Mechanical Properties of High Density Polyethylene/Chromium Trioxide under Ultraviolet Rays

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Abstract

High density polyethylene was chosen as it is a commodity polymer, easily available at economical price and easy to process. This research studies the effect of ultraviolet ray and the addition of chromium trioxide (CrO₃) on the mechanical properties in the ratio (0.05%, 0.1%) and two periods of irradiation (25 and 75) hours. The mechanical properties are flexural strength, tensile strength, and hardness. Scanning electron microscope studies the fracture surfaces of samples before and after UV and CrO₃. The best improvement in flexural strength occurs at (0.05%) CrO₃ proportions after 25 hours of UV exposure. Maximum enhancement in tensile strength occurs at 0.1 % CrO₃ after both periods (25,75) hours.

Keywords: HDPE, ultraviolet ray, CrO₃, mechanical properties, stabilizer

INTRODUCTION:

Polymers are long-chain molecules consisting of a series of small repeating molecular units (monomers) that are commonly made from compounds of carbon but are also made from inorganic chemicals, such as silicates and silicones. These repeating monomer units exhibit strong covalent bonds that form chains, which are also frequently linked by strong primary bonds and/or weaker secondary bonds.[1]

Polymers are light weight, corrosion resistance materials but are not suitable for use at high temperatures. They are less stiff, less strong and less tough than most metals.[2]

Thermoplastics have linear chain configurations where chains are joined by weak secondary bonds. The secondary bonds holding adjacent macromolecules together are a direct result of the formation of molecular dipoles along the length of the polymer chain. Secondary bonds are much weaker than primary bonds, which accounts for the low melting temperatures, low stiffness, and low strength exhibited by many thermoplastic polymers.[1,2]

High density polyethylene (HDPE) is widely used for economic and environmental reasons. HDPE is often used in medical applications because it exhibits excellent chemical resistance. A variety of polyethylene (PE) medical products are sterilized by gamma irradiation. The crystalline structure of HDPE is orthorhombic. HDPE is a ubiquitous material with versatile properties and is widely used due to its mechanical strength, low cost, excellent biocompatibility, easy process ability and resistance to chemical and biological attack.[3,4]

Properties of HDPE can be further manipulated by the addition of organic or inorganic particles into the polymer matrix. It is used extensively in many fields, including agricultural and food-packing films. [5]

High density polyethylene is a very useful commodity plastic with high chemical resistance, excellent electrical insulation, environmental resistance, and easy moldability. [6]

The mechanical and thermal properties of HDPE depend on the relative amounts of crystalline and amorphous contents present in the polymer, crystal structure, molecular weight, and branching. The properties of polyolefins have been exploited by the addition of various kinds of fillers to achieve the desirable properties at reasonable cost. Addition of a filler to a polymer changes its microstructure like crystallization, glass transition, crosslinking, phase splitting, and orientation, which are closely related to various types of molecular motions. [7]

Properties of HDPE can be further manipulated by the addition of organic or inorganic particles into the polymer matrix. HDPE is a stable material due to its carbon-carbon bonds, causing their slow degradation. HDPE’s low rate of degradation is one of the reasons that new alternatives for disposal reduction. [5,8]

Chromium(VI) rarely occurs naturally, but is usually produced from anthropogenic sources. Chromium(VI) compounds are more stable. Chromium Trioxide or Chromium (VI) Oxide is red dark color flakes solid, odorless. CrO₃ is stable Reactive with organic materials. Chromium oxides gain significant attention due to their diverse technological application in various industries. CrO₃ is an important compound for automobile industries due to its high corrosion resistance properties, used for plating the chromium on car body and other auto components. It can be used in various pharmaceutical and chemical industries. [9,10]

The high energy of the solar radiation (200-400 nm), generally known as Ultra Violet radiation (UV) can cause some undesirable effects in living creatures and may also
reduce service life of materials due to its high energy. Approximately all the radiation of wavelength below 290 nm is filtered out by the ozone layer in earth’s atmosphere. The large doses, especially in the short UVB range (280-315 nm) may cause harmless effects such as sunburns, skin cancer, photo keratitis, photo dermatoid. With the alarming increase in the rate of ozone layer depletion in the earth’s atmosphere, the risks involved due to prolonged exposure to solar UV radiation are increasing day by day. The science and technology of UV stabilizers have evolved over the years and today a wide range of UV stabilizers are available commercially. [11,12]

UV degradation is often the result of exposure of polymers to ultraviolet rays and has been a challenging problem to material engineers because autoxidation reactions that occur as the product is exposed to UV rays have immediate impacts on properties that determine the service life of the product. Some results of UV degradation are discoloration, viscosity changes, char formation, cracking and loss of adhesion. Many synthetic polymers are not UV-stable and are susceptible to cracking and discoloration as a result of exposure to UV rays. [13,12]

Sofia (2004) studied the effects of the ozone-generating UV light treatment of thin high-density polyethylene (HDPE) films were monitored with the quartz crystal microbalance (QCM) technique both in the presence of ozone and without it. The films were further characterized by X-ray photoelectron spectroscopy, optical microscopy, and atomic force microscopy. She found that the ozone not only modified the surface properties of the HDPE films but also etched away the polymer layer. An average etching rate of 0.48 nm/min was determined. UV light exposure of the polymer film in an argon atmosphere resulted only in minor degradation of the films; the presence of ozone was needed to cause the destruction and loss of material. The QCM technique was a straightforward method for the monitoring of the kinetics of the ablation induced by the UV–ozone treatment process. [14]

Donald E. Duvall, Dale B. Edward (2011) studied a typical HDPE pipe compound includes the base HDPE resin, carbon black added at 2 – 3 weight percent to protect the material against oxidative degradation from exposure to UV radiation. Processing stabilizers (antioxidants to prevent oxidation during pipe extrusion at 350°F – 400°F) and other antioxidants intended to provide protection against oxidation caused by long term exposure to water containing dissolved air (oxygen) and other oxidative agents such as water disinfectants. [15]

Bhupendra 2013 studied the photo stabilizing of HDPE monofilaments with hindered amine light stabilizers (HALS) and UV absorbers at varying stabilizer concentrations. The films were assessed for UV resistance by exposure to simulated outdoor weathering conditions in artificial weathering apparatus and testing the exposed samples at regular intervals for retained tensile properties. Films of HDPE of varying thickness and containing different concentrations of photostibilizers were also prepared. The UV protective ability of the films was assessed by measuring Ultra Violet Protection Factor (UPF). The results indicate that UV absorbers improve the stability of the filaments significantly. [11]

Kuria and others (2014) studied the absorption of ultraviolet-light by conventionally processed PE films. The PE film samples were submitted to UV from fluorescent lamp at 20°C & relative humidity 40% for two hours. Transmission, reflection, and emission spectra, from which absorption was inferred, were obtained with an optical spectrum analyzer. They studied also the natural degradation under solar action of PE films for a period of up to 150 days. Degradation was analyzed by change of the storage modulus using a DMA instrument. Evidence of chromophoric sites was inferred from the absorption of UV light in the range (250-400) nm. [16]

Yan and others 2014 were focused in this research on characterizing hardness evolution in irradiated high density polyethylene (HDPE) at elevated temperatures. Hardness increases with increasing gamma ray dose, annealing temperature and annealing time. The kinetics of defects that control the hardness are assumed to follow the first order structure relaxation. The defects that control hardness in post-annealed HDPE increase with increasing dose and annealing temperature. The structure relaxation of HDPE has a lower energy of mixing in crystalline regions than in amorphous regions. [4]

Barbosa and others (2015) were obtained HDPE monofilaments using different extruders and post-extruder equipment. Drawn and undrawn monofilaments (draw ratio 7:1) were irradiated with 10 MeV electron beams in air at room temperature at 25, 50, 75, 100 and 125 kGy doses to induce a network structure. The fibers were examined by mechanical properties measurements. The tensile properties of irradiated fibers decreased but elongation-at-yield for undrawn and elongation-at-break for drawn fibers boosted by increasing irradiation dose up to 125 kGy. [17]

EXPERIMENTAL PART:

Equipment:

1. Twin Screw extrusion machine of polymer: Model SLJ-30A, screw diam.30mm, heating power 3kw, main motor 4kw, and speed is (0-320) rpm.
2. Saw Electrical Device (Einhell RT-SB305U).
4. UV Radiation Device: Xenon lamp intensity 2.3w/m², wave length (300-350) nm.
Sample Preparation:

Sample preparation process including three stages:

First: the extrusion granules of HDPE (100g) through fine slot of the twin screw extruder machine at 190°C and cooled by air without any addition. The flakes of chromium tri-oxide with two ratios (0.05g CrO₃, 0.1g CrO₃) are added to (100g) HDPE in the extrusion machine.

Second: after extrusion process, each polymer sheet (net HDPE, HDPE-0.05%CrO₃, PP-0.1%CrO₃) has been cut into samples of (tensile, flexural, and hardness tests) by using saw electrical device. Tensile and flexural specimens follow ASTM D638 and ASTM D790 respectively.

Third: prior the mechanical tests, grinding has been carried out for each sample by applying grinding machine.

RESULTS & DISCUSSION:

Figs. (1&2) showing the load-deformation curves of neat HDPE before and after (25,75) hours of ultraviolet radiation. The tensile strength decreases with increasing the time of ultraviolet irradiation. The reduction in tensile strength occurs according to the free radicals formation. These radicals react with oxygen molecules to form peroxides which lead to polymer chain scission and the oxidation degradation.[17]
Figure 3: Tensile strength of HDPE+0.05%CrO$_3$ before and after 25h UV.

Figure 4: Tensile strength of HDPE+0.05%CrO$_3$ before and after 75h UV.

Figure 5: Tensile strength of HDPE+0.1%CrO$_3$ before and after 25h UV.
From Figs. (3&4) it can be shown the decreasing in tensile strength of HDPE after (0.05 CrO$_3$) incorporation as compared with neat HDPE, this behavior reflects the brittle nature of chromium trioxide. There is slightly improvement in tensile strength after 25 hours of UV radiation. According to the stabilizing effect of chromium trioxide against UV degradation, the tensile strength improves at low radiation dose 25 hours. The period 75 hours of UV irradiation slightly decreases the load and increases the deformation (reduction in tensile strength). The stabilizer chromium trioxide is ineffective at high radiation dose. The decrement in tensile strength increment in deformation belongs to oxidation process (oxidative degradation) which caused by the presence of oxygen molecules in the system during the irradiation as well as increment in deformation The oxygen molecules cannot diffuse into crystallites and chain scission only occurs in the amorphous region.[17].

It can be observed from Figs. (5&6) that the proportion (0.1%) of chromium trioxide diminishes the tensile strength due to the stiff nature of the ceramic additive (CrO$_3$). On the other hand there is an increment in tensile strength after (25&75) hours of radiation and slight increase in deformation with 75 hours. This improvement can be attributed to the effect of CrO$_3$ as stabilizer against ultraviolet radiation because the role of chromophoric sites in the absorption of ultra violet light in the range (250-400) nm.[16]

**Figure 6:** Tensile strength of HDPE+0.1%CrO$_3$ before and after 75h UV.

![Tensile strength graph](image)

**Figure 7:** Flexural strength of HDPE before and after 25h UV.

![Flexural strength graph](image)
It can be seen from Fig. (7&8) the load-deformation curves of 3-point bending test for neat HDPE before and after irradiation. For pure HDPE, maximum load is 0.06 KN against 3.5 mm deformation. The maximum load of HDPE after 25 hours of ultraviolet irradiation remains constant versus decreasing in deformation. On the other hand the flexural strength of HDPE after 75 hours reduces with increment in deformation with raising the deformation. The reduction in flexural strength with radiation time belongs to oxidative degradation.

From figures (9&10) it can be seen the decreasing in flexural strength at 0.05% CrO3 sample as compared with neat HDPE because of the brittle nature of chromium trioxide additive. 25 hours of irradiation enhances the flexural resistance with constant deformation. The reason behind this improvement in flexural strength is due to the stabilization effect of chromium trioxide versus ultraviolet radiation where the irradiation effect of HDPE differs depending on the presence of additives. The activity of absorbs UV rays belongs to the existence of chromophores in the polymeric materials.[16]
The duration of 75 hours of ultraviolet exposure reduces the brittle strength into a level very near from the flexural strength of (HDPE+0.05) sample without UV radiation as well as slight increase in deformation. The reduction in flexural strength according to the irradiation process belongs to chain scission, formation of peroxide radicals and oxidative degradation which generally causes material weakening.\[12\]

Figs. (11&12) showing the steadiness of maximum flexural load of HDPE +0.1 as compared with pure HDPE with slight increase in deformation after 0.1% CrO\textsubscript{3} addition. The flexural strength of HDPE+0.1 after 25 hours of UV radiation also stays constant against little rising in deformation. There is a reduction in flexural strength after 75 hours of ultraviolet exposure (reduction in both load & deformation). This behavior reflects the ineffectiveness of 0.1% CrO\textsubscript{3} as stabilizer versus UV radiation. The polymer understudy suffers from degradation due to thermo oxidation reactions which swearing in breakage.\[8\]
Figure 12: Flexural strength of HDPE + 0.1\%CrO\textsubscript{3} before and after 75h UV.

Figure 13: Hardness of HDPE/HDPE(0.05\%CrO\textsubscript{3}, 0.1\%CrO\textsubscript{3}) before and after UV.

Figure (13) explicates the values of shore D hardness against irradiation time. HDPE is a semi-crystalline material, so the defects affecting hardness in HDPE occur in crystalline regions because polymer chains in crystalline region are denser than those on the amorphous region. The hardness change is attributed to the variation of defects in both microstructure and molecular structure according to the increasing in radiation dose. Cross linking enhances the resistance to wear and cut through and resistance to heat. The hardness of neat HDPE increases with irradiation dose according to crosslinking. Polyethylene mainly crosslinks because of its structure. On the other hand the hardness of HDPE after (0.05\% & 0.1\%) CrO\textsubscript{3} addition reduces monotonically with increasing the time of irradiation due to the stabilizing effect of CrO\textsubscript{3} by absorption of UV radiation instead of HDPE and works as chromophores.
Figure 14: SEM for HDPE/HDPE+(0.05%CrO₃, 0.1%CrO₃) before and after 25h UV.
Fractography contains the examination and explanation of fracture surfaces. As shown in Fig. (14) interpret the fractography of tensile specimens before and after the reinforcement and irradiation to 25h UV. Ductile fracture of HDPE in (a) is distinguished by material stretching related to the febrile nature of the polymer response to stress. After 25h of irradiation the brittle fracture is clear because the crosslinking effect. After addition of CrO3 all specimens shutter in a brittle fracture with ductile manner by crazing. Craze appear to look like cracks, but they are load bearing, with fibrils of material bridging the two surfaces.

CONCLUSIONS:

1. The tensile and flexural strength of HDPE decrease with raising the irradiation time according to photo-oxidation.
2. The tensile strength of HDPE reduces with increasing the proportions of CrO3 additive
3. Maximum enhancement in tensile strength due to stabilizer can be obtained at 0.1CrO3 after both periods (25, 75) hours of UV irradiation.
4. The best improvement in flexural strength occurs at 0.05CrO3 after 25 hours as a result of stabilization versus UV degradation.
5. Shore D hardness of HDPE increases against the radiation dose because of the cross linking.
6. The addition (0.05-0.1) CrO3 reduce the hardness according to stabilizer absorption of UV radiation instead of HDPE.

REFERENCES