

Characterisation and Performance of Low-Density Poly Ethylene-Corn Flour Composites

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Abstract

This study aims to investigate the effects of corn flour fillers on the mechanical and thermal properties and surface morphology of low-density polyethylene composites. Low-density polyethylene (LDPE) and low density polyethylene/corn flour (LDPE/CF) with different loadings of CF (5%-20% w/w) were prepared in an internal mixer type Z-Blade mixer at 190°C and rotor speed of 50 rpm. Dynamic mechanical analysis (DMA), Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and tensile tests were analysed to investigate thermal and mechanical properties. Tensile tests displayed an increase in the tensile strength and modulus with the increase of CF loadings. The results of DMA tests showed significant improvements for the storage modulus and glass transition temperature, T_g . The results of TGA indicated that the addition of higher amounts of CF enhanced thermal stability.

Keywords

LDPE, CF, Thermal stability, Tensile strength, Storage of modules

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1. INTRODUCTION

A composite is mainly composed of a mixture of two or more of materials that have a different chemical composition, and that usually are insoluble in each other [1-3]. 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 were utilised as conventional composites and had a broad application [4-7]. Polymers with natural fillers are eco-friendliness because polymer – natural filler composites are more accessible to recycle, may be used as alternatives to existing products [8-10]. The incorporation of natural fillers into a polymer widely produced substantial changes in the mechanical properties of the composites. However, a problem appears when trying to mix natural fillers with plastics like polyolefins such as LDPE, HDPE, PP, and PVC [11-13]. This problem is one of the differences as a result of the hydrophilic nature of natural fillers such as corn flour. 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 [14-17]. However, there was a general improvement in the mechanical properties of the polymer composites in comparison to those of the polymer matrix [18-20]. Previous studies investigated of the DMA results showed that the incorporation of jute fibres 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 [21-23]. This study aims to investigate the improvement of the thermal and mechanical characterisations of LDPE plastic reinforced corn flour (CF) as a natural additive.

2. MATERIALS AND METHODS

2.1. Materials

Low-density polyethylene (LDPE) polymer was supplied from SABIC chemical company, KSA, The corn seeds were collected fresh from local farms.

2.2. Corn Flour Treatments

The corn seeds were dried by using a microwave oven at the temperature range of 60 to 70°C for 24 hours to remove the moisture after that they cracked to small parts and then passed through a molecular sieve (150-micron mesh size).

2.3. LDPE Composite Preparation

LDPE composites were melted and mixed with different ratios of corn flour filler in a shear mixer at a rate about 50 rpm with the continued mixing for 7 min to achieve the homogenous between

the CF and LDPE matrix. The mixture was poured out into metal moulds and compressed, starting from $20 \text{ kg}\cdot\text{cm}^{-3}$ and then increased to $100 \text{ kg}\cdot\text{cm}^{-3}$ within 7 min. After 24 h, the samples were removed from moulds and left for a day to make more curing.

2.4. Characterisations

2.4.1. Mechanical tests

The tensile tests were done on a Universal machine, model Instron 1130 tester, according to standard ISO 527-1, using a load of 1000 N and the test speed is $2 \text{ mm}\cdot\text{min}^{-1}$.

2.4.2. 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 $35\times 9\times 1.5 \text{ mm}$. A heating rate was 10°C at a fixed frequency (1 Hz), and the range of temperature was between 30 to 150°C .

2.4.3. Thermogravimetric analysis)TGA(

LDPE and LDPE-CF composite samples were tested by utilising 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 $10^\circ\text{C}\cdot\text{min}^{-1}$. The activation energy for decomposition (E_a) was calculated utilising Horowitz-Metzger (HM) equation.

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

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

α = the decomposed fraction and is specified as $= (C_i - C) / (C_i - C_f)$.

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

$\theta = T - T_{\max}$

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

2.4.4. Differential scanning calorimetric analysis (DSC)

The thermal characterisation of LDPE and LDPE/CF composites were determined by using a TA Q-10 thermal analysis apparatus. The temperature range was used between of 30 to 220°C

at a heating scan rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ 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 $287 \text{ J}\cdot\text{g}^{-1}$. Subsequently, the samples were cooled to 40°C at the rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and cooling rates and the corresponding melting temperature (T_m), crystallisation temperature (T_c) and degree of crystallinity were recorded from the heating and cooling curves.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties

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

Table 1. Mechanical properties of LDPE and LDPE composites

The samples	Tensile strength (MPa)	Modulus of elasticity (MPa)	Elongation at Break (%)
Pure LDPE	25.8 ± 3.2	189.5 ± 22	9.5 ± 0.8
LDPE / 5 % CF	26.2 ± 1.5	220.4 ± 15	8.2 ± 0.5
LDPE / 10 % CF	29.5 ± 2.7	238.5 ± 25	6.5 ± 0.2
LDPE / 20 % CF	33.5 ± 2.5	260.5 ± 30	3.8 ± 0.7

3.2. Dynamic Mechanical Analysis of LDPE Composites

The storage modulus of LDPE and LDPE composite samples was investigated to improve steadily with the addition of CF 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 composites 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% CF into LDPE, respectively, compared to that of LDPE matrix (Figure 2). The loss factor ($\tan \delta$) of LDPE and LDPE composites are shown in Figure 2. There were significant changes in loss factor (the peak highest of $\tan \delta$) for 10 and 20 wt% CF into PP, compared to that of a lower loading level of CF and pure LDPE (Figure 2). The transition glass temperature (T_g) was determined from a maximum peak in $\tan \delta$ that increased with an increase of the CF loading level into LDPE. The value of T_g was about 120°C in the LDPE matrix, compared to that of 10wt % (121.5 °C), 10 wt% CF (130 °C), and 20 wt% (135.5 °C) of 5, 10, and 20 wt% CF into LDPE, respectively The presence of a higher content of CF may enhance the flexibility and reduces the molecular mobility of the LDPE polymer molecular chain.

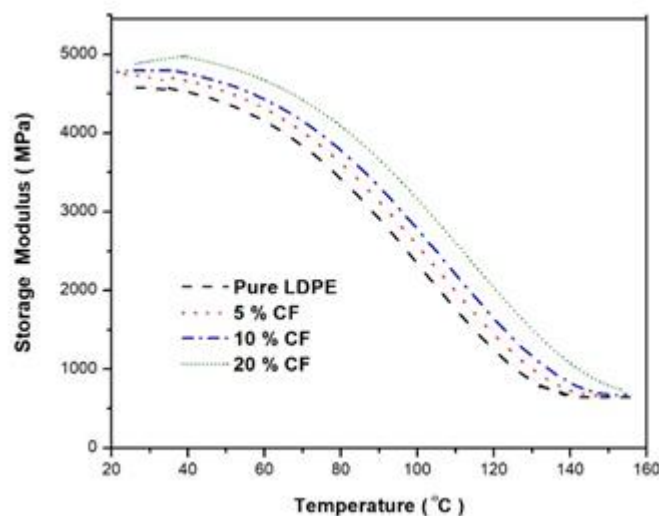


Figure 1. The storage modulus of LDPE and LDPE composites

3.3. Thermal Analysis of LDPE and LDPE/CF Composites

The results of thermal degradation for the LDPE matrix and LDPE/CF composite samples are shown in Table 2. T_i defines as the initial degradation temperature and is a relevant factor in determining the thermal stability. The maximum degradation temperature T_{max} and residue at 600°C % are shown in Table 2. The incorporation of 10 wt % CF into LDPE can prominently increase both T_i and T_{max} of the LDPE composites by 99.7 and 52.8 °C, respectively. The presence of the CF is to make more stability to the LDPE matrix and gives higher crosslinking between the CF fillers and the pure LDPE. Table 2 showed that T_i , T_{max} , and residual yield were

increased by increasing the content of CF. Table 2 indicated that T_i was about 455.8°C while T_i of 5, 10, and 20% CF 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%CF composite (525.4°C).

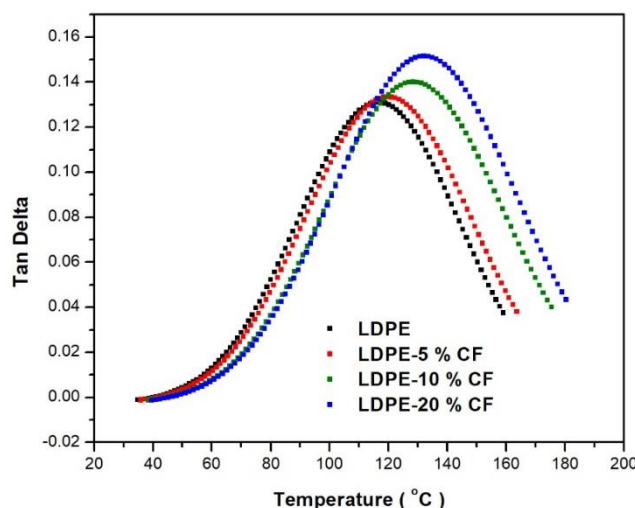


Figure 2. The loss factor ($\tan \delta$) of LDPE and LDPE composites

Table 1 showed that the residue percentage of 5, 10, and 20 % CF into LDPE increased by 15.7%, 18.2%, and 21.2 respectively, by comparing with that of pure LDPE (14.5%). Figure 3 exhibited the Arrhenius plots for the activation energy (E_a) for the decomposition of LDPE and LDPE composites. The effects of blend composition and compatibilisation on the E_a of LDPE and LDPE composites are given in Table 2. The value of E_a in 20% CF /LDPE composites was 141.6 $\text{KJ}\cdot\text{mol}^{-1}$ while E_a for 10 wt%, 5 wt%, and LDPE matrix was 123.8, 124.2, and 118.3 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. It was seen that the higher addition (10 wt% CF) into LDPE increased the E_a in the LDPE matrix.

Table 2. Thermal properties of LDPE and LDPE composites

System	$T_i \pm 0.1$ (°C)	$T_{max} \pm 0.1$ (°C)	E_a ($\text{KJ}\cdot\text{mol}^{-1}$)	Residue yield at (%)
Pure LDPE	455.8	472.6	118.3	14.5
5 wt% CF	477.5	474.5	124.2	15.7
10 wt%CF	510.4	499.3	123.8	18.2
20 wt%CF	555.5	525.4	141.6	21.4

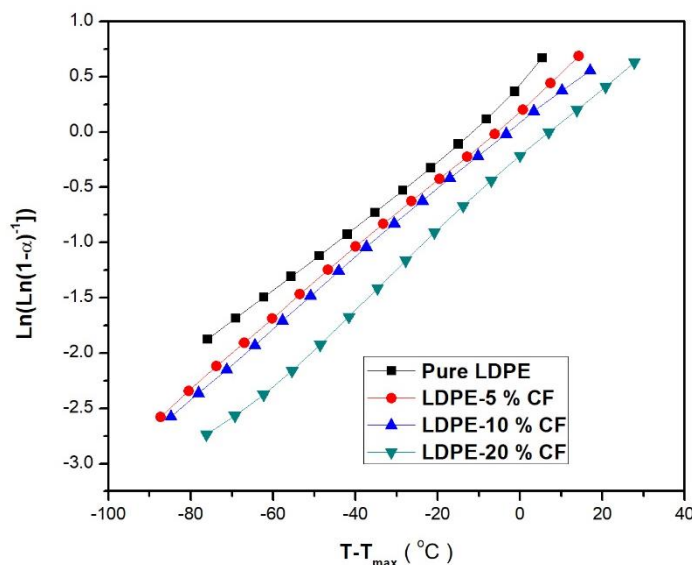


Figure 3. Arrhenius plots of calculating the activation energy for LDPE and LDPE composites

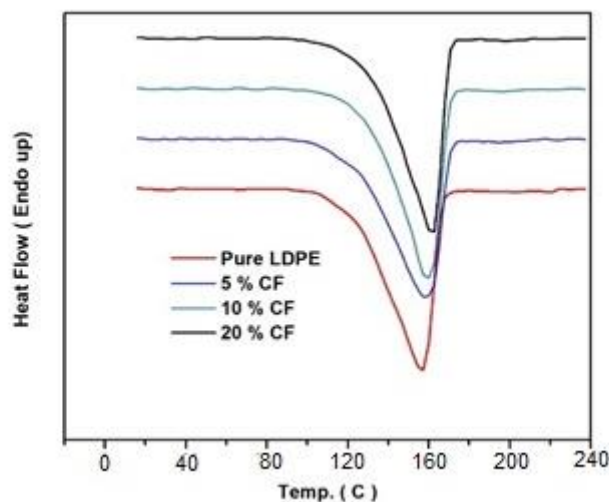


Figure 4. DSC thermogram curves of LDPE and LDPE composites

3.4. Crystallisation Behavior of LDPE composites

Thermal Properties of LDPE composites were analysed using DSC, and the thermogram curves were shown in Figure 4. The crystallinity degree of the LDPE composites was quantitatively measured by subtracting the filler mass contribution. From Table 3, the melting enthalpy (ΔH_m) increased with increase in the CF content into LDPE. The ΔH_m value of 20 wt% CF into LDPE increased (195.2 J/g), compared to the lower contents 5 wt.%, 10 wt.%, and pure LDPE (190.7 J/g, 191.5 J/g, and 189.8 J/g). In the case of CF into LDPE, T_m shifted to a higher temperature (161.7 °C), compared to that of 5 wt%, 10 wt% CF, and pure LDPE (158.4 °C, 159.2 °C, and 155.5 °C), respectively. The high melting points can probably be attributed to the increase of LDPE matrix crystals. The crystallisation points of LDPE and LDPE composites showed no significant changes in LDPE and LDPE composites (Table 2). LDPE composites exhibited

higher endothermic crystallisation points, compared with the LDPE matrix. 20 wt.% filled LDPE showed a higher crystallinity (27.4%) while LDPE crystallinity was 24.5%.

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

The samples	T_m (°C)	ΔH_m (J/g)	X_c (%)
Pure LDPE	155.5	189.8	24.5
LDPE / 5 % CF	158.4	190.7	24.8
LDPE / 10 % CF	159.2	191.5	25.2
LDPE / 20 % CF	161.7	195.2	27.4

4. CONCLUSIONS

The effect of CF content in LDPE polymer has been investigated. It has been found that The higher values of CF 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 LDPE matrix. 20% CF into LDPE was higher storage of modulus than that of pure LDPE. The LDPE composites with a higher loading (20 wt%) of CF 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 increase as the CF content increase. Overall results confirmed that CF contents are more effective and reinforce the LDPE matrix.

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