Utilizing Organic Aromatic Melamine Moiety to Modify Poly(Vinyl Chloride) Chemical Structure and Micro CuO That Plays an Important Role to Enhance Its Photophysical Features

Mohammed Hussein Al-Mashhadani[1*], Ekhlas Abdulkhadiar Salman[1], Amani Ayad Husain[2], Mustafa Abdallh[1], Muna Bufaroosha[3], and Emad Yousif[1]

[1]*Department of Chemistry, College of Science, Al-Nahrain University, 64021, Baghdad, Iraq*

[2]*Polymer Research Unit, College of Science, Al-Mustansiriyah University, 10052, Baghdad, Iraq*

[3]*Department of Chemistry, College of Science, UAE University, 15551, Al-Ain, UAE*

** **Corresponding author:***

email: mo_chemical@yahoo.com

Received: November 6, 2021
Accepted: July 30, 2022

DOI: 10.22146/ijc.70263

Abstract: *Three arms Schiff base unit based on melamine moiety was synthesized and introduced to polyvinyl chloride (PVC) to produce a modified PVC polymer. The polymer composite of new modified PVC polymer was blended with micro copper oxide as a reflecting mirror of UV light to enhance the photostability of PVC. Three different concentrations of micro copper oxide (0.01–0.03 wt.%) were mixed with the modified PVC and cast as a thin film. The photostability test has shown high resistance to photodegradation upon exposure to UV light. In this work, different approaches were applied to examining doped modified PVC's thin film efficiency against photodegradation after exposure to UV light for 300 h in an ambient atmosphere. The exhibited studies, such as infrared spectroscopy and weight loss percentage, have demonstrated the improvement of photophysical properties for modified PVC and blended modified films in comparison to blank PVC polymeric films. These outcomes are so interesting as they could contribute to reducing the consumption of PVC around the world hence its waste causing huge environmental problems for the marine ecosystem.*

Keywords: *aromatic; photo-stabilizers; micro copper oxide; FTIR; melamine*

INTRODUCTION

Plastics have a wide range of chemical and physical qualities as well as inexpensive manufacturing costs. They are mass-produced and used in a variety of industrial applications [1-3]. However, in recent years, both academic and industrial companies have been under intense work to address issues arising from the usage of plastics. For example, the amount of trash produced, the composition of that waste, and its negative impact on the ecosystem. Another major challenge is how to enhance the characteristics of plastics for long-term usage [4-6]. Polyvinyl chloride (PVC) is a flexible thermoplastic used in various applications, from food wrapping to equipment used in medicine. PVC is an inexpensive polymer easy to make and has excellent features. On the other hand, it has low thermal and mechanical stability.

Furthermore, when irradiated by ultraviolet (UV) radiation for lengthy periods, especially at high temperatures, the most prevalent types of synthesized PVC undergo a specific de-hydrochlorination process [7-8]. Because of the HCl molecules released, such processes result in the making (C=C) double bonds inside the polymer structure, cracking, discoloration, deformation, and a defect in the mechanical qualities of polymeric films [9-11]. Furthermore, PVC degrades slowly in landfills in natural settings [12]. As a result, at the numerous disposal sites where PVC trash ends up, it must either be burnt or collected and recycled [13]. PVC incineration creates harmful by-products that damage the environment as well as soil and groundwater [14]. Thus, including different stabilizers in the polymeric chemical structures might be a way to improve PVC characteristics and enhance its stability against heat and UV light [15-16]. The PVC stabilizers should be well-matched with the polymer and not change the product's color. The additives' main features are stability against harsh conditions, non-volatile, and inexpensive to manufacture [17-18]. Highly aromatic organic molecules, organometallic materials, inorganic nano-compounds, and Schiff bases are the most often used PVC stabilizers [19-22].

On the other hand, additives having heavy metals are not an amazing way to protect PVC for a long time because they have a propensity to leak out, generating ecosystem and human health issues. Because titanium dioxide is an efficient UV light absorber, it may be utilized as a PVC additive [23-24]. Nevertheless, titanium dioxide is a photocatalyst and speeds up the weathering and deterioration of PVC surfaces [25].

As a result, novel PVC stabilizers that are proficient, easy to manufacture, aromatic, and work as light stabilizers still have the potential to be developed. Melamine is a fragrant, odorless, low-cost, very stable material and not toxic. It is employed in a variety of industrial settings, including corrosion inhibitors [26-29]. Previous studies used copper oxide particles as photo stabilizers for paint media [30]. However, a new approach in this study was followed by using copper oxide microparticles as PVC additives. It used micro copper oxide, which should work as a reflecting mirror, which reflects the UV light from the surface of the polymeric films and prevents the chemical structure damage of it. Thus, the copper oxide was chosen because it is cheap and available. Also, it was used as an example to open the door for a new stabilization mechanism that could be expanded for many other metallic oxides.

■ EXPERIMENTAL SECTION

Materials

Petkim Petrokimya (Istanbul, Turkey) has supplied PVC generously for this work. The supplied PVC has a K value of 67. The copper oxide was purchased from Sigma-Aldrich company as a powder, with particle size < 10 µm and purity of 98% since it was used without any further purifications. All other chemicals are purchased from Sigma Aldrich (Gillingham, UK).

Instrumentation

The final PVC composite films have a thickness of about 40 µm measured via Digital Caliper DIN 862 micrometer (Germany). In order to run a photodegradation experiment, A QUV tester instrument was used to simulate the exposure to sunlight under laboratory conditions. The UV light was centered at 313 nm with an intensity of 6.43×10^{-9} ein dm^{-3} s^{-1}. UV rays irradiated all the samples for a maximum of 300 h irradiation time.

Procedure

Synthesis of three arms Schiff base unit based on melamine moiety (3)

Dimethylformamide (DMF) (40 mL) was used to dissolve (0.50 g, 4 mmol) of melamine under stirring at 120 °C completely. An excess of aromatic aldehyde (1.61 g, 13.2 mmol) dissolved in 5 mL DMF in addition to acetic acid (glacial) (0.2 mL) was mixed with the previous solution. The reaction was then heated up to refluxed (6 h). After cooling to ambient temperature, toluene was added to crash out the precipitate. The precipitate was filtrated and thoroughly rinsed with toluene and methanol. The pure target product was dried under a vacuum [19].

Synthesis of PVC/3 films

A 0.25 g of PVC polymer was dissolved in tetrahydrofuran (THF). A few drops of pyridine were then added to the above solution, followed by the addition of compound **3** (0.05 g) to the previous mixture. The solution was heated to reflux for 3 h and then cast on a glass mold. The solution was then kept in a dry place to let the solvent evaporate at room temperature. The resulted films have a thickness of about 40 µm.

Prepare PVC/3 micro copper oxide films

The modified PVC polymer with copper oxide composite was prepared by dissolving the PVC/3 polymer (0.3 g) in THF (5 mL) with different concentrations (0.01, 0.02, and 0.03 wt.%) of micro copper oxide. The solution was heated to reflux for 4 h to give the PVC-3/CuO composite. The solution was then kept dry to let the solvent evaporate at room temperature to give the final product.

Weight loss method

The weight alterations of the samples are calculated using Eq. (1). The changes in the weight of the samples pre (W1) and post (W2) illumination with ultraviolet light are used to determine the percentage of the change.

$$\text{Weight loss \%} = \frac{W1 - W2}{W1} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Synthesis of Aromatic Melamine

The synthesis route of **3** is accomplished according to the procedure described by previous literature [19]. First, melamine was condensed with an excess of 4-hydroxybenzaldehyde in the existence of acetic acid, as shown in Fig. 1. Then, the final product **3** was obtained as a pale yellow powder in a 73% yield.

Modification of PVC Chemical Structure

In recent times many attempts have been tried to modify the chemical structure of PVC to enhance its properties [31-32]. This work used melamine as a highly aromatic moiety to modify the chemical structure of PVC polymeric chains, as shown in Fig. 2. A very small amount of melamine was used compared to polymer; melamine molecules replaced a few chlorine atoms. The reaction has likely followed SN2 mechanisms due to the

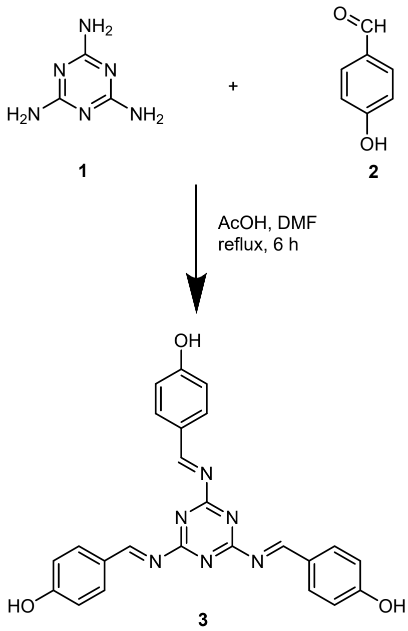

Fig 1. Synthesis of melamine Schiff base **3**

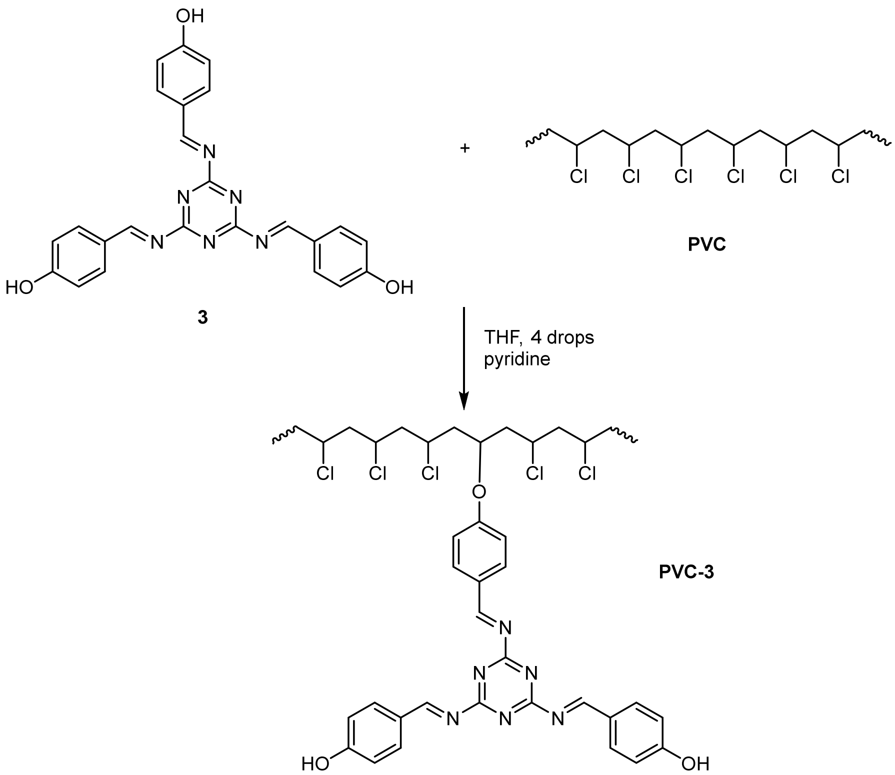

Fig 2. Modification of PVC chemical structure

steric hindrance, as a slightly similar mechanism was described in previous research [33]. The product was identified using FTIR spectroscopy. Hence it noticed the Schiff base peak at 1776 cm^{-1} as well as the decreasing of the intensity of the OH band. It is clear evidence that almost all of the melamine was replaced by chlorine from one side. This is possible due to steric hindrance effects since the molecule prefers to react from one side rather than strictly hindrance situations with making cross-linking. However, there is a possibility that a very trace amount reacted from two or three sides, but the majority reacted from only one side. The idea is to use a very small amount of aromatic units so it does not affect the chemical or physical properties of the polymer; at the same time, it provides very good photoprotection for the polymer. Melamine in a small amount was not changing the features of PVC, and it works as an excellent UV absorber due to its high aromaticity. This work also used micro CuO particles to enhance the photo-stability of PVC films, proposing a new stabilization mechanism, as will be discussed in the next section.

The Blending of Modified PVC with a Trace Amount of Micro CuO

After that, the modified polymer was mixed with different percentages of micro copper oxide (0.01, 0.02, and 0.03 wt.%) to get a blend of modified PVC with micro copper oxide. It was thought that micro CuO could work as a reflecting mirror of sunlight and protect the polymer from degradation. Fig. 3 is an animated diagram that shows how melamine and micro copper oxide can protect the PVC from photodegradation.

Utilizing the FTIR Technique to Examine Modified PVC Stability

The prepared polymeric films described in the experimental section were irradiated by UV light for 300 h of blank and blended PVC films. The photodegradation of polymeric films was monitored using the FTIR technique (4000–400 cm^{-1}) because the PVC undergoes an elimination process by releasing HCl molecules when irradiated by UV light, which leads to the formation of alkene groups. Furthermore, it is possible

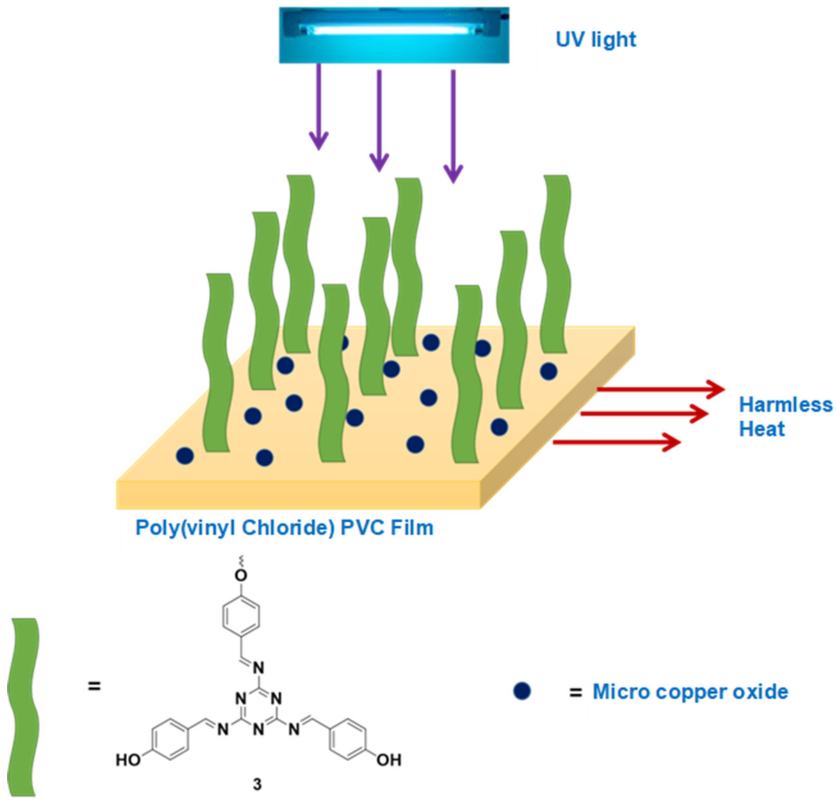

Fig 3. Animated diagram of photostability for modified PVC doped with CuO

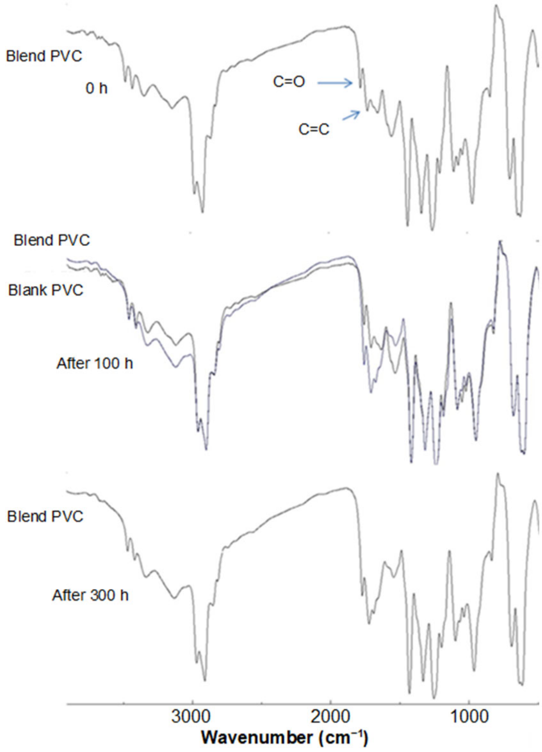

Fig 4. Infrared spectrums of PVC blended with micro copper oxide (0.01 wt.%)

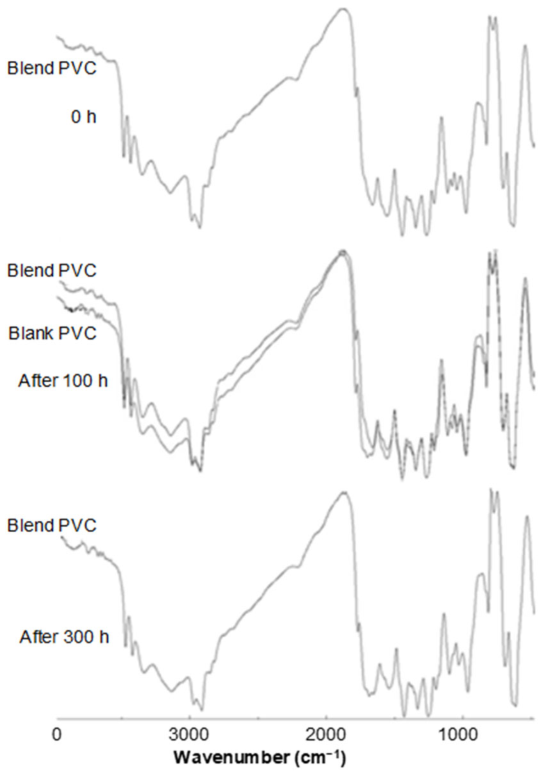

Fig 5. Infrared spectrums of PVC blended with micro copper oxide (0.03 wt.%)

to oxidize the polymeric chains and form carbonyl groups in the presence of oxygen. Therefore, both alkene (C=C) and carbonyl (C=O) groups could be monitored using FTIR, which shows peaks at 1660 and 1720 cm^{-1}, respectively. Fig. 4 and 5 clearly show that blend modified PVC has very good stability against UV light matched to blank PVC, as shown in Fig. 4 and 5 after 100 h irradiation.

Weight Loss Percentages Approach to Monitor the Stability of PVC

Another approach was utilized to exhibit the efficiency of blend modified PVC, which is the weight loss percentage against irradiation time, as shown in Fig. 6. In all cases, it is obvious that the weight loss percentage increases with increasing the irradiation time. This is because the PVC chemical structure has the ability to undergo an elimination reaction and release HCl molecules when irradiated by UV light. This leads to reducing the molecular weight of the polymer and increasing the weight loss as this is the main known defect of PVC materials. Hence, it was taken and weighed for both blank and blend PVC in an interval time of 50 h. Using micro CuO particles with modified polymer has enhanced the photostability of PVC. Another result was obtained from this study that increasing the percentage of micro copper oxide can decrease the degradation of polymeric film. Hence, micro copper oxide works as a reflecting mirror of UV light in this case. It is important to mention that modified

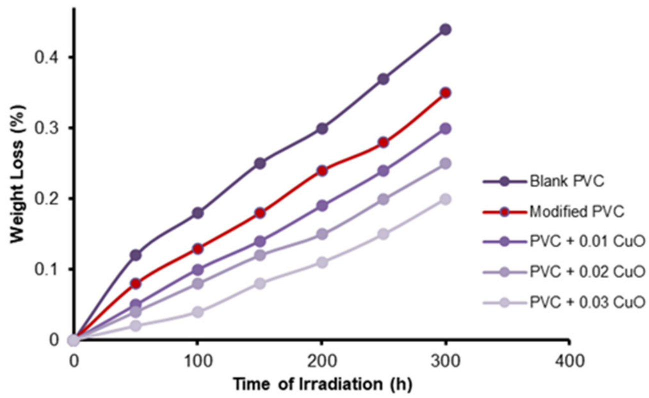

Fig 6. The loss of weight percentage of PVC mixed with different concentrations of micro copper oxide at 300 h of irradiation

PVC has provided good protection for PVC polymeric films compared to blank PVC. This is because melamine has a highly aromatic system, which absorbs UV light and works as a UV blocker. This protects the PVC chemical structure from photodegradation after exposure to UV light.

■ CONCLUSION

To summarize, this study used a highly aromatic organic molecule (melamine) to modify the chemical structure of PVC and utilized FTIR to identify the product. This modification was done to enhance the photophysical properties of PVC. Hence, melamine has a highly conjugated system and absorbs in the UV region. Copper oxide (CuO) was added to modified PVC in different concentrations. It is thought that CuO could work as a reflecting mirror of UV light and protect PVC films from degradation. Two approaches, FTIR spectra and weight loss were considered to examine the stability of blend PVC compared to blank PVC. Both studies were in agreement and proved that modifying the structure of PVC with a very small amount of aromatic molecules and blending it with micro CuO particles can improve the properties of the polymer and reduce its photodegradation.

■ ACKNOWLEDGMENTS

We would like to thank Al-Nahrain University for its support during this research.

■ AUTHOR CONTRIBUTIONS

Conceptualization and experimental design were done by Mohammed H. Al-Mashhadani, and Ekhlas A. Salman. The experimental work and data analysis were done by Amani Ayad Husain and Mustafa Abdallh. Meanwhile, writing–original draft preparation was done by Muna Bufaroosha, and writing–review and editing by Emad Yousif.

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