

CHARACTERIZATION AND MODIFICATIONS OF LOW-DENSITY POLY ETHYLENE-NANO CELLULOSE CRYSTALLINE COMPOSITES

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Abstract

The incorporation of nanocrystalline cellulose (NCC) with different ratios into the LDPE matrix was investigated by using the mechanical and thermal tests. The LDPE composites were prepared in an internal mixer type Z- Blade mixer at 190°C and rotor speed of 50 rpm. The results obtained showed that the higher addition of NCC improved the mechanical properties. The thermal stability was increased as the NCC loading into LDPE increased. From the results of DSC data, the crystallinity of LDPE nanocomposites improved. The flow properties of LDPE composites were investigated by determining the Melt Flow Index (MFI).

Keywords: LDPE, NCC, Thermal stability, Tensile strength, Storage of modules

Introduction

A composite is mainly composed of a mixture of two or more of materials that have a different chemical composition, and that usually is insoluble in each other (Błaszczak *et al.*, 2010; Awad *et al.*, 2017; Khalaf *et al.*, 2017). The significant aim of using these materials is to create better properties compared to that of the individual components. Polymer composites filled with natural additives used as conventional composites and

have a broad application (Ghafari-zadeh *et al.*, 2018; Khalaf *et al.*, 2018) Natural fillers filled polymers are eco-friendliness because polymer – natural filler composites are more accessible to recycle, may be used as alternatives to existing products. The incorporation of natural fillers into a polymer widely produced substantial changes in the mechanical properties of the composites (Goyal *et al.*, 2016; Hamzeh *et al.*, 2018). However, a problem appears when

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trying to mix natural fillers with plastics like polyolefins such as LDPE, HDPE, PP, and PVC. This problem is one of the differences as a result of the hydrophilic nature of natural fillers such as nitrocellulose. The mechanical properties of the untreated LDPE composites were observed, due to the reinforcing effect imparted by the natural fillers which allowed a uniform stress distribution from the continuous polymer matrix to the dispersed fibre phase (Luyt *et al.*, 2006; Awad *et al.*, 2016; Awad *et al.*, 2017). However, there was a general improvement in the mechanical properties of the polymer composites in comparison to those of the polymer matrix (Reddy *et al.*, 2006; Roy *et al.*, 2006; Mubarak *et al.*, 2018). Previous studies investigated of the DMA results showed that the incorporation of jute fibers into HDPE increased the modulus and stiffness of the matrix with reinforcing effect imparted by the natural fillers that allowed a higher degree of stress transfer at the interface (Wang *et al.*, 2006; Zhang *et al.*, 2006). This study aims to improve the thermal and mechanical behavior of LDPE reinforced natural fillers (NCC) composites.

Materials and Methods

Materials

Provided Low-density polyethylene (LDPE) was supplied from SABIC chemical company, KSA, The nano cellulose crystalline (NCC) was provided from Sigma-Aldrich (USA) without further purification.

LDPE Composite Preparation

The NCC filler with various ratios (5, 10, and 20 wt.%) was blended and melted with pure LDPE matrix, utilising a shear mixer at a rate about 50 rpm with the continued mixing for 10 min to achieve the homogenous between the NCC and LDPE matrix. The produced mixture was poured out into metal molds and compressed, starting from 20 kg·cm⁻³ and then increased to 100 kg·cm⁻³ within 7 min. The composites were taken out from the molds and left for a day to make more curing.

Characterizations

Mechanical Tests

The tensile tests were carried out by using on a Universal machine, model Instron 1,130 tester, according to standard ISO 527-1, using a load of 1,000 N and the test speed is 2 mm.min⁻¹.

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) was applied out using a TA instruments model DMA-2980. The dimensions of the samples were of 35×9×1.5 mm. A heating rate was 10°C at a fixed frequency (1 Hz), and the range of temperature was between 30 to 150°C.

Thermogravimetric Analysis (TGA)

LDPE and LDPE/NCC composite samples were tested by utilizing TGA instruments type (TGA Q500; TA Instruments) under a nitrogen atmosphere. The temperature range was from 30 to 600°C. All samples were tested at a heating rate of 10°C·min⁻¹. The activation energy for decomposition (E_a) was calculated utilizing Horowitz-Metzger (HM) Equation.

$$\ln \left[\ln (1 - \alpha)^{-1} \right] = E_a \left[E_a \theta / RT_{\max}^2 \right] \quad (1)$$

$$\alpha = \frac{C_i - C_f}{C_i} \quad (2)$$

- α = the decomposed fraction and is specified as $= (C_i - C_f) / C_i$.
- C = the mass at a temperature chosen, C_i the mass at the initial temperature (T_{ons}) and C_f is the mass at final temperature.
- E_a = the activation energy for decomposition.
- $T_{\max}$ = the temperature at a maximum rate of mass loss.
- R = the universal gas constant
- θ = $T - T_{\max}$.

Kinetic plots were made with $\ln[\ln(1-\alpha)^{-1}]$ versus θ .

Differential Scanning Calorimetric Analysis (DSC)

The thermal characterization of LDPE and LDPE/NCC composites were determined by using a TA Q- 10 thermal analysis apparatus. The temperature range was used between 30 to 220°C at a heating scan rate of 10°C·min⁻¹ under a nitrogen atmosphere. In the first heat run, all samples were annealed at 220°C for 5 min to eliminate the thermal history. The degree of crystallinity (X_c) of LDPE and LDPE composites was calculated from the heat of fusion (ΔH_m) of the second heating cycle with the following relation.

$$X_c = \left(\frac{\Delta H_m}{(1-\phi)\Delta H_m} \right) \times 100 \quad (3)$$

Where, ΔH_m is the heat of fusion for 100% crystalline LDPE, which has taken 287 J·g⁻¹. Subsequently, the samples were cooled to 40°C at the rate of 10°C·min⁻¹ and cooling rates and the corresponding melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity were recorded from the heating and cooling curves.

Results and Discussions

Mechanical Properties

The results of the stress-strain curves are exhibited in Figure 3. The tensile strength and modulus of elasticity were increased with the incorporation of NCC contents of 5-20 wt% into the LDPE matrix. Table.1 showed that tensile strength increased with adding a higher loading level (20 wt% NCC) compared to that of pure LDPE matrix. The tensile strength of LDPE/ 5 wt.%NCC, LDPE/10 wt.%NCC, and 20 wt.% NCC composites were increased by 1%, 14%, and 30%, respectively. The tensile modulus of LDPE/ 5 wt%, 10 wt%, and 20 wt% NCC composites increased by 16%, 26%, and 37%, respectively, compared with LDPE matrix (Table.1). In contrast, elongation at the break decreased by 60%, 31.5, and 14% of 20, 10, 5 wt% NCC in LDPE matrix, compared to that of LDPE (Table 1). Overall mechanical results exhibited better tensile strength and modulus for the higher loading level (10 wt%)

NCC into LDPE, compared with that of lower loading levels of NCC and LDPE matrix.

Dynamic Mechanical Analysis of LDPE Nanocomposites

The storage modulus of LDPE and LDPE nanocomposite samples was investigated to improve steadily with the addition of NCC contents. Figure 1 showed that the temperature dependence of the storage modulus of the control and composite samples. The values of storage modulus for LDPE nanocomposites were higher than that of pure LDPE throughout the temperature range. The storage modulus increased by 9.2%, 4.2%, and 2.06%, and 20 wt% of 20, 10, and 5% NCC into LDPE matrix, respectively, compared to that of LDPE matrix (Figure 1). The presence of a higher content of NCC may enhance the flexibility and reduces the molecular mobility of the LDPE polymer molecular chain.

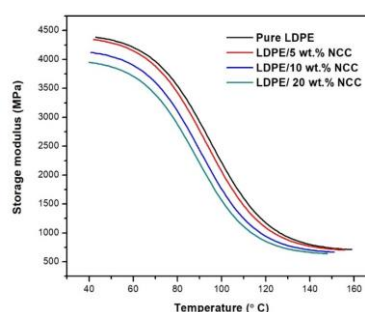


Figure 1. The storage modulus of LDPE and LDPE nanocomposites

Thermal Analysis of LDPE and LDPE/NCC Nanocomposites

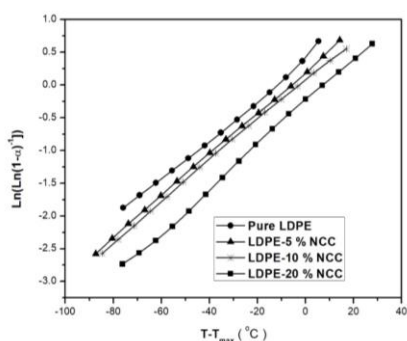
The results of thermal degradation for the LDPE matrix and LDPE/NCC nanocomposite samples are shown in Table 2. T_i defines the initial degradation temperature and is a relevant factor in determining thermal stability. The maximum degradation temperature T_{max} and residue at 600°C % are shown in Table 2. The incorporation of 10 wt % NCC into LDPE can prominently increase both T_i and T_{max} of the LDPE composites by 99.7°C and 52.8°C, respectively. The presence of the NCC is to make more stability to the LDPE matrix and

Table 1. Mechanical properties of LDPE and LDPE composites

Samples	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
LDPE	30.5±2.5	200.7±20	5.5±0.8
LDPE/5 wt% NCC	31.7±2.4	208.4±12	5.9±0.6
LDPE/10 wt%NCC	33.5±1.8	218.5±22	4.5±0.2
LDPE/20 wt%NCC	39.6±3.2	±25	2.5±0.09

Table 2. Thermal properties of LDPE and LDPE nanocomposites

System	$T_i \pm 0.1$ (°C)	$T_{max} \pm 0.1$ (°C)	E_a (KJ·mol ⁻¹)	Residue yield (%)
Pure LDPE	455.8	475.5	122.5	18.7
5 wt.% NCC	481.5	478.8	123.7	19.8
10 wt.%NCC	514.5	495.5	127.5	22.5
20 wt.%NCC	535.7	520.5	138.5	27.5

**Figure 2. Arrhenius plots of calculating the activation energy for LDPE and LDPE nanocomposites**

gives higher crosslinking between the NCC fillers and the pure LDPE. Table 2 showed that T_i , T_{max} , and residue yield were increased by increasing the content of NCC. Table 2 indicated that T_i was about 455.8°C while T_i of 5, 10, and 20% NCC into LDPE was 477.5°C, 510.4°C, and 555.5°C, respectively. Table 2 displayed that T_{max} of pure LDPE was 472.6°C, compared to that of LDPE- 20 wt% NC composite (525.4°C).

Table 2 showed that the residue yield of 5, 10, and 20 % of NCC into LDPE was increased by 15.7%, 18.2%, and 21.2% respectively, by comparing with that of pure LDPE (14.5%).

Figure 2 is exhibited the Arrhenius plots for the activation energy (E_a) for the decomposition of LDPE and LDPE composites with different temperatures. The effects of blend composition and compatibilization on the E_a of LDPE and LDPE nanocomposites are given in Table 2. The value of E_a in 20% NCC/LDPE nanocomposites was 138.5 KJ·mol⁻¹ while E_a for 10 wt%. NCC, 5 wt%.NCC and the LDPE matrix was 127.5, 123.7, and 122.5 kJ·mol⁻¹, respectively. It was seen that the higher addition (10 wt% NCC) into LDPE increased the E_a in the LDPE matrix.

Crystallization Bbehavior of the NCC Filled LDPE Nanocomposites

Thermal Properties of LDPE and LDPE nanocomposites were analyzed using DSC, and the thermogram data are shown in Table 3. The crystallinity degree of the LDPE nanocomposites was quantitatively measured by subtracting the filler mass contribution. From Table 3, the melting enthalpy (ΔH_m) was increased with increasing of the NCC content into LDPE. The ΔH_m value of 20 wt% NCC into LDPE was about (198.5J/g), compared to the lower contents 5 wt.%, 10 wt.%, and pure LDPE (192.5 J/g, 195.2 J/g, and 189.8 J/g). In the case of 8 wt.% NCC into LDPE, T_m was shifted to a higher temperature (167. 7°C),

Table 3. The results from DSC thermogram curves properties for LDPE and LDPE nanocomposites

The samples	T_m (°C)	ΔH_m (J/g)	X_c (%)
Pure LDPE	24.5	189.8	155.5
LDPE / 5 % NCC	25.4	192.5	160.2
LDPE / 10 % NCC	27.5	195.2	163.5
LDPE / 20 % NCC	29.2	198.5	167.7

compared to that of 5 wt%, 10 wt% of NCC, and pure LDPE (163.5 °C, 160.2 °C, and 155.5 °C), respectively. The high melting points can probably be attributed to a rise of LDPE matrix crystals. The crystallization points of LDPE and LDPE nanocomposites showed no significant changes in LDPE and LDPE composites (Table 3). LDPE nanocomposites were exhibited higher endothermic crystallization points, compared with the LDPE matrix. 20 wt. % filled LDPE showed a higher crystallinity (29.2 %) while LDPE crystallinity was about 24.5% (Table 3).

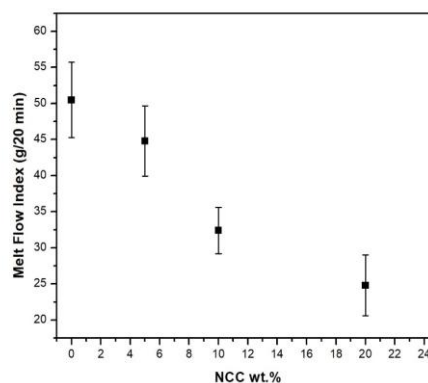
Melt Flow Index

Melt flow index (MFI) replicates the flexibility of flow for a molten polymer and is generally working in combination with melt flow rate (MFR) to define different grades of polyolefins (Sirin *et al.*, 2012). The flow and viscosity of polymers were increased with the incorporation of NCC fillers, thus a decrease of MFI for LDPE composites. Figure 3 showed that the effect of NCC content on the melt flow index based on LDPE composites. However, MFI was decreased with increasing of NCC content into LDPE (Figure 3). The higher amount of NCC (20 wt. %) was displayed a lower value of melt flow index (25.5 g.20 min⁻¹) by comparing with that of lower contents of NCC (5 wt.% and 10 wt.%) and the LDPE matrix (45.2 and 32.8 g. 20 min⁻¹ and 52.7 g. 20 min⁻¹), respectively.

Conclusions

The effect of NCC content in LDPE polymer has been investigated. It has been found that the higher values of NCC fillers in LDPE improved the thermal and mechanical properties of LDPE. The LDPE composites showed higher tensile strength and modulus of

elasticity compared to that of the LDPE matrix. 20% NCC into LDPE was higher storage of modulus than that of pure LDPE. The LDPE nanocomposites with a higher loading level (20 wt%) of NCC exhibited higher thermal stability by comparing with that of pure LDPE. From endothermic DSC curves, it is observed that the melting points, the melting enthalpy (ΔH_m) and crystallinity points of LDPE composites increased with increasing the NCC contents. Overall results confirmed that NCC contents are more effective and reinforce the LDPE matrix.


Figure 3. Melting flow index (MFI) of LDPE and LDPE nanocomposites

References

- Alidadi-Shamsabadi, M., Behzad, T., Bagheri, R., and Nari-Nasrabadi, B. (2015). Preparation and characterization of low-density polyethylene/thermoplastic starch composites reinforced by cellulose nanofibers. *Polym. Composite.*, 36(12): 309-2316.
- Awad, S. (2011). Influence study of (Vitamin C) absorption on the mechanical properties of (Polyethylene

- terephthalate) drinking bottles. *J. Univ. Anbar Pure Sci.*, 5:31-36.
- Awad, S.A. and Khalaf, E.M. (2017) Evaluation of thermal and mechanical properties of Low-Density Poly Ethylene (LDPE)-Corn Flour (CF) composites.
- Awad, S.A. and Khalaf, E.M. (2018). Improvement of the chemical, thermal, mechanical and morphological properties of polyethylene terephthalate-graphene particle composites. *B. Mater. Sci.*, 41(3):67.
- Blaszczak, P., Brostow, W., Datashvili, T., and Lobland, H.E.H. (2010). Rheology of low-density polyethylene+ Boehmite composites. *Polym. Composite.*, 31(11): 1,909-1,913.
- Ghafari-zadeh, S.B., Fr  chette, M.F., and David, E. (2018). Fabrication and Dielectric, Mechanical, and Thermal Properties of Low-Density Polyethylene (LDPE) Composites Containing Surface-Passivated Silicon (Si/SiO₂ Core/Shell Nanoparticles). *Polym.-Plast. Technol. Eng.*, 57(4):327-334.
- Goyal, M., Goyal, N., Kaur, H., Gera, A., Minocha, K., and Jindal, P. (2016). Fabrication and characterization of low-density polyethylene (LDPE)/multi walled carbon nanotubes (MWCNTs) nanocomposites. *Perspect. Sci.*, 8:403-405.
- Gray, N., Hamzeh, Y., Kaboorani, A., and Abdulkhani, A. (2018). Influence of cellulose nanocrystal on strength and properties of low-density polyethylene and thermoplastic starch composites. *Ind. Crop. Prod.*, 115:298-305.
- Khalaf, E. and Awad, S. (2016). Improvement of Chemical and Thermal Properties of Polyethylene Terephthalate (PET) by Using Multi-walled Carbon Nanotubes (MWCNTs). *Int. J. Mater. Sci. App.*, 5(6):297-301.
- Khalaf, E. and Awad, S. (2017a). Improvement of chemical, thermal, and mechanical properties of Polypropylene by using corn flour. *Usak Univ. J. Mater. Sci.*, 6:15-25.
- Khalaf, E. and Awad, S. (2017b). Improvement of mechanical and water absorbance properties of Low-Density Poly Ethylene (LDPE) by using White Kaolin powder (WK). *J. Adv. Chem. Sci.*, 3:426-427.
- Khalaf, E. and Awad, S. (2017c). Improvement, the Performance of Polyurethane (PUR), Y-290 Resin as Coating of Oil Pipeline by Using Multi-Walled Carbon Nanotubes (MWCNTs). *Eng. Technol. J.*, 35, Part A, p. 845-848.
- Luyt, A.S., Molefi, J.A., and Krump, H. (2006). Thermal, mechanical and electrical properties of copper powder filled low-density and linear low-density polyethylene composites. *Polym. Degrad. Stabil.*, 91(7):1629-1636.
- Mubarak, Y.A. and Abdulsamad, R.T. (2018). Effects of microcrystalline cellulose on the mechanical properties of low-density polyethylene composites. *J. Thermoplast. Compos. Mater.*, (In press).
- Reddy, C.S., and Das, C.K. (2006). Propylene-ethylene Copolymer Filled Nanocomposites: Influence of Zn-ion Coating upon Nano-SiO₂ on Structural, Thermal, and Dynamic Mechanical Properties. *Polym.-Plast. Technol. Eng.*, 45(7):815-820.
- Roy, P.K., Surekha, P., Rajagopal, C., Chatterjee, S.N., and Choudhary, V. (2006). Accelerated aging of LDPE films containing cobalt complexes as prooxidants. *Polym. Degrad. Stab.*, 91(8):1791-1799.
-   irin, K., Balcan, M., and Do  an, F. (2012). The influence of filler component on mechanical properties and thermal analysis of PP-LDPE and PP-LDPE/DAP ternary composites. In: *Polypropylene. InTech.*, p. 345-356.
- Wang, Z., Lu, M., Li, H.-L., and Guo, X.-Y. (2006). SWNTs-polystyrene composites preparations and electrical properties research. *Mater. Chem. Phys.*, 100(1):77-81.
- Zhang, Q., Rastogi, S., Chen, D., Lippits, D., and Lemstra, P.J. (2006). Low percolation threshold in single-walled carbon nanotube/ high-density polyethylene composites prepared by melt processing technique. *Carbon*, 44(4):778-785.