An investigation of the improvements of mechanical and thermal properties of high-density polyethene/nano clay composites

Sameer A. Awad [1]*, Eman M. Khalaf

[1]Department of Chemistry, College of Education for Pure Science, University Of Anbar, Ramadi 31001, Iraq

S. A. Awad (0000-0002-9194-719X), E. M. Khalaf (0000-0001-7887-6158)

Abstract

The incorporation of different loadings of nanoclay (NC) into high-density polyethylene (HDPE) was studied. A series of different ratios of NC (2, 4, and 8 wt %) in fixed particle size, 300μm was blended with HDPE matrix and prepared via melt mixing process. The tests of thermal decomposition behaviour of HDPE and HDPE composites were investigated by utilising thermal gravimetric analysis (TGA). The mechanical properties of HDPE reinforced with different ratios of nanoclay particles were determined by tensile strength, Young's modulus, and elongation at break. The results of the TGA indicated that the highest thermal stability was shown by the HDPE treated with 8 wt % of NC. The tensile strength, Young's modulus, and elongation at break were improved with increasing of NC loadings into HDPE matrix compared to that of HDPE without filler. The highest interfaces of nanoclay into the HDPE matrix were led to a decrease in the brittle behaviour and enhanced the high crosslinking of the HDPE matrix. The SEM micrographs showed that the HDPE/8 wt % more homogeneous and no voids on the surface by comparing to that of HDPE matrix.

Keywords: Nanoclay, High-density polyethylene, Thermal decomposition, Mechanical properties

1. INTRODUCTION

Polymer nanocomposites have been commonly utilised in several fields as industrial, construction, and medical applications regarding their excellent chemical, physical, and mechanical characterisations [1-3]. Researchers mainly focused on the improvement of thermal and mechanical properties of developed composite materials. Polymer nanocomposites include nano-sized fillers which display superior properties at a lower loading than conventional composites [4]. The polymeric materials are usually nominated based on their inherent properties, availability, cost, and manufacture's finding. High-density polyethylene (HDPE) is the most common matrix which is utilised for composite material development. [5-7].

High-density polyethylene is commonly utilised in industrial applications as a result of its distinctive mechanical and physical properties when compared to those of many other thermoplastic materials. HDPE has been modified with reinforcements, such as nanoclay, nano calcium carbonate ($CaCO_3$), carbon nanotubes (CNT), graphite nanofibers na-nocarbon [8]

Several researches have been focused on finding the clay loading that will produce the ideal thermal and mechanical properties for the desired application [9-11]. Heydari-Meybodi et al. concluded in their study that Young's modulus increased with an increase in clay loading from 5 wt % to 7 wt % into polymers [12]. Tannuri et al. also displayed that the utilise of 4 wt.% of nanoclay fillers in the HDPE matrix improved the tensile strength and storage of modulus [13]. Khan et al. presented the flexural strength of the nanoclay/epoxy nanocomposites increased with increasing nanoclay loading but decrease back after 3.0 wt.% of nanoclay [14]. They also found that the flexural modulus of the nanocomposite increased with adding nanoclay [14]. Faruk and Matuana found that HDPE matrix has significantly improved both the flexural strength and modulus of the HDPE/wood-flour composites by the addition of nanoclay [15]. The purpose of this study was to investigate the possibility of using nanoclay modifier to enhance the thermal and mechanical properties of the HDPE matrix.

2. METHODOLOGY

2.1 Materials

High-density polyethylene (HDPE) was supplied from SABIC chemical company, KSA. The nanoclay used was the type (Cloisite 30B) and was obtained from Southern Clay Products (USA). Nanoclay contains organically modified nanometer scale which layered by magnesium aluminium silicate platelets. Moisture content is ≤ 2%, and the particle size is approximately 2 μm.

2.2 HDPE/NC composite preparation

The HDPE/NC composite films were synthesised by mixing the HDPE with different loadings of 2, 4, and 8 wt.% of nanoclay using an internal mixer type (Haake HBI system 90, 300 ccs, fill factor 0.8). Before melt mixing, the HDPE and the NC were preheated in a vacuum oven at 80 °C for 8 hours. HDPE was fed into the twin screw extruder at the rate of 8 kg/h, and the NC was added regularly at the melting zone. All samples were then continuously mixed for 10 minutes at 160 °C with a rotor speed of 50 rpm. The HDPE/NC composite was pressed under 25 MPa at 170 °C for 5 min and then cooled down at room temperature for 4 hours.

3. ANALYTICAL METHODS

3.1 Thermogravimetric analysis (TGA)

HDPE and HDPE/NC composite samples were tested by utilising TGA instruments type (TGA Q500; TA Instruments) under a nitrogen atmosphere and a temperature range from 25 °C to 650 °C at a heating rate of 10 °C·min⁻¹. All samples were weighted within the range (5-10 mg). The thermal decomposition temperature of the samples was tested and monitored the decomposition of samples within the above temperature range.

3.2 Tensile strength tests

Composite samples were tested by using the Instron tensile machine model (Testometric, M500-50AT, UK). The crosshead speed was about 20mm/min. Tensile measurements of the samples were carried out at the room temperature using a device equipped with a 10 KN load cell. Dog-bone-shaped samples with overall dimensions of 16.3 × 1.9 × 0.5 cm were prepared, the tests were done according to the American Society for Testing and Materials (ASTM-D 638. Three samples were tested for each analysis of samples. Charpy impact strength measurement was used by using A CEAST Resil IMPACTOR. The instrument was connected with a 4J hammer at room temperature.

3.3 Water absorption

Water absorption samples were immersed entirely in distilled water mass of the samples was reported at various content times. The samples were dried with tissue paper to remove water from the surface of samples before weighing by utilising a sensitive balance. Four samples for each composition were dried in an oven for 24 h at 80 °C. The water absorption was achieved according to the ASTM D 570-98 method. The water absorption (W_A) of samples was calculated, utilising the following equation:

$$W_A(\%) = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

Where: W_0 is the weight of the original specimen and W_t is the weight of the immersed sample in time.

3.4 Scanning electron microscopy (SEM)

The morphology of the surfaces for HDPE and HDPE/nanoclay composite were examined with JEOL, JSM 840A scanning electron microscope with a voltage of 10 kV. The surface of the samples was coated with thin layers of gold.

4. RESULTS AND DISCUSSION

4.1 Thermal decomposition of HDPE nanocomposites

Thermal decomposition behaviour of the pure HDPE and HDPE/NC composite samples are given in Figs 1 and 2. The maximum decomposition temperature (T_{max}), the initial decomposition temperature (T_i) and residual yield % at 650 °C are summarised in Table 1. Fig. 1 shows the TGA of the HDPE and HDPE/NC composites. T_i has represented the initial decomposition temperature and is a relevant factor, indicating thermal stability [12]. The differential of thermogravimetric analysis (DTG) curves of HDPE/NC composites is shown in Fig. 2. The addition of 8 wt % of NC filler was exhibited higher initial decomposition temperature at 386.4 °C compared to that of pure HDPE at 380.5 °C (Table 1). The presence of the NC fillers found to enhance the thermal stability of the HDPE matrix and provide good interfacial adhesion between the HDPE matrix and NC fillers. The decomposition at T_{10} showed a higher decomposition in HDPE/8 wt % NC (389.5 °C) while the T_{10} of pure HDPE was 385.4°C. The 8 wt % of NC in the HDPE matrix has a higher temperature at loss decomposition (T_{50}) that was 397.8 °C compared to that of pure HDPE (390.5 °C) as are shown in Table 1.
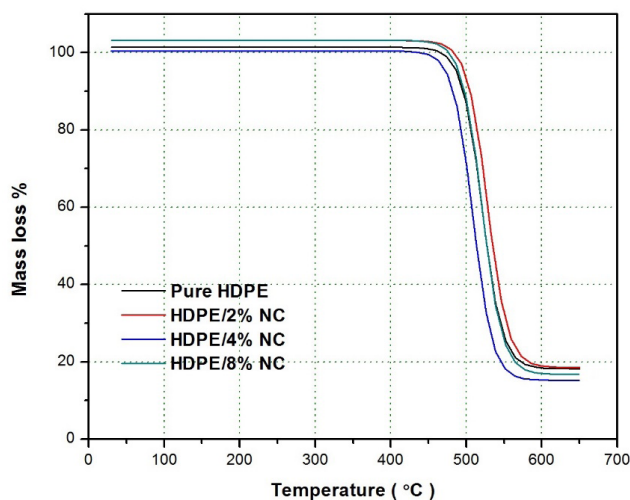

Fig.1 TGA thermogram curves for pure HDPE and HDPE/NC composites.

From the data in Table 1 that are showed that the residual yield % exhibited higher values of 4 wt %, 8 wt %, and 12 wt

Ibrahim Ozbay, Tamer Aydiner, Gürkan Yilmazoglu, Hafize Celik, Levent Aksel, Harun Yeni, Metehan Bayramoglu, Erdem Aydogmus

% NC (15.2%, 17.8%, and 19.5%), respectively, by comparing with the pure HDPE that was about 13.2% (Table 1). The DTG curves in Fig. 2 showed the temperature at maximum rates. The results showed that the T_{max} of 8wt.%NC in HDPE was (410.7 °C) while the T_{max} of pure HDPE was (395.6 °C).
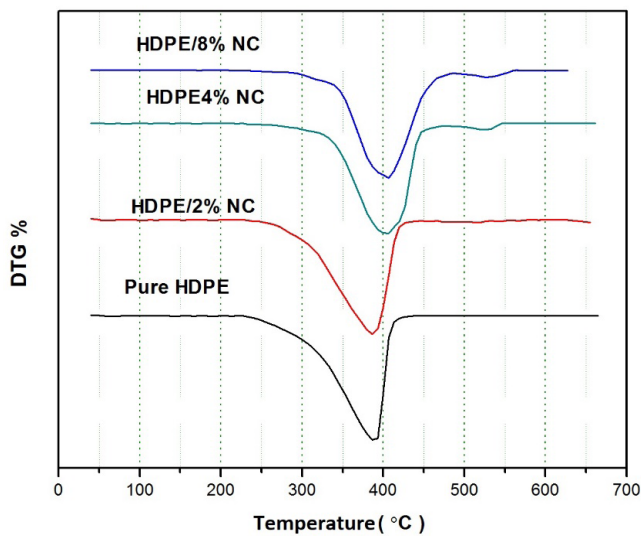

Fig. 2 DTG curves for pure HDPE and HDPE/NC composite samples

Table. 1 Thermal decomposition results of pure HDPE and HDPE/NC composite samples

Composites	$T_{ons.}$ (°C)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)	Residual yield (%)
Pure HDPE	380.5	385.5	390.5	395.6	13.2
HDPE/2wt.%NC	381.7	387.2	391.4	396.8	15.2
HDPE/4wt.%NC	383.8	388.2	395.2	403.5	17.8
HDPE/8wt.%NC	386.4	389.4	397.8	410.7	19.5

4.2 Mechanical analysis of composites

The tests of tensile properties can evaluate the impacts of adding NC fillers in HDPE. The mechanical properties of HDPE/NC composites were improved with the incorporation of NC contents of 2-8%. It is evident from Table 2 that tensile strength increased with adding further amounts of NC fillers (2-8%) to pure HDPE, compared with pure HDPE. From Figure 4, it can be shown that the higher content 8% NC increased to 19.54 MPa by comparing with pure HDPE 12.74 MPa. The results of the Young's Modulus are shown in Table 2 and which was displayed rising in the modulus of elasticity 96.18 MPa, 98.88 MPa, and 110.64 MPa of 2 wt.%, 4 wt.%, and 8 wt.% of NC in HDPE, respectively when the weight ratios of NC were increased while Young's modulus of pure HDPE was 95.22 MPa. The elongation at break versus blend composition of HDPE/NC composite was displayed a decreasing pattern for all blends composition (Table 2). The results of elongation at break are exhibited in Table 2 which are shown that a higher value of elongation at break 290.9%, of pure LDPE, compared with 8wt.% NC 255.5%. The impact strength of LDPE incorporated increased with increasing the loading of NC. The values of the impact strength of LDPE/2wt.%, 4wt.%, and 8wt.%NC were 5.87 KJ.m^{-2}, 6.88 KJ.m^{-2}, and 7.22 KJ.m$^{-2)}$ compared to that of pure LDPE that was (5.52 KJ.m^{-2}). Lei et al. (2007) were reported that the flexural and tensile strength of HDPE/pine composites increased

about 20 and 24%, respectively, with the incorporation of 1% clay; however, then decreased slightly as the clay content increased to 3%. The tensile modulus and tensile elongation were also increased with the addition of 1% clay. The impact strength was lowered by about 7% by 1% clay but did not decrease further as more clay was added [16].

Table .2 Mechanical properties results of pure HDPE and HDPE/NC composites.

Composites	Tensile stress (MPa)	Young's modulus (MPa)	Elongation at break %	Impact strength (KJ.m^{-2})
Pure HDPE	12.74 ± 0.55	95.22 ± 3.56	290.9 ± 30.5	5.52 ± 0.35
HDPE/2wt.%NC	13.43 ± 0.72	96.18 ± 4.78	285.5 ± 35.5	5.87 ± 0.27
LDPE/4wt.%NC	15.65 ± 0.65	98.88 ± 3.85	267.8 ± 28.7	6.88 ± 0.47
LDPE/8wt.%NC	19.54 ± 0.85	110.64 ±6.54	255.5 ± 24.5	7.22 ± 0.53

4.3 Water absorbance of composite

Water absorptions of HDPE/NC composites are shown in Fig. 3. Water absorption increased with increasing the time of immersion for all samples. Swelling or absorption behaviour due to water uptake was examined, utilising the equation (1). The results in Fig. 3 were exhibited that the addition of nanosilica into the pure HDPE has shown a reduction in the percentages of water absorption with an increase of nanoclay loadings. It was evident that the percentage of water absorption is higher for pure HDPE compared to that of HDPE incorporated nanocaly 8wt. % NC. The rate of water absorbance at the beginning of immersion time was the highest in HDPE/NC composite samples compared with that of pure HDPE. After immersion to 250 h, water absorbance of HDPE increased significantly by 4.5% compared to that of HDPE/NC composites with different loads of 2%, 4%, and 8% (4.2%, 1.6%, and 0.95%) that increased with increasing immersion time to 250 h (Fig. 3).
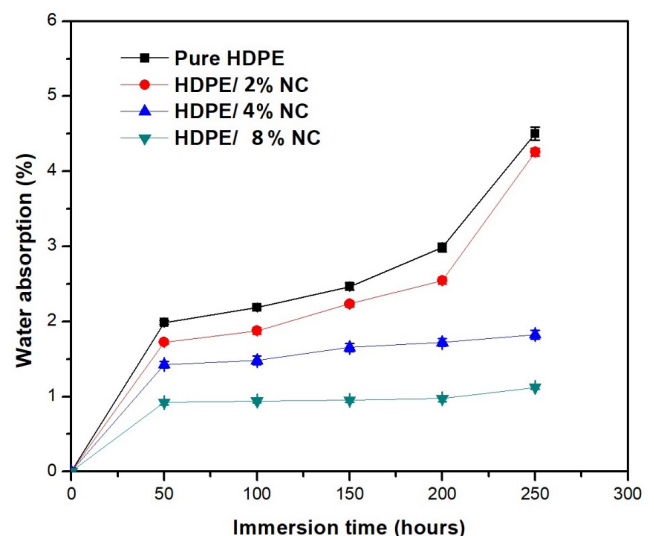

**Fig.3** Water absorption of LDPE and HDPE /NC composites

4.4 Surface morphology analysis of HDPE/NC composites

SEM micrographs of pure HDPE and HDPE/12wt % of NC composite are presented in Fig. 4(A) and (B), respectively. From Fig. 4 (A), it can be seen that pure HDPE exhibited

more voids and ductilities, while for the HDPE incorporated with 8 wt % NC showed more smooth and homogeneous between the particles. The nanoclay particles reduced and decreased the voids on the HDPE surface and exhibited more adhesion between the molecules of HDPE and nanoclay (Fig. 4B).
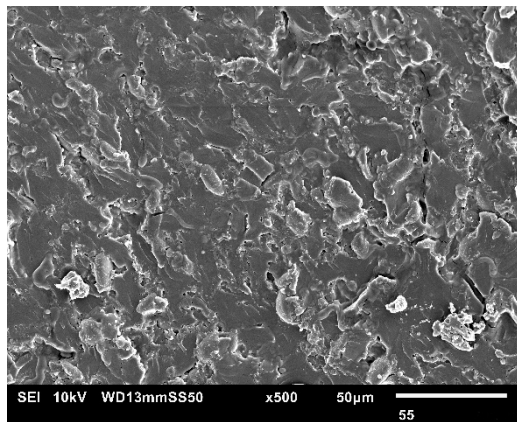
(a)
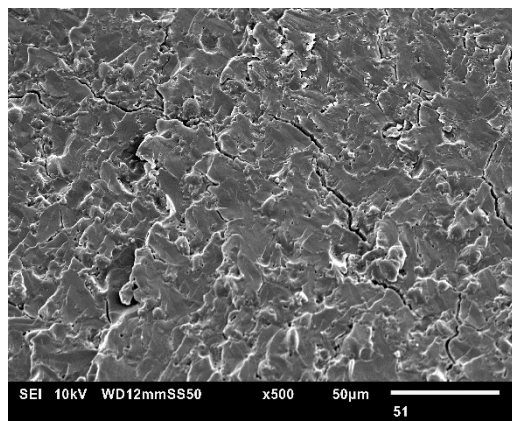
(b)

Fig. 4 SEM micrographs of Pure HDPE (A) and HDPE/8%wt.NC composite

5. CONCLUSIONS

The additions of NC fillers in the HDPE matrix have achieved improvements in the thermal and mechanical properties of HDPE nanocomposites. The thermal stability increased with increasing of NC contents into HDPE. The tensile strength and Young's modulus of (HDPE/NC) composite slightly improved with the incorporation of the filler 2-8%. Elongation at break was decreased slightly with increasing NC contents. The higher values of NC in pure HDPE enhanced higher thermal stability by comparing with pure HDPE.

REFERENCES

[1] Verdejo, R., Bernal, M. M., Romasanta, L. J., Lopez-Manchado, M. A. (2011). Graphene filled polymer nanocomposites. Journal of Materials Chemistry, 21(10): 3301-3310, DOI:10.1039/C0JM02708A.

[2] Blaszczak, P., Brostow, W., Datashvili, T., Lobland, H. E. H. Rheology of low-density polyethylene-Boehmite composites, Polym. Compos, 31(2010): 1909-1913, DOI:10.1002/pc.20987.

[3] Pinto, F., Carotenuto, G., Meo, M. (2015). Preparation and thermo-mechanical characterisation of graphene nanoplatelets/low-density polyethylene composites. Journal of Thermoplastic Composite Materials, 28(6): 745-761, DOI:10.1177/0892705713489702.

[4] Supri, A., Salmah, H., Hazwan, K. (2008). Low density polyethylene-nanoclay composites: the effect of poly (acrylic acid) on mechanical properties, XRD, morphology properties and water absorption. Malaysian Polymer Journal, 3(2): 39-53.

[5] Awad, S. A., Khalaf, E. M. (2019). Investigation of improvement of properties of polypropylene modified by nano silica composites. Composites Communications, 12: 59-63, DOI: 10.1016/j.coco.2018.12.008.

[6] Youssef, A. M., El-Gendy, A., Kamel, S. (2015). Evaluation of corn husk fibers reinforced recycled low density polyethylene composites. Materials Chemistry and Physics, 152: 26-33, DOI: 10.1016/j.matchemphys.2014.12.004.

[7] Awad, S. A., Khalaf, E. M. (2018). Characterisation and Performance of Low-Density Poly Ethylene-Corn Flour Composites. Aksaray University Journal of Science and Engineering, 2(2): 171-179, DOI: 10.29002/asujse.432715.

[8] Sepet, H., Tarakcioglu, N., Misra R. (2016). Investigation of mechanical, thermal and surface properties of nanoclay/HDPE nanocomposites produced industrially by melt mixing approach. Journal of composite materials, 50: 3105-3116, DOI: 10.1177/0021998315615653.

[9] Yang, W., Ge, L., Lv, H., Xia, M., Ji, X., & Yao, Z. (2016). Mechanical and thermal properties of low-density polyethylene composites filled with dye-loaded shell powder. Journal of Applied Polymer Science, 133(42): DOI: 10.1002/app.44118.

[10] Awad, S. A., Khalaf, E. M. (2018). Investigation of improvement of thermal and mechanical properties of polypropylene/nano clay composites. International Journal of Chemistry and Technology, 2(2): 129-134, DOI: 10.32571/ijct.430058.

[11] Awad, S. A., Khalaf, E. M. Evaluation of thermal and mechanical properties of Low-Density Poly Ethylene (LDPE)-Corn Flour (CF) composites. International Journal of ChemTech Research, 10(3): 230-235.

[12] Heydari-Meybodi, M., Saber-Samandari, S., Sadighi, M. (2015). A new approach for prediction of elastic modulus of polymer/nanoclay composites by considering interfacial debonding: experimental and numerical investigations. Composites Science and Technology, 117: 379-385, DOI: 10.1016/j.compscitech.2015.07.014.

[13] Tanniru, M., Yuan, Q., Misra, R. (2006). On significant retention of impact strength in clay–reinforced high-density polyethylene (HDPE) nanocomposites. Polymer, 47: 2133-2146, DOI: 10.1016/j.polymer.2006.01.063.

[14] Khan S.U., Iqbal, K., Munir, A., Kim, J-K. (2011). Quasi-static and impact fracture behaviours of CFRPs with nanoclay-filled epoxy matrix. Composites Part A: Applied Science and Manufacturing, 42: 253-264, DOI: 10.1016/j.compositesa.2010.11.011.

[15] Faruk, O., Matuana, L.M. (2008). Nanoclay reinforced HDPE as a matrix for wood-plastic composites. Composites Science and Technology, 68: 2073-2077, DOI: 10.1016/j.compscitech.2008.03.004.

[16] Lei, Y., Wu, Q., Clemons, C.M., Yao, F., Xu, Y. (2007). Influence of nanoclay on properties of HDPE/wood composites. Journal of Applied Polymer Science, 106: 3958-3966, DOI: 10.1002/app.27048.