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Effect of Processing Technique on LDPE Thin Films and sheets

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Abstract: *LDPE (low density polyethylene/Graphene (G) nanocomposites were fabricated using solution casting to produce thin films and using compression molding to produce sheets. The mechanical and physical properties of thin films and sheets were evaluated. The results indicated that LDPE thin films and their nanocomposites have enhanced tensile properties compared to LDPE sheets and their nanocomposites. Moreover LDPE/G thin films had Melt flow index and higher thermal stability results compared to LDPE/G sheets and their nanocomposites. Controlling the mechanical and physical properties is a fundamental factor in LDPE packaging applications and membrane technology. To the best of our knowledge, this is the first study that presents the effect of processing technique and the effect of G nanofiller content on LDPE films.*

Keywords: *Graphene, LDPE, Mechanical properties, Nanocomposites*

I. INTRODUCTION

The physical dimensions of thin film materials are related to their microstructure that strongly influence their mechanical properties [1]. The mechanical behavior of thin films is an important technological issue in applications as microelectronics, integrated optoelectronics data storage, and micro-electro-mechanical systems (MEMS) [2-5]. In many cases, the reliability and performance of such devices are strongly influenced by their mechanical properties. It is now well known that the mechanical properties of thin metal films can be substantially different from those of their bulk counterparts. Specifically, the tensile stress of thin films can exceed that of bulk materials of the same composition and grain size by a factor of three to ten [6]. LDPE was selected, since it is the most commonly used polymer in packaging industry. LDPE is a thermoplastic made of ethylene monomers used for synthetic membrane preparation. It is opaque and robust enough to be virtually unbreakable and at the same time a quite flexible polymer. It is unreactive at room temperature although it is slowly attacked by strong oxidizing agents, and some solvents will cause its softening or swelling. Moreover, it has excellent resistance to diluted and concentrated acids, alcohols, bases and esters. In addition, it entails good resistance to aldehydes, ketones and vegetable Oils. Furthermore, it has easy processability properties, flexibility and high elongation modulus, which makes it suitable for packaging materials such as foils, trays and plastic bags, both for food and non-food purposes. It was also used as protective coating on paper, textiles. However, despite LDPE's numerous advantages, it suffers from poor resistance to oxidizing agents and hydrocarbons [7-8]. The shortcomings of LDPE are minimized with the addition of nanofiller to either sheets or thin films. Graphene (G) nanofiller attracted an enormous amount of scientific interest due to its exceptional physical properties. G incorporation improves thermal and mechanical properties of polymers. However, the hydrophobic nature and low polarity of LDPE have made effective dispersion of nanofillers difficult [9]. Meanwhile the experimental procedure prove that the dispersion of G in LDPE thin films produce higher tensile strength, Lower melt flow index (MFI) and enhanced thermal stability than LDPE sheets.

II. EXPERIMENTAL PROCEDURE

2.1. Materials

Low density polyethylene (LDPE) was purchased (AG trading, Egypt) in the form of pellets (hardness = 68 Shore, density= 0.919 g/cm^3 MW = 28000, Tm around 120 °C. Tg < -100 °C). Xylene (Sigma, Aldrich, anhydrous, ≥ 99%) was used as a solvent for LDPE. Graphene nanofiller (Sky Spring Nanomaterials, Inc. USA), was mixed with LDPE to produce the PNC thin films**.**

2.2. Thin Film Processing

To prepare the LDPE thin films, 20g of LDPE pellets was dissolved in 200mL of xylene solvent at 75 ºC. The mixing of F and G with LDPE occurred with constant stirring for 24hrs with a VWR® Standard Analog Shaker, to form a clear homogeneous solution. The LDPE/F and LDPE/G filtrate were poured into two separate flattened containers and left to dry at room temperature to form thin films with a 0.2 mm thickness, as shown in Fig. 1.

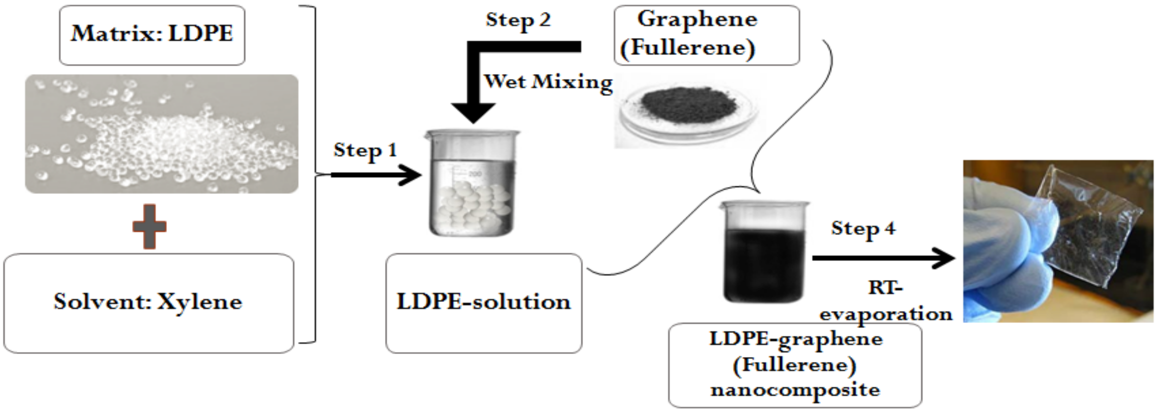

Figure 1. Fabrication of LDPE Membrane

2.3. Sheets Processing

2.3.1. Mechanical (Dry) Mixing

A turbula mixer (Turbula T2F, Switzerland) was used to mix the LDPE pellets with G powder in-situ. During the process, the mixing speed was set to 96 rpm for 1 hour. The mixer works by moving the mixing container in a three dimensional motion of rotation, translation, and inversion.

2.3.2. Hot Compaction

This process was mainly adding LDPE/G (dry form) mixture into a preheated mold and by applying heat and pressure, the molding material takes the shape of the mold cavity. Pressure was applied on the mold using the heated plates of the hydraulic press. Molding was carried out at 150°C, 2 tons (±0.1) for 10min.

2.4. Tensile testing

The yield tensile strength of the previously prepared LDPE thin films, sheets and nanocomposites was evaluated through an axial tensile test. The test was conducted using an Instron universal testing machine with 100KN capacity. To insure the axial uniform load distribution on the membrane-thin sheets, a fixture was designed as a transition between the flat grips of the machine and the thin films. The guidelines for the dimensions of the membrane samples were cut in accordance with ASTM Standard Method D 882-91 [10]. The initial grip separation was set at 30 mm. The testing was performed at the preselected strain values to insure that testing occurred within the uniform plastic deformation. A strain rate of 2 mm/min was employed for all tested samples.

2.5. Melt Flow Index

The viscosity of the LDPE/G was measured using a melt flow indexer (MFI) (A Ray-Ran Co. England melt flow systems). Four grams of polymer sample was packed properly inside the extruder barrel to avoid formation of air pockets. A piston was introduced, which acted as the medium responsible for the extrusion of the molten polymer. The sample was preheated for a specified amount of time. After preheating, a specified weight was introduced to the piston. Examples of standard weights are 2.16 kg and 5 kg. The weight exerted a force on the molten polymer and it immediately started flowing through the dye. A sample of the melt was taken after a desired period of time and was accurately weighed. For flow rate consistency, it was important to make sure that the extrudate was free of voids. The weight of the resulting material strips was measured every 0.5 min. The specified flow range to drive the melt through the column was in g/10 min.

2.6. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) experiments were carried out to determine the variation in the thermal degradation temperature of LDPE by TGA analyzer Q series (Thermo Fisher Scientific, USA). Heating rate of 20 °C/min was used to raise the temperature of 10-14 mg samples from room temperature up to 700 °C under nitrogen purge flow rate of 50 ml $min^{-1.}$The nitrogen gas valve and the TGA release valve were opened. The sample pan was cleaned and carefully placed with tweezers onto the sample platform. The instrument was tared. The sample was then placed in the center of the sample pan. The appropriate inputs were entered into the Q50-TGA program as dictated by the experiment parameters. Then the run started. Once the run was finished, the pan was carefully cleaned with a propane torch.

III. RESULTS

3.1. Tensile properties of LDPE films and sheets and their nanocomposites

The presence of G-nanofiller within LDPE thin films offered resistance to the movement of the polymer chains which led to an enhancement in the mechanical strength. This agreed with the findings of Checchetto et., al. where the enhancement of tensile properties depended strongly on the properties of the nanofiller, and the nanofiller-matrix interface in both LDPE thin films fabricated by solution casting and in LDPE sheets manufactured by compression molding [11]. The tensile strength of LDPE films in Figure 2a gradually increased from 20 MPa to 38 MPa at 0.1 wt. % G and further to 52 MPa at 1 wt. % of G. This corresponded to an overall increase in strength up to160 % at 1 wt. % G addition. The enhancement accompanied with G nanofiller could be due to the restacking of G nanoclusters in the polymer matrix [12]. It was also reported that the tensile strength of LDPE increased by a factor of 2.5 with the addition of G nanofiller [13-14].

On the other hand, there was an increase in tensile strength in LDPE sheets reinforced with G from 20 MP at 30 MPa at 0.1 wt. % G and further to 38 MPa at 1 wt. % of G as shown in Fig. 2. The improvement in tensile strength of thin films was higher than the improvement in LDPE sheets by 70 %. These observations may be attributed to the difference in temperature during manufacturing the thin film (80 °C) compared to the temperature (150 °C) at which the LDPE sheets was fabricated. In order to explain the previous behaviour of LDPE sheets, one must study the compression molding of LDPE sheets thoroughly. The LDPE/G nanocomposite was placed in the mould and heated under pressure within the plates of the press. When the reaction completed, the polymer nanocomposite sheet was cooled and ejected. Crystallinity played an essential role in determining the tensile strength of the LDPE sheet [15]. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure. The melted LDPE cooled and the chains began to fold on each other but could not form regular structures (like crystals). Hence, the low degree of crystallization affected the tensile strength [16]. Another possible explanation could be due to the small chains that melted early during processing and they were subjected to heat and friction until all the longer chains melt, therefore small chains acted as initiators for degradation thus decreasing the tensile strength [17].

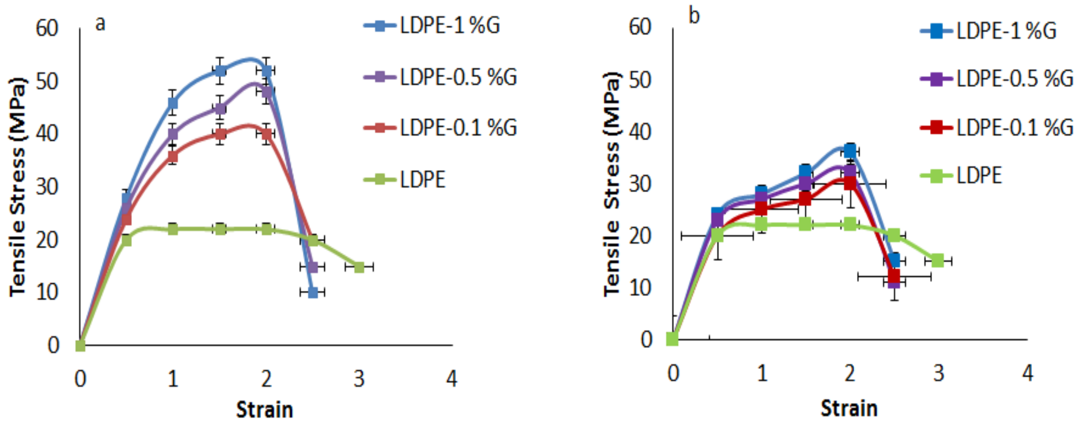

Figure 2. Stress-strain curve for LDPE and LDPE nanocomposite membranes a) LDPE thin film b) LDPE sheet

3.2. Melt Flow Index (MFI) of LDPE films, sheets and their nanocomposites

It is observed in Fig. 3 that the MFI of LDPE and nanocomposite thin films are a function of the nanofiller content. There was a decrease in MFI upon addition of G nanofiller from 0.3 to 0.05 g/10 min at 1 wt. % G. This was most probably due to the formation of clusters leading to less dispersion and higher shear force within the polymer matrix thus decreasing the MFI of the polymer nanocomposite [18]. It was reflected from the results that the 0.1 wt. % G showed a higher melt flow index (lower viscosity) than 0.5 wt. % and 1 wt. % G. The same behavior could be concluded upon addition of G nanofiller to LDPE sheets. There was a decrease in MFI upon addition of G nanofiller from 2 to 0.7 g/10 min at 1 wt. % G. However, there was a dramatic decrease in MFI (an increase in viscosity) within LDPE/G thin films due to the high viscosity of the polymer solution that formed during solution casting. The polymer segments are surrounded by solvent molecules rather than by other polymer segments increasing the flow of the solution. The increase in viscosity explained the decrease in MFI of thin films [19]. On the other hand, there was an increase in the applied pressure on the LDPE sheets increasing the melting temperatures. The increase in melting temperature caused a decrease of viscosity leading to a high melt flow index as shown in Fig. 3 [20]

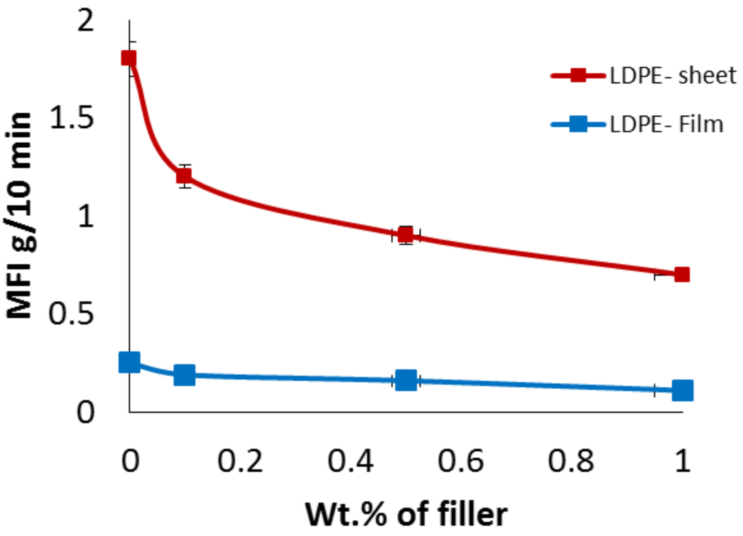

Figure 3. Melt flow index for LDPE films, sheets and their nanocomposites

3.3. Thermo Gravimetric Analysis of LDPE films and sheets and their nanocomposites

TGA of LDPE and nanocomposite thin films, sheets is outlined in Fig. 4. The G nanofiller act as a physical cross link which limits the movements of macromolecular chains of LDPE. It can be concluded that the addition of G nanofiller leads to a remarkable improvement of LDPE thermal stability. The glass transition temperature increased from 160 ºC (at 0.1 wt. % G) to 290 ºC (at 1 wt. % G). This enhancement could be explained by the barrier effect of the carbon which resulted in the improvement of the resistance to thermal degradation and so in hindering the diffusion of the decomposition products from the bulk polymer onto the gas phase. This stabilization effect could be attributed to the increased interfacial interactions between the G nanofiller and the LDPE and to the fine dispersion of the fillers within the LDPE matrix, which led to an increase in activation energy for thermal degradation especially in the thin film fabrication [21].

It can also be noticed that the addition of G nanofiller led to an improvement of the LDPE thin films thermal stability with a higher % (60 % at 1 wt. % G) compared with addition of G nanofiller to LDPE sheet, which improved from 150 ºC (at 0.1 wt. % G) to 190 ºC (at 1 wt. % G). This is probably due to the solvent loss in solution casting process of thin films. The solvent loss led to reduced chain mobility thus increasing the glass transition temperature of the film [22]. In case of LDPE sheets and their nanocomposites, there was more time available for the orientation to relax towards an equilibrium state with greater chain mobility leading to a decrease in glass transition temperature as shown in Fig. 4 [23].

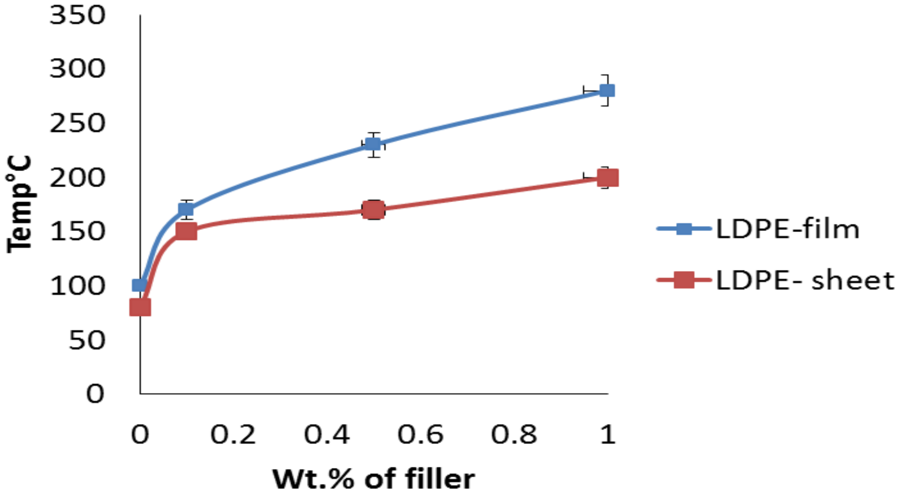

Figure 4. Temperature versus Wt. % of nanofiller for LDPE

IV. CONCLUSION

In conclusion, the fabricated thin films with thickness (0.2 mm) showed enhancement in tensile properties, thermal stability and lower MFI compared to LDPE sheets (0.5 mm). Moreover the effect of addition of G nanofiller enhanced the tensile strength of both thin films and sheets by 160 % and 70 % respectively. There was a decrease in MFI upon addition of G nanofiller in thin sheets with 65 % and 80 % decrease in MFI for the LDPE films. On the other hand, the addition of G nanofiller increased the glass transition temperature for both LDPE thin films and sheets by 90% and 30 % respectively. The effect of G nanofiller is significantly shown with the thin films due to the high surface area to volume compared to sheets.

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