



## Nanocatalyst for the Degradation of Plastic Waste to Produce Paints

Shams N. Almutalabi, Mohammed Alzuhairi , F. A. Hashim

Materials Engineering Dept., University of Technology-Iraq, Alsina'a street, 10066 Baghdad, Iraq.

\*Corresponding author Email: <mailto:mohammed.a.alzuhairi@uotechnology.edu.iq>

### HIGHLIGHTS

- Chemical recycling of plastic water bottles by Depolymerization process.
- Improving the specifications of paints materials by polyethylene terephthalate

### ARTICLE INFO

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### ABSTRACT

Recycling consumed commercial polymers is considered a highly important issue that chemists and engineers must take care of to develop the proper recycling techniques. The main objective of this study is to find a radical solution to the problems of plastic waste by recycling plastic waste (water bottles) and studying the effect of the produced Degraded Polyethylene Terephthalate (DPET) on the properties of paints. DEPT was added in six quantities to the paint mixture (1, 3, 4, 5, 7, and 14 grams). The paints were evaluated using various tests, including scanning electron microscopy (SEM), viscosity, adhesion, brightness, color, ultraviolet reflectance, and accelerated weathering. Testing the paint mixtures showed that the samples were not affected by weather conditions. This indicates the improvement of the paint mixtures by adding quantities of DPET. This study concludes that the catalyst ratios used succeeded in cracking DPET and avoided the need for large quantities of the catalyst. The use of DPET in various material applications reduces the cost due to the low cost of DPET production. The use of PET in sustainable applications conferred a radical solution to plastic waste problems worldwide. In this work, mixing plastic waste products, after their treatment, in the preparation of paint mixtures successfully contributed to improving the required specifications.

## 1. Introduction

Plastics are a widely used, non-harmless group of materials composed of long atomic chains, with carbon as the only or principal component. Plastics, polymers, and pitches are all used in the same way in a generic sense. According to a September 2018 research by the Central Pollution Control Board (CPCB), which extrapolated data from 60 major cities, the world generates around 25,940 tons of plastic waste daily. About 94 percent of this amount is recyclable thermoplastics like PET and PVC. Any large group of materials made up of other natural or inorganic components, such as oxygen, hydrogen, nitrogen, and carbon, in whole or in part, is referred to as plastic material. At the same time, being hard in their finished state, they can form fluid at some point throughout the manufacturing process and, along similar lines, capable of being framed into a variety of shapes, most typically by applying heat and weight, either independently or in combination. Plastics are lightweight, strong, and versatile; therefore, they can be employed in many applications.

Consequently, in response to daily life requirements, the use of plastics increases. Plastic waste is also being increased along these lines. As a manufactured polymer, plastic has replaced unique materials in virtually every aspect of our lives. It has become a significant part of the life of our general population. In the last few decades, the age of plastics in nature has increased by 17-fold. In addition, there are 18 synchronized extended uses of plastic materials. Plastic security and durability have steadily improved over time. There are groups of 20 materials that are now considered an alternative for materials resistant to various natural restrictions; the twenty-first century has created a new form of globalization. The literature focuses on converting waste plastics to gasoline by hydro-treating and hydro-breaking them. Much research and testing have been carried out to reveal the chemical components of pyrolysis fuel created by this activity. In 2016, waste bottles were used on the asphalt pavement to extend the life of the pavement while also lowering pollutant levels. PET was added as an additive to the bitumen mixture to address relevant issues. Six different weight percentages (%w/w) of PET) were added to the bitumen to create the samples.

According to the findings, increasing the amount of PET% content increased the modification. This addition provided maximum flexibility and hardness and improved resistance to permanent deformations and engineering properties [1].

In 2017, monomers and oligomers of bis (2-hydroxyethyl) terephthalate (BHET) were synthesized using a glass condenser for chemical recycling at 190°C from nano-zinc oxide with varying particle sizes and weight ratios. As a result, different monomers and dimers were formed [1].

The use of an additional heater in the bubble column reactor. The chemical depolymerization of PET using the shutdown system of ethylene glycol nitrogen glycolysis process, a PET catalyst, and nitrogen in a three-stage bubble column using a Nanocatalyst, SiO<sub>2</sub> with different weight ratio based on the weight of PET and nitrogen preheated to 100°C in 2018. The final product of (PET) depolymerization was thoroughly characterized using FTIR, AFM, and CHN tests [2]. Microorganisms isolated from soil samples were also tested for their PET biodegradability. Thirty-eight bacterial isolates were isolated from ten soil and material waste samples collected at four different waste disposal locations in Baghdad city at different times. The results showed that the saffron sample produced most of the isolates while the other produced fewer. During the screening process, the abilities to grow in liquid containing PET powder and create the liquid region on PET-MSM agar were all taken into account [3]. Pyrolysis, which converts plastic waste into valuable products in heat, has been identified as the most appropriate chemical recycling technique [4]. It also entails the development of blends containing various combinations of depolymerized Polyethylene Terephthalate (DPET), an Unsaturated Polyester Resin, and Ravemul VV/55 to reduce pollution by recovering plastic waste. The tests show that the presence of unsaturated polyester resin improves mechanical properties and increases cohesiveness [5]. Plastic production has risen considerably in recent decades, and end-of-life products made of plastics discarded in large quantities in landfills pose a serious threat to the entire planet. Attempts to solve the problems of recycled plastics have been made in various ways (for example, chemical or mechanical recycling), resulting in exceptionally cost-effective, reasonable, and ecologically friendly products. Because of its wide range of applications and ease of manufacture, the cost of producing plastic is reduced. The main advantages of employing polymers for many purposes include:

- The use of a variety of ways of treatments is used to produce various types of plastic items.
- Thermoplastic polymers are used in some formulation, strengthening, and filler applications.
- Currently, several manufacturing procedures are employed to make low-cost plastic goods [6].

Recycling has numerous advantages regarding environmental issues, such as lowering pollution levels and saving energy and money. Primary recycling is the process of reusing materials in their primary form. Moreover, it is inexpensive [7].

In the packaging sector, PET is used in the material industry. It is a high-strength, transparent, and safe semi-crystalline thermoplastic polyester. Because of its excellent chemical and physical properties, it is an indispensable material with various applications. The disposal of polyethylene terephthalate waste, on the other hand, has produced severe economic and environmental concerns due to its increasing use and non-biodegradability. As a result, PET waste management has become a significant issue for communities. However, according to a study of community environmental awareness, recycling is still the most sustainable treatment option for polyethylene waste [8].

Manufacturing of PET can be performed by using pure ethylene glycol and terephthalic acid, which are generated from crude oil. The initial result of heating the monomers of Bis (2-hydroxyethyl) terephthalate and the low molecular weight polymers together is a mixture of the two compounds. Accelerating the reaction and the addition of excessive ethylene glycol drips leaves the PET as a viscous molten liquid. The second phase, i.e. polymerization, which takes place in the solid-state at low temperatures, is required to produce PET. All unstable impurities, such as glycol-free, water, and acetaldehyde, are removed. Excellent mechanical qualities, like creep resistance, hardness, stiffness, and enough flexibility to resist explosion and break under pressure, need a high molecular weight. In addition, it is challenging to purify a polymer after it has been made; thus, the purity of the raw components is essential. High molecular weight polymers with excellent purity are required for food packaging applications to improve reactions and ensure the practical economy; the catalysts are used in very low concentrations. Antimony trioxide, titanium salts, germanium, manganese, zinc, cobalt, and magnesium are the most common catalysts [9]. PET stands for poly (ethylene terephthalate); this polyester resin is manufactured from terephthalic acid and ethylene glycol, or dimethyl terephthalate and ethylene glycol. Furthermore, it produces around 18 percent of all polymers produced globally, with over 60% of its output going to bottles, which account for roughly 30% of global PET use [10].

Since the mid-to-late 1940s, PET has been utilized to make textile fibers. Nathaniel Wyeth invented the PET bottle in 1973, and it became popular in the 1980s produce beverage bottles. PET was consumed in the production of almost 700 million pounds in 1987. In 2000, global polyester production was estimated to be between 25 and 30 million tons. However, by 2012, this amount had risen to 55 million tons, with PET accounting for the majority of the total. Because of the high demand for textile applications, polyester usage has increased rapidly in the fiber and resin molding industries and food markets, and packaging to replace glass bottles. Today, the global market controls two polyethylene terephthalates: bottle-grade PET and fiberglass PE. In addition to colorings, PET differs in the kind and amount of common monomers, catalysts, and stabilizers. Polyethylene terephthalates for textile fibers have a molecular weight of 15,000-20,000 g/mol, indicating a natural viscosity of 0.55 to 0.67 g. PET fiber grades used in practical threads like tire cords have high molecular weights and viscosities. In its amorphous state, PET is Glass - Clear. The mean molecular weight varies between 24,000 and 36,000 g/mol, indicating high viscosity. The other grades of PET are used to make packaging films and audio and video tapes [11].

Every year, a large number of PET bottles are discarded in landfills. The quantity of PET bottles is expected to grow to 583.3 billion by 2021. Bisphenol (BPA) (a chemical used to make plastics solid) is very hazardous to human health and contains very harmful compounds in these bottles. In addition, plastic bottles are non-biodegradable because they take 700 years or longer to degrade. As a result, only about 10 % of these PET bottles are recycled. More than 300 million tons of plastic are produced worldwide, with just 10% of that being recycled and more than 7 million tons ending up in the oceans. PET bottles are formed

of 100% recyclable plastics. Still, they do not biodegrade or photodegrade for many years, which means they break down into polymers, which absorb poisons over time and pollute seas and seaways, as well as soil and animals. This takes a long time to break down and decompose in landfills, resulting in environmental damage. Every second, around 20,000 plastic bottles are produced Figure 1 [12].

PET waste products are generated in huge quantities worldwide these days. Because PET is not biodegradable, this waste poses a serious environmental threat [13]. Waste landfills, open burning, and recycling are all options for disposing of PET waste and polymers today. On the other hand, these methods are unsuccessful in environmental protection. The waste landfill is the world's simplest and oldest waste disposal method. Yet, it has resulted in many problems, including land occupation, groundwater pollution, improper disposal, and resource waste. As a result, reprocessing (recycling) these plastic materials is the best alternative. For handling PET waste, recycling is an effective and practical solution [14].

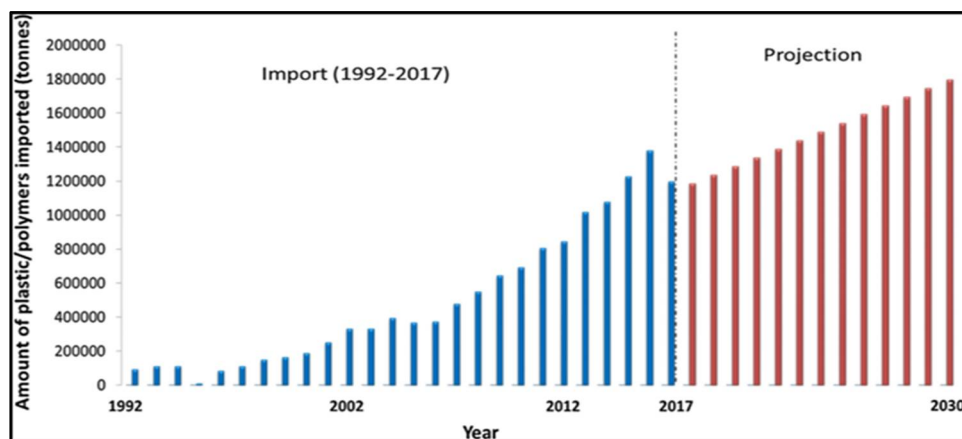


Figure 1: Projection of plastics around the world

## 2. Raw Materials and Preparation Methods

The procedure devised in this study is that waste PET bottles had to be cleaned and then dried; they were cut into square chips to a particle size of  $(3 \times 3)$  mm. The chemicals used were of high purity and were used without purification. Ethylene glycol (EG) was used as a solvent for glycolysis mixed with magnesium oxide as catalysis.

In the first step, the amounts of (100) gm of PET, (116) ml of Ethylene Glycol (EG.) (4:1, EG: PET, molar ratio), and (0.5% ) MgO catalyst were mixed in (190 °C) for 5 hours until the mixture became in the resin state. Heat treatment included total condensation (reflux) in a closed system. Then, with no material loss, in glass condenser was performed, followed by the separation of the unreacted ethylene glycol solution from the previous mixture. This experiment produced DPET, as shown in Figure 2.



Figure 2: Materials used in this work. (a) The unsaturated waste plastic bottles (PET), (b) Ethylene Glycol (EG.), (c) Magnesium Oxide (Nano catalyst)

In the second step, at a ratio of (50) gm for each product, both calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) catalyst, which is a fine white powder with a molecular weight of (74.09) g/mol, and the DPET powder were mixed. Next, a boiling flask containing the sample was introduced into a heating mantle using a temperature controller; the boiling flask was heated to (270 °C) with a 90% heater performance for fast DPET melting. Within 10 minutes, the vapor began to fill the condenser pipe. Then the mixture started to break down and disintegrate after 45 minutes. Figure 3 demonstrates the closed system.

For the preparation of the paint samples, mixtures of paints and appropriate proportions of DPET were made to improve the specifications of the paint mixture.

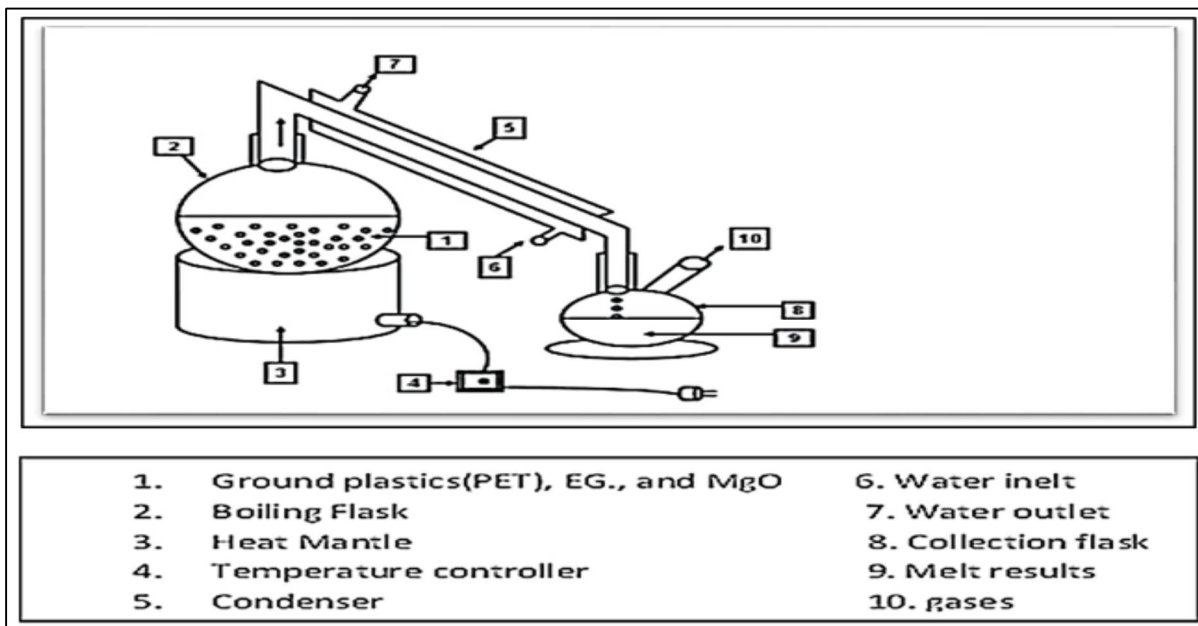


Figure 3: The closed system of chemical depolymerization for the process

The properties of the paint mixtures were examined by applying relevant tests for brightness, color, adhesion, ultraviolet reflectance, accelerated weathering, and viscosity. These tests were conducted in the Ministry of Industry and Minerals / Industrial Research and Development Authority / National Center for Packaging. To prepare the paints mixture, the standard factory proportions of the materials mentioned in Table 1 were mixed in an electric mixer with various additives of DPET (1, 3, 4, 5, 7, and 14 grams), which were added to replace the styrene material, to obtain six mixtures, as shown in Table 2. After 30 minutes of continuous mixing, the temperature rose to (50°C) through the interaction between the materials. The temperature was measured using a laser thermometer. Finally, the mixture was left to cool for (2 hours). During the preparation work, protective clothing, paws, and a mask were worn for safety because of the strong smell of ammonia and other chemicals. See Figure 4 for the paint mixtures preparation process.

Table 1: Properties of primary materials

Materials	Active Role	Chemical formula	Quantity (gm)
Styrene acrylic copolymer emulsion	Increases adhesion	C <sub>8</sub> H <sub>8</sub>	200
Hydroxide Ammonia	Dissolves the mixture components to facilitate mixing	NH <sub>4</sub> OH	3
Sodium hexameta phosphate	Keeps the mixture soft	Na <sub>6</sub> [(PO <sub>3</sub> )] <sub>6</sub>	6
Calcium carbonate	Inexpensive material that increases the amount of mixture	CaCO <sub>3</sub>	1,150
Titanium dioxide	Increases glossiness and hardness	TiO <sub>2</sub>	100
Hydroxyl propyl methylcellulose	Increases viscosity	C <sub>56</sub> H <sub>108</sub> O <sub>30</sub>	6
Polyacrylate ammonium salt	Increases ductility	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	8
Water	Water is a basic component of paint dyes, which is environmentally friendly, unlike oily paints that use benzene	H <sub>2</sub> O	650
Mergal (Türkçe)	Insect poison	C <sub>4</sub> H <sub>5</sub> NOS	6
Silicon	Increased resistance to weather conditions (temperature, etc.)	.....	4
Foam ester	Eliminates bubbles	.....	6

**Table 2:** Quantities of materials

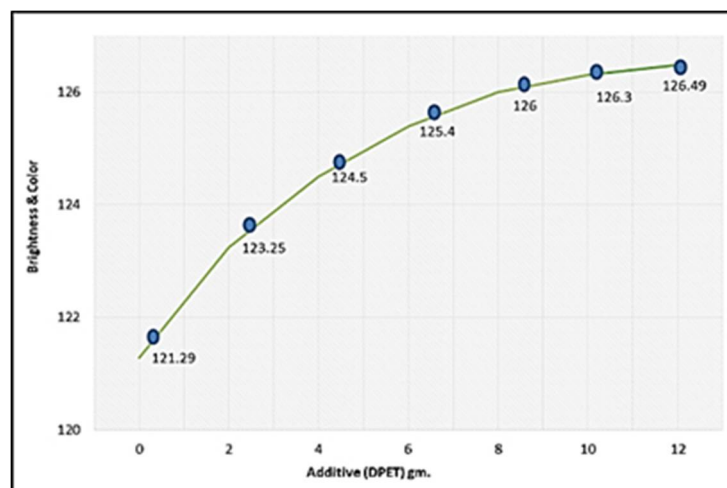
DPET powder (gm.)	Styrene material (gm.)
0	200
1	199
3	197
4	196
5	195
7	193
14	186

**Figure 4:** Mixing process

### 3. Results And Discussion

#### 3.1 Brightness and color test for paint mixtures

The results showed that the brightness and color gradually increased from 121 to 126 (this test is without units) by the gradual increase of the added DEPT up to 14 gm, as shown in Figure 5. Due to the exposure of materials to weather conditions, which causes a change in composition and shape, it is necessary to improve these materials and maintain their external shape by adding polymers. The most probable reason for this increase is the interlocking and the increase in the cohesion between the paint materials and the DPET polymeric molecules. This is because the polymer molecules are linked to each other in a chain-like manner that increases the color stability and brightness of the materials [15].

**Figure 5:** The effect of DPET addition on the brightness and color of paints

#### 3.2 Ultraviolet reflectance test for paint mixtures

The results showed that ultraviolet rays' reflectivity increases gradually from 242 to 249.5 with the gradual increase of the added DEPT up to 14 gm, as shown in Figure 6. The ultraviolet rays have enough energy to break the bonds inside the materials. Therefore this effect may result in cracking on the surface of these materials and peeling colors. For this reason, polymeric materials are used as inhibitors of the effect of ultraviolet rays on materials due to their nature of strong bonds[16].

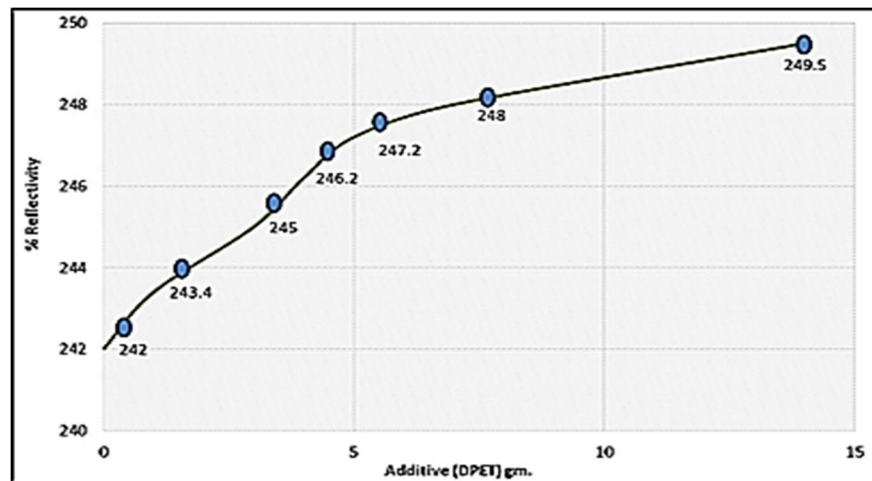


Figure 6: The effect of DPET addition on the UV reflectance of paints

### 3.3 Adhesion test for paint mixtures

The results showed that the adhesion increases gradually from 99 Mpa to 141 Mpa with the gradual increase of the added DEPT up to 14 gm, as shown in Figure 7. The most probable cause of this increase is the interlocking between paint components and DPET molecules, as well as the impact of the OH functional group in DPET [15].

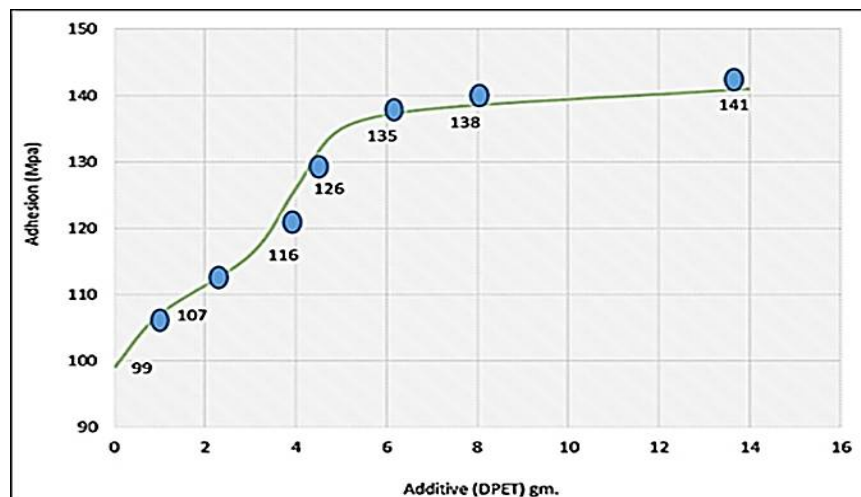


Figure 7: The effect of DPET addition on the adhesion of paints

### 3.4 Accelerated weathering test for paint mixtures

Tests in accordance with this practice are used to evaluate the stability of dyes materials when exposed outdoors. The relative durability of dyes in outdoor use can be very different depending on the location of the exposure because of differences in ultraviolet radiation, time of wetness, temperature, pollutants, and other factors, according to ASTM D 4364. So, when the material is exposed to atmospheric agents, such as chemical solutions, fluctuating humidity, light, ozone, heat, and ultraviolet radiation (UV), some properties will deteriorate. The deterioration signs include a change in the color of the paint that becomes darker, the occurrence of crusting, and its transformation into a state of bombardment (brittle). Therefore, the resistance of these materials can be improved by adding polymeric materials that prevent this deterioration. In this study, the results indicate no change in the dyes materials, which indicates the strength and hardness of the material. of the results imply the because the addition of DPET prevented the paint material from the interaction with external conditions, avoiding the impacts of humidity and other environmental factors [15].

### 3.5 SEM test for paint mixtures

The paint mixture with 4 gm. DPET + 196 gm. styrene showed a regular rounded structure, as demonstrated in Figures 8a, b, and c, with a diameter of about 30 nm [16].

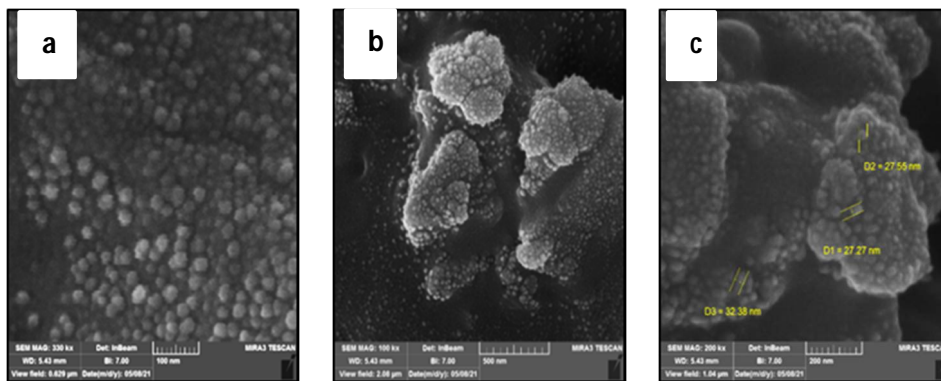


Figure 8: Scanning electron images of paints with nano-structure

## 4. Conclusion

From the results of the investigation, it has been found that:

- The results proved that the addition of the polymeric material led to an improvement in the properties of coating materials, such as adhesion resistance and weather resistance.
- Painting of plastic containing multi polymer structures has excellent mechanical resistance and good cohesion.
- The fabricated paints can be used as adhesives, repair paste, decoration paints, and foundation paint and have extremely good resistance to weather in normal Iraqi conditions [5].

## Author contribution

All authors contributed equally to this work.

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## Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

## Conflicts of interest

The authors declare that there is no conflict of interest.

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