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# Quartz Crystal Microbalance (QCM) as an efficient tool for studing UV stabilization of PVC by $TiO_2$ and CuO nanoparticles

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**Abstract**

In recent years, industrialization has necessitated the widespread use of polymers in many fields. Polymers due to their desirable properties such as high durability and flexibility and resistance to electric current and heat. have played their role well in construction, industrial, automotive, health and other applications. The studied polymer in this research is polyvinyl chloride, which is one of the most widely used polymers in the world after polyethylene. The main problem in the use of polymers is the destructive effect of sunlight on polymers used outdoors**.** fractures and cracks and formation of gypsum on the surface of polymers and financial losses and even in some cases, destruction of docks and aircraft fuselages can cause casualties of UV radiation of sunlight. In this paper, in order to increase the lifespan of PVC against UV radiation, TiO2 and CuO nanoparticles in the polymer structure have been used. QCM is used as a mass sensitive sensor to study the stabilizing effect of metal oxide nanoparticles in PVC matrix. Results showed that both $TiO_2$ and CuO nanoparticles can enhance durability of PVC against UV degradation while CuO has much better performance in this regard.

**Keywords**: QCM, PVC, UV Resistance, TiO2 and CuO nanoparticles

## Introduction

The climatic conditions of agiven region are considered to select the materials used for constructional and industrial applications; In the past, traditional materials such as wood and cement were used for most constructional and industrial uses. In the twentieth century, advances in technology have intensified the use of polymers for most everyday, technical and industrial uses. In this regard, the twentieth century is known as the era of plastic or polymer. Meanwhile; polyvinyl chloride is one of the most widely used polymers in the world, which is used in a wide range of applications such as construction, automotive, healthcare, electronics and sports [1-3]. The advantages of PVC include compared to other plastics, transparency, lightness, recyclability, high hardness and mechanical properties, excellent thermal and electrical insulation, resistance to a variety of acids, salts, alcohols, bases and fats.

But the problem of using commercial polymers, such as PVC, is that these polymers undergo photolytic and photooxidative reactions when exposed to the sun's ultraviolet rays [4]. Polymers with chromophore groups, such as double bond carbon-carbon (C=C) and carbonyl groups (C=O), absorb UV energy emitted from the sun; Chromophore groups may be exist in the regular structure of the polymer, either as a result of existing impurities or through the thermal processes of the materials involved in the reaction. Absorption of UV energy by polymers with chromophore groups can cause light reactions and photochemical reactions [5, 6]; The onset of photochemical decomposition reactions can occur through free radical mechanisms and lead to the formation of hydroperoxides and chain breakage, ultimately leading to catastrophic damage of the polymer structure and destructive effects on the polymeric material, including discoloration of the polymer surface and severe mechanical damage to the polymers, the occurrence of which severely affects the performance of the product.

Polymer discoloration is caused by chemical changes in the structure of the polymer, which causes the polymer to turn yellow or darken, and the combination of water and UV rays is another adverse effect of weathering and can cause erosion and fading of some surfaces. As this process continues, the surface additives disappear and the degradation of the polymer substrates begins, which will affect the beauty of the polymer. These phenomena cause the destruction of effective parameters in the performance of products such as mechanical properties of materials such as tensile strength and impact resistance of materials; Therefore, before using materials, the performance of building products (especially in terms of longevity) in certain environments should be checked. In this research, an attempt was made to modify the structure of the polymer by introducing metal nanoxides in its structure and then the QCM method was used to track and monitor the mass reduction due to the degradation of the modified polymer against UV radiation. As a result of using the QCM method, information is available for online monitoring, so this method can be used as a sensitive mass sensor to study the mechanism of degradation and the stabilizing effect of various materials against UV rays.

Quartz crystal microscale (QCM) is an online sensor of biological, chemical and physical sensors with good features such as cost-effectiveness, high resolution and mass sensitivity [7]. The principle of operation of QCM is based on frequency fluctuation proportional to the mass changes deposited on the crystal surface; And what makes this sensor so diverse is that it can be used with a variety of coatings for a wide range of analyzes [8].

The QCM consists of two electrodes around a thin quartz plate that induce deformation in the crystal by applying AC voltage across the crystal. In this method, the Sauerbrey equation is used to relate mass changes and frequency changes:

$$\Delta m = -\frac{C}{n}\Delta f \qquad (1)$$

In this equation, the mass of the added layer is denoted by m, the frequency changes due to the addition of the layer on the crystal is denoted by f, and C is a constant in the equation and corresponds to the properties of quartz and N is the harmonic odd numbers, which can be 1, 3,5, 7, etc.

In a 2008 study by Dr. Mir Mohseni et al., A simple and inexpensive method for quantitative determination in solution was presented, which was based on a nickel oxide-modified quartz crystal electrode with PCA. High sensitivity and selectivity to the test solutions showed that the result was a linear response for the sensor at a Hys concentration of 2000-200 mg / L[9].

**Experimental**

To evaluate the stability of pure PVC polymer and structurally modified polymer against UV light, QCM machine was made and used in the laboratory. The schematic and real shape of the set-up and QCM circuit made in the laboratory can be seen in Figures 1 and 2.

To build the QCM sensor, a UV lamp with a peak wavelength of 390 nm and a power of 15 w, quartz crystal in parallel resonance mode, Calpits oscillator and ten digits Frequency meter were used**.** First, a suitable amount of PVC with known physical and chemical properties was dissolved in tetrahydrofouran (THF) solvent and a certain amount of polymer was precipitated on the crystal by droplet and evaporation of the solvent with a microliter pipette. A suitable UV light source (15w-280nm) was used to irradiate UV rays on the precipitated polymer.

The same test procedure was repeated with nanoparticle and PVC solutions dissolved in THF solvent. Frequency change diagrams per time were recorded and monitored as a measure of polymer degradation against UV rays.

**Result and Discussion**

Dropping polymer solutions on quartz crystals was performed with a microliter pipette and PVC was deposited on the crystal in a rigid and uniform manner. Frequency was recorded at regular intervals as shown in Figure 3. According to the Sauerbrey equation, the changes in frequency and deposited mass on the crystal are inversely related**,** that is, when a drop of solution is placed on the crystal, a sudden decrease in frequency is observed, which is caused by the droplet hitting the crystal surface, Then, with slow evaporation of the solvent from the crystal surface, a slow increase of frequency is observed in the diagram. Finally, with complete evaporation of the solvent, a relative stabilization of the frequency in a constant number (less than the initial frequency) was observed. This is due to the complete evaporation of the solvent and the fixation of a thin layer of PVC on the crystal, so the difference of the two frequency classes in the diagram can be attributed to the mass of PVC deposited on the crystal.

In Figure No.1, the non-uniformity of the frequency class distances can be explained by the different size of the droplets on the crystal and the possible difference in the density of the solution in different parts of the cell containing the solution (due to different densities of PVC, nanoparticles and THF).

After dropping, each crystal was exposed to direct UV radiation for approximately 240 h and the effect of each nanoparticle on the degradation of

polyvinyl chloride polymer against UV light was investigated.
As shown in Figure 2, UV light causes the gradual degradation of the polymer deposited on the quartz crystal and the frequency increases due to the reduction of mass on the crystal; However, the final frequency did not reach the initial frequency (frequency of the quartz crystal before dropping) of the crystal after 240 hours of exposure to UV light. This indicates that after this period of direct UV light irradiation, only the polymer precipitated in the drip step 4 is degraded, and a longer UV exposure must be established for complete polymer degradation.
The same test procedure was repeated with the modified polymer structured with nanoparticles and the diagrams obtained in Figures 3 to 6 are given; According to the diagrams, it can be seen that if UV stabilizers such as metal nanoxides are used, the degradation process of the polymer against UV rays will be slower and as a result, the curve will increase with a slower slope in a given time.

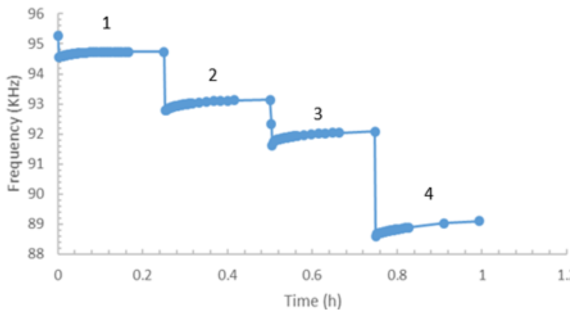


**Figure (1) QCM frequency changes during drip of 4 drops of PVC solution in THF on quartz crystal.**

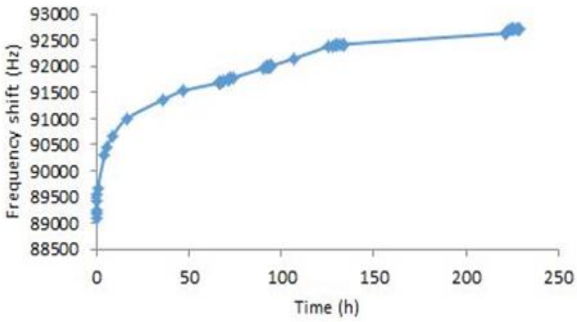


**Figure (2) frequency changes vs. time during degradation of PVC deposited on quartz crystals exposed to UV radiation.**

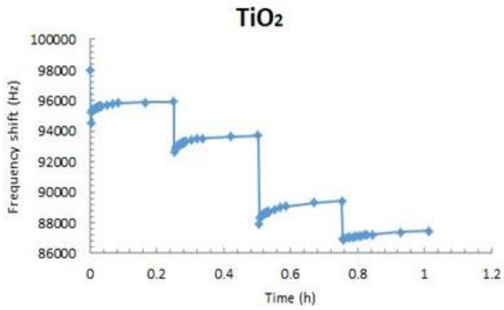


**Figure (3) QCM frequency changes during drip of PVC+$TiO_2$ solution in THF on quartz crystal.**

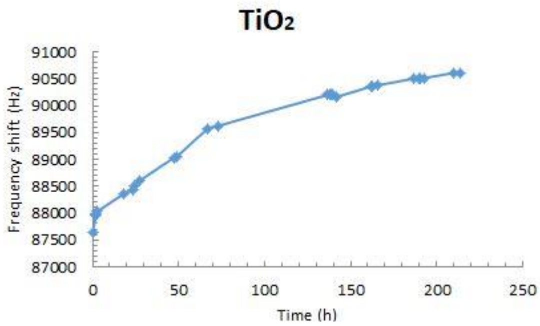


**Figure (4) frequency changes vs. time during degradation of PVC+$TiO_2$ deposited on quartz crystals exposed to UV radiation.**

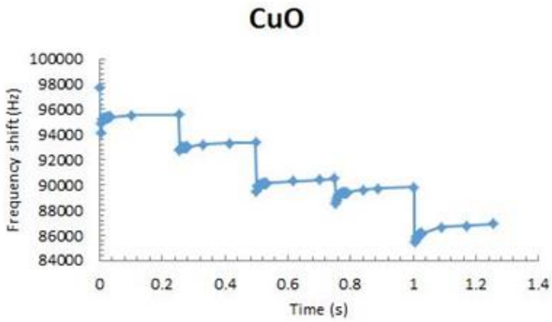


**Figure (5) QCM frequency changes during drip of PVC+CuO solution in THF on quartz crystal.**

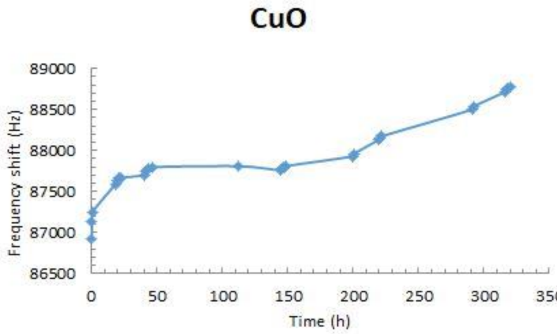


**Figure (6) frequency changes vs. time during degradation of PVC+CuO deposited on quartz crystals exposed to UV radiation.**

Figure 7 indicated a general comparison of frequency shift vs. time for pure PVC, PVC+$TiO_2$, PVC+CuO. As can be seen from Figure 7,both $TiO_2$ and CuO nanoparticles considerably lower the frequency shift in QCM indicating that PVC polymer is degsaded more slowly in the presence of UV radiation.

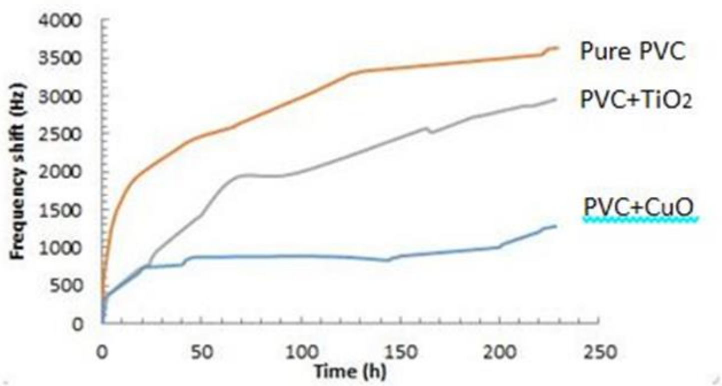


**Figure 7- Comparison of degradation of Pure PVC and PVC with $TiO_2$ and Cuo metal nanoxides.**

**Conclusions**

In this study, using the conrentional QCM method, which is a method based on instantaneous changes in mass based on frequency changes, the structural UV performance improvement of PVC polymer was studied using TiO2 and CuO metal nanoxides. QCM is used as a mass sensitive sensor to study the stabilizing effect of metal oxide nanoparticles in PVC matrix. Results showed that both TiO2 and CuO nanoparticles can enhance durability of PVC against UV degradation while CuO has much better performance in this regard.

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