Study of the degradability of polyethylene by catalyzing nanoparticles of zinc oxide

Alaa Ali Hassan
Department of Environmental Science, College of Environmental Science and Technology, University of Mosul
Email: aala91hassan@gmail.com

Ahmed Noori Mahmood
Department of Environmental Science, College of Environmental Science and Technology, University of Mosul
Email: ahmednoori@uomosul.edu.iq

Abstract—Polymer composite materials were manufactured as the base material made of low density ethylene using the thermal fusion method, the base material was supported using ZnO powder present in the Nano-form at a rate of (30-50) nm and in volumetric ratios by adding (5,10,15,20,25), Thermally treated models were treated Thermally manufactured takes three (3.6,9) and (40.60.80) degrees of heat. The models were subjected to a range of mechanical tests that included (surface solidity tests, shock resistance examinations), XRD x-ray scans and SEM (scanner electronic microscope) tests. The results showed that by grafting the materials in different proportions with nanomaterials, it was found that the optimum ratios that lead to the best case of improvement in mechanical properties were within 15%, and the treatment time had an effect on changing the mechanical properties shown by the manufactured models, Also the temperature had an effect on the mechanical properties of the manufactured composite material. As for the results of the X-ray spectrum for all models, a composite spectrum appears between crystalline materials and the spectrum of random matter, and the presence of sites in the spectrum that appear in the form of phases related to nanomaterials. Lastly, The scanning electronic microscope (SEM) examinations showed that the surface of the model contains nanoclusters (Quantum dots), these clusters are distributed in a way that gives the form of high bonding between the common materials which is evidence of the presence of a high surface energy for the polymeric material compound (the manufactured material with additives).
Introduction

Human activities in the past decades have raised serious issues related to the environment and its preservation, including air pollution, poor waste management, water scarcity, resource depletion, the spread of plastic waste, pollution and environmental degradation ... etc. (Zhongming et al., 2021). Nanomaterials are a promising and effective tool to overcome the main challenges in modifying treatment methods that help protect the environment and apply new nanomaterials within this area to serve as environmental detergents. This has enabled researchers to make polymeric materials of great interest to the possibility of improving their properties in general, and physical properties in particular through techniques and mechanisms that can be considered among the few and medium-implemented mechanisms and techniques (Ahmeda et al., 2017).

The Nano-additive technology of polymeric materials has been used to improve some properties of materials and get rid of the inactivity to self-decomposition. Huge amounts of plastic have been dumped into the oceans and other environments. According to United Nations reports and statistics issued in 2019, every day the equivalent of a garbage truck loaded with plastic is thrown into the ocean, equivalent to 13 million tons annually, until the pollution reached epidemic proportions of more than 100 million Tons of plastic over the past decades alone (Chenje, 2007), 80% - 90% of which come from sources on Earth, The world is also witnessing the purchase of about one million plastic water bottles every minute, while the use of single-use plastic bags reaches 5 trillion units every year. Also there are 13,000 pieces of plastic garbage per square kilometer of oceans around the world, and according to United Nations estimations the production of 4 Plastic cans produce a level of greenhouse gas emissions equivalent to traveling one mile in a medium-sized car, and it has been found that carbon dioxide emissions into the atmosphere for the production of one form of polyethylene from start to finish are equivalent to about 2440 kg per 1000 kg of production. (Webb et al., 2012)

Over the past years, researchers have turned to Nanotechnology and this term has become a major focus in the world, resulting in a huge leap in all branches of science, engineering and many applications in various medical, economic, agricultural, vital and environmental fields. (Keiper, 2003; Ramsden, 2016). Although nanotechnology is relatively new, the existence of devices that contain structures with nanoscale dimensions is not new, and that these structures date back to the beginning of the Earth’s life and the beginning of life on it.

The term (nanocomposites) is also used to express the addition of nanoparticles to other ordinary materials to manufacture new materials, \ this results in a significant improvement in the properties of these materials. For example, adding carbon nanotubes to another material changes the electrical and thermal conductivity properties of the nanocomposites. (Hashim, 2011). The addition of other types of nanoparticles also leads to improve the optical properties, electrical
insulation properties, as well as mechanical properties such as hardness and strength. Researches is being conducted to obtain nanocomposites with properties and characteristics that differ from the original materials. Among the known nanocomposites are polymeric nanocomposites. The addition of nanoparticles to materials gives them many unique qualities and properties that can be used in many fields.

For example, carbon tubes are not corroded and do not burn under normal conditions, and they can be added to plastic to make it conductive and other applications. (Diwan & Bharadwaj, 2005; Yokoyama et al., 2008). The presence of chemicals in the nanoscale within the nanoscale gives it several new features and properties different from its previous properties in the traditional measurement. The most important of which is the increase in the surface area and the activity of the surface of the body. It is known that reducing the size of the body will lead to its tendency to be affected by the behavior of the basic units that make up that body (atoms and molecules) and thus show properties different from the characteristics of bodies of traditional measurement such as the change in physical properties such as the melting point, and qualitative properties such as the dielectric constant. Even changes in the activity and solubility of materials and all related properties (mass and heat transfer) in addition to changes in the speed of reactions and these changes in the properties resulting in the measurement of particles are called the measurement effect and this occurs as a result of changing the association between atoms, molecules and components of those bodies. (Yokoyama et al., 2008).

Also, the atoms and molecules on the surface are very active, which facilitates their association with other materials, giving properties different from the properties of large objects, and this is what happened by adding ZnO to low-density polyethylene.

**Model manufacturing**

**Materials used:**

**Base material:** The base material used for fabricating the models in this paper consists of raw material LDPE (low density poly ethaline), which was prepared by (ExxonMobil) company, which includes low density polyethylene resin with characteristics of (LDPE LD 051.LQ).

**Added nanomaterials:** ZnO powder was used in a Nano form with distinctive properties and mixed with low-density polyethylene that has been prepared by (Central Drug House) company, where the average particle size of nanomaterials was within (5±50) nm. These materials have been added in volume proportions as follows (5%, 10%, 15%, 20%, 25%) because there is a large density difference between the base material and the additive.

**Weight measurements:**

The weight rate of the LDPE model was 15 gm and the weights used from the additives were determined by using a sensitive balance of up to (0.0000001 ± g).
Casting molding: Casting molds are made of aluminum plates with a thickness of (1 mm) and the dimensions of the manufactured models have been approved with measurements (10 x 10 x 120 mm). In order to obtain a model with these dimensions after the casting process and surface treatments, the dimensions of the mold require an increase of (5%) for each dimension as a maximum.

Surface treatments: All tests conducted on manufactured models depend on the regularity of the dimensions of the model as well as on the uniformity of the surface. Therefore, after completing the model hardening process, the model is treated with silicon carbides smoothing papers with grit sizes # (400, 1000, 2000) respectively, where the treatment is with the roughest smoothing paper first and then the less finally the least.

Mechanical tests: including

Surface Hardness Examination: The surface hardness of the manufactured models was determined by using a prick hardness measuring device, and the device used is of a type (N.S.S.), Japanese origin. This device measures the surface hardness by pricking events on the surface of the model, through this shock, the device can determine the value of the surface hardness directly and show the amount of this value on the scale on the top of the device, since this scale contains an indicator that directly determines the value of the hardness.

Shock resistance test: The ability of the manufactured models to resist shock was determined using the (Charpt Impact Test), which depends in the basis of its theory on measuring the maximum amount of energy that can be tolerated by the model before any breaking or crushing can happen in the model’s form and in a batch of energy within a very short period of time, by using the (Izod Charpy Tension Impact Test Instrument), which is manufactured by (Testing Machines, Inc, Amityville New York).

X-ray tests: X-ray diffraction (XRD) is a versatile, non-destructive analytical method for analyzing properties of materials such as phase composition, structure, texture, and various powder samples, solid samples, or even liquid samples. (Al-Jubouri, 2017). X-ray diffraction tests were carried out for the manufactured models using a Dutch-origin Shematdu type device, the tube used was (Cu) Ka and The temperature were (±25°C).

Electronic Microscope: In order to obtain a clear magnified image, the wavelength of the rays directed at the object must be smaller than its measurements. (Dunlap & Adaskaveg, 1997)

Therefore, the wavelength of light must be determined, as the wavelength of visible light is between (380-750) nm, while the wavelength of the electron beam can be controlled and minimized to 3 nm, and its magnification can reach to a million times, and some electron microscopes can show even the circumference of separate atoms in one of the samples, and through it we will obtain more accurate images.
The examination of the samples was carried out using a scanning electron microscope (SEM) type (TESCAN) model (MIRA3), the scanning electron microscope is distinguished from the rest of the optical microscopes by using electrons instead of light waves, as it gives a detailed and magnified three-dimensional image (3D) and the image is in black and white because it does not depend on light waves.

Results and Discussion

Mechanical tests:
- Surface solidity tests

Figure (1-1) represents the amount of change in the value of surface solidity tests of Nano-additive-backed base material models with different temperatures and thermal treatment periods for ZnO materials at (3,6,9). The results showed that the hardness value increases gradually with temperature, as the difference between the different aggregates is based on the improvement in the amount of surface hardness, and this depends on the difference in the geometrical composition of the different materials, which are in the form of powders to reinforce the base material, as each A material from the supporting materials that has a geometrical spatial arrangement according to its chemical composition (Hany & Fahad, 2019). After this strengthening process and the emergence of this result, we must define the hardness as the ability to make an impact on the surface of the material, that is, the higher the resistance of the material to the impact, the higher the surface hardness. This case is affected by two main factors, the ability of the base material & the backing material to resist the impact and the optimal containment of the polymeric materials of the nanostructure powder.

Also we must remember that the properties of polymeric materials increase their plasticity with increasing temperatures within the permissible range through the principle of thermal annealing, as we find the increase in the hardness values in the models at a temperature of 80°C is higher than 40°C, 60°C, respectively. We find that this formula was able to show the best containment of reinforcement powders when it is at a certain critical rate, less than this percentage the polymer chains don’t reach the stage of the ideal full of vacuum structure, while more than this percentage will be excess of reinforcement powder leading to a defect in the cohesion of the base material and the synthesis of the support material.

The properties of nanomaterials that increase the rigidity and strength of materials have resulted in a high rigidity in all models at the same temperature, while this ratio is lower at 60°C temperature in all models due to the low impact of factors on changing the properties of polymer matter, and less at 40°C which showed a solidity below 80°C And respectively.
The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 3 hours.

The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 6 hours.

The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 9 hours.

Figure 1.1. The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 6 hours.

- **Shock resistance tests**

Figure (1-2) represents the change in the shock resistance value of the models of the base materials supported by nano-additives with different temperatures and heat treatment periods for (ZnO) materials at (3,6,9) and represents the amount of change in the shock resistance values of the base materials supported by the
materials Added in a nano form consisting of nano-zinc oxide (ZnO), it is noted that there is an improvement in the ability of the base material to resist shock after strengthening it. The model then obtains the highest state of improvement at the highest degree of the thermal effect (80°C), while the improvement decreases when the temperature decreases. For the purpose of explaining the behavior of the models in causing a change in the material’s ability to resist shock, we basically have to understand that the shock resistance is in fact the material’s ability to resist cracking and fracture under the influence of the forces applied to it, and that this resistance is often little when the material is of brittle hardness (Brittle) due to the inability of this material to contain the energy resulting from the external influence and to distribute the external stress placed on it and not to be concentrated at specific points, while we find that the more plastic property in the material (Ductile), the shock resistance increases in order to enhance the property of the material’s ability to transfer external energy imposed on it at a specific point and distributed to the rest of the body. (Hou et al., 2008)

The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 3 hours

The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 6 hours
The hardness of the prepared samples as a function of the Zno nanoparticle addition ratio for a heat treatment time of 9 hours

Figure 2.1. Represents the values of the shock resistance of the models supported by ZnO at different temperatures and heat treatment periods.

**X-ray tests**

**Model ZnO + matrix**
**Treatment time 60°C**

X-ray spectrum of the model system shows a presence in the spectrum as a result of the effects of the base material on ZnO as the peaks of ZnO approached the peaks of the base material in this case, which means that by increasing the temperature, a state of blocking is likely to appear on the ZnO compound so that the amount of active substance entering this model becomes less than the amount of active substance entering the model where the temperature has affected the effectiveness of the material so that part of the material is likely to have been associated with the underlying substance, causing peak values to converge. The rest of the observations were diagnosed again with a relative decrease in the kα phase and reaching a ratio approaching the kο phase, so we can say that the temperature may have affected ZnO in terms of the effectiveness of the substance and that it has also affected the severity of the appearance of secondary emergencies and is thus highly likely to be a material that may be energy-receivable and storeable, which is the result of the intended proof.
Figure 3.1. Represents the X-ray spectrum of the matrix supported by ZnO powder and for 15% at 60°C

**Electron microscope scans:**

**The ZnO+Matrix model**

The model shows a combination in which the quantum diameters are in the range of 133.01 nm with class-shaped clusters which means that there is high surface energy, this energy has been reflected in a kind of irregular surface nature with the formation of gaps that make the level of energy handling at the multiple level (i.e. the beam can be handled more than once).

The mixing composition between the base material and the additive is closer to being a physical mixture than a chemical reaction, as the nano-additives still form independent units that are not mixed with the composition of the polymeric material, and the polymeric material remained as the incubating material. This result may not agree with the results of the X-ray examination in terms of appearance, but it agrees with it if the subject was looked at in a more in-depth manner. Apparently, on the surface but what is inside the composition of the polymeric material may give another case or another description.
**Figure (5-1)** for EDS shows that the main phases are the Kα and Kβ phases with the disappearance of the Lβ and Lα phase, and this means that the material was formed in the form of the basic phase with showing the role of the effect, which appears in the Kβ phase, and the Lα phase appears due to the influence of external factors effect with the presence of an additive, which means that this phase has disappeared due to the addition of a substance that is likely to be an antimatter of the substance that exhibited this phase.

Figure 4.1. Shows images of the polymeric base material with Zno under a scanning electron microscope.
The conclusions

In the end showed that nanomaterials can play the role of energy storage material and rearrange it to the structure it contains in a way that can stimulate the self-decomposition of polymeric materials and based on this talk this method can be a way to manufacture a polymeric substance that has the characteristic of self-decomposition.

References


