 3, it is clear that the abundance peak in Figure 2 is for carbon atom as the film contains only polystyrene. However Figure 3 demonstrates the appearance of new peaks at the region of nitrogen, sulfur and oxygen, which is due to the presence of the Schiff base compound in the prepared films.

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\begin{array}{c}
\text{AcOH, reflux 4 h} \\
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Scheme 1: Synthetic rout of compound (4).
Figure 1: Schematic diagram shows the Irradiation of doping polystyrene/Schiff base by sunlight.

Figure 2: EDX spectra obtained for polystyrene (blank) film.
The EDX technique was performed to investigate the chemical compositions of the materials, while the Scanning electron microscopy (SEM) technique was established to identify few properties related to the surface topography of the material. Both of these two techniques have been widely used to study different types of material surfaces. The surface features of the polymer films such as the shape and size were studied by using the SEM technique, and it was also used to investigate the homogeneity of polymeric films Figure 4. Figure 4 (a and b) shows SEM images of blank polystyrene film before and after irradiation with the UV light so it can be compared with doped films. Figure 4 (a) demonstrates smooth and homogenous surface of the polystyrene (blank) film. Both polystyrene and polystyrene/Schiff bases thin films were irradiated by ultraviolet ray at 313 nm for 300 h. Figure 5 shows SEM images at various magnifications for PS/Schiff base blend and it can be seen clearly that the blend polystyrene film form interesting phenomena (cotton-like fibrous) after irradiation under UV light [28]. Irradiation of the PS film that containing Schiff base for 300 h leads to the production of crescent-like in comparison to the ones obtained in the absence of any additive, this may be due to the photo-degradation by UV light.
4. Conclusions

A novel Schiff base has been synthesized and utilized as stabilizer to reduce the photo degradation of polystyrene films under sunlight. The EDX patterns demonstrated clear evidence on the influences of Schiff base compound within the polymeric films. They showed that the main element in both blank polystyrene and polystyrene/Schiff base films is the carbon atom. It also showed the appearance of new bands which are due to the incorporation of the Schiff base. The irradiation of blank polystyrene by UV light for long time produced cotton-like material however polystyrene-having the Schiff base produced crescent-like material after irradiation. The crescent-like material was formed due to the presence of compound 4 within the polymeric structure, long time irradiation, or decreasing the photo-degradation process of the polymer. Obviously, Schiff bases improved the photo-stability of the polystyrene films under irradiation.

Figure 5: Top view of SEM images of crescent-like for PS/1 blend after irradiation
a) 100 µm, b) 50 µm, c) 20 µm and d) 10 µm.
5. References

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