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Miscibility Improvement of LDPE/PVA Blends with Maleic Acid Additions

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Abstract: Mixing two types of polymers usually results in an immiscible blend, especially when using polymers with different polarities; therefore, a compatibilization process using suitable compatibilizers to improve miscibility is required. In this work, a low-density polyethylene (LDPE)/poly vinyl alcohol (PVA) blend was improved by adding maleic acid as compatibilizer. A twin-screw extruder was used to prepare blend samples, and the LDPE and PVA were mixed with different weight proportions. To identify the compatibility and miscibility of these blends, several tests were conducted, including Fourier transform infrared (FTIR), mechanical property observation, density testing, scanning electron microscopy (SEM), morphology examination, and differential scanning calorimetry (DSC). The results showed that mechanical properties and density were enhanced by the addition of maleic acid to the blends. SEM and Digital microscope results also showed good interaction between blend components when maleic acid was added to the blends.

Keywords: Miscibility, LDPE/PVA blend, maleic acid.

1. Introduction

A large proportion of the total tonnage of plastics currently used mainly consumer products or non-load bearing application is made up of commodity plastics such as polyethylene (PE), polyvinyl alcohol (PVC), polypropylene (PP), and polystyrene (PS). However, high performance plastics with good combinations of light weight, stiffness, and toughness and wide ranges of temperature applications have been developed; these are known as engineering plastics. The use of engineering plastics has been growing in the areas previously dominated by the use of metal and ceramics, but frequently, the requirements of new applications are not naturally met by an individual engineering plastic.

Thus, the development of new polymers in order to improve marketable products has continued, and polymer blends that are more economical, suitable, and widely accepted have been developed by many plastics manufacturers. Polymer blends can be customised to meet the requirements of particular applications, which is of growing importance, and such blends can be easily and readily adjusted to meet performance and cost objectives in new or changing markets, as polymer blend properties are functions of their composition [1].

Usually, when mixing two or more polymers, an immiscible polymer blend results; these are characterised by the large domain size of the dispersed phase. These blends are thus distinguished by their rough, discontinuous morphologies and poor adhesion between phases [2].

Generally, weak interfacial adhesion and thus poor mechanical performance, results from incompatibility in most polymer blends; therefore, the manipulation of the phase structure by controlling the interfacial interactions between the constituent parts is the biggest challenge in the field of multiphase polymer blending. The use of a third component, a compatibilizer, to create a finer and more stable morphology with good adhesion between the phases and thus improve the mechanical properties of the final product is one of traditional methods for improving adhesion between phases (interfacial tension reduction) [3].



Compatibility depends on the chemical and physical structures of the blend constituent parts that emerge from the thermodynamic interactions between blend components [4]. Therefore, in order to create useful polymer blends, dispersion and interfacial adhesion between the phases of multiphase polymer systems must be controlled [5].

Low-density polyethylene (LDPE) is a lightweight long-branch polymer with very little moisture absorption, good corrosion and chemical resistance, and high impact resistant. It is used mainly for casting and blown films [6].

Poly(vinyl alcohol) (PVA) is a non-poisonous artificial polymer that dissolves in water, and in some cases in ethanol, but which is insoluble in other organic solvents. PVA is a semi-crystalline polymer with a melting temperature between 180 and 230 °C depending on the level of hydrogen bonding in the crystals. The polymerization and hydrolysis degrees determine the physical characteristics and functional uses of PVA [7][8][9].

In the present work, 5% wt. of maleic acid was added to LDPE and PVA using a twin-screw extruder at 35 rpm and 150 °C. The mechanical and thermal properties of these mixes were investigated. SEM and digital microscopy of the blends were conducted an FTIR used to analyse the chemical structure.

2. Experimental Part

2.1. Materials

The materials used in this research were

Low-density polyethylene, obtained from Amir Kabir Petrochemical Company, Iran, as pellets; relevant properties of LDPE are given in Table 1,

Polyvinyl alcohol (PVA), obtained from Yonghui Chemical Holdings Limited Company, China; relevant PVA properties are shown in Table 2, and

Maleic Acid (C₄H₄O₄), supplied by Shijiazhuang Lemandou Chemical, with properties as shown in Table 3.

Table 1. Properties of LDPE.

Properties	Unit	Value
Density	g/cm ³	0.923
MFR(190 °C/2.16 Kg)	g/10 min	0.25
Hardness	Shore D	41-46
Tensile strength	MPa	4-16
Melting point	°C	110

Table 2. Properties of PVA

Properties	Unit	Value
Density	g/cm ³	1.19-1.31
Glass transition temperature	°C	85
Molecular weight of repeat unit	g/mol	44.00

Table 3. Properties of Maleic Acid

Properties	Unit	Value
Density	g/cm ³	1.59
Melting point	°C	135
Boiling point	°C	202
Molar mass	g/mol	116.07

Table 4. Polymeric blend percentages.

(LDPE/PVA)% wt.	Maleic acid wt.
(100/0)	-
(90/10)	5
(80/20)	5
(70/30)	5
(60/40)	5
(50/50)	5
(40/60)	5

2.2. Blend preparation

LDPE pellets, PVA, and Maleic acid were mixed together at room temperature in the proportions seen in Table 4. A twin-screw extruder model SLJ-30A was used to form blend sheets, with the screw speed set to 35 rpm. The temperatures used for zones 1 and 2 were 135 °C and 150 °C, respectively. Finally, the molten material passed through two rotating cylinders to form thin flat sheets of 2 mm thickness, which were then cut into the required sample shapes according to ASTM-D.

3. Characterisation Methods

Tensile tests were performed using a universal testing machine (model WDW 5 E) according to ASTM D638-IV at a cross-head speed of 10 mm/min. A Shore D Hardness test (TH 210 FJ) was used to measure the hardness of blend samples according to ASTM D 2240. An average of three readings in different locations and at different points for each sample was taken. A high precision density tester type GP-120 S, which contained distilled water at room temperature as per ASTM D-792, was used to measure the density of blend samples at room temperature; this test depends on Archimedes' principle. A Fourier transform spectrophotometer (FTIR) was used to identify changes in the chemical structure for polymeric blends with different compositions through band values, using an FTIR analysis instrument Type IR Affinity-1 made in Kyoto, Japan. The device was first calibrated using KBr, and then the sample powder and KBr were mixed (mix ratio 99% KBr); the mix was then pressed into tablet-shaped semi-transparent forms for radiation penetration. Scanning electron microscopy (SEM) used to examine the miscibility of the polymer blends. The samples were cut into small pieces (1 x 1 cm) to fit into the device. To achieve good electric conductivity, all samples were first sputtered with gold on the surface along the edge. A digital microscope model AM4815T Dino-Lite Edge was used to examine the morphology of the blended samples at magnification rates of 20x to 220x. Differential scanning calorimetry (DSC) measurements were also carried out by using a DSC i-series (CW-05G) instrument under a nitrogen atmosphere at a heating rate of 10 °C/min. The blend was heated from 25 to 250 °C with a blend weight of 10± 0.5 mg.

4. Results and Discussion

4.1. Mechanical properties

Figure 1 shows the effect of PVA content on the tensile strength of LDPE/PVA blends with and without the addition of maleic acid. The tensile strength of blended LDPE/PVA decreases as the PVA content increases in this circumstance. This reduction in tensile strength is due to the poor interfacial adhesion between LDPE and PVA, which have different polarities that cause poor stress transfer between matrix LDPE and dispersed phase PVA. Due to the strong intramolecular hydrogen bonds between hydroxyl groups, PVA forms agglomerates that result in the poor dispersion in LDPE at higher PVA contents. That means that the interaction between PVA-PVA is more favourable than that between PVA-PE [10].

Where maleic acid was added to the blends of LDPE/PVA, the tensile strength was increased significantly. This was due to maleic acid's abilities to improve PVA dispersion and enhance the interactions between LDPE and PVA, which are related to the increased ester cross linkages as the maleic acid becomes grafted onto the LDPE and reacts with the hydroxyl groups in the PVA. The modulus of elasticity for LDPE/PVA blends are increased as the PVA amount increases due to the stiffening effect of PVA, which is stiffer than LDPE. The hydrogen bonds in PVA create a higher modulus than seen in the semi-crystalline LDPE, which have no hydrogen bonds. For this reason, in a non-enhanced mix, the elasticity drops and the stiffness is increased, as PVA tends to agglomerate in the LDPE matrix to form three-dimensional reticulate structures. With the addition of maleic acid, the modulus shows the same result for many mixes of LDPE/PVA, but is increased at 40% PVA; this increment is due to the additional cross-linking and better interaction between LDPE and PVA, as shown in Figure 2.

The elongation at break of the blend drops with an increase in PVA percentage, as shown in Figure 3. As the PVA content is increased, the elongation become more drastic due to poor interactions between the LDPE and PVA, which lead to more facile crack propagation. The presence of maleic acid allows the elongation at break to be higher than that of plain LDPE/PVA at PVA contents between 10 and 30%. This is due to the ability of maleic acid to improve PVA dispersion and enhance interaction between LDPE and PVA, as shown in Figure 3; this result is in agreement with [11].

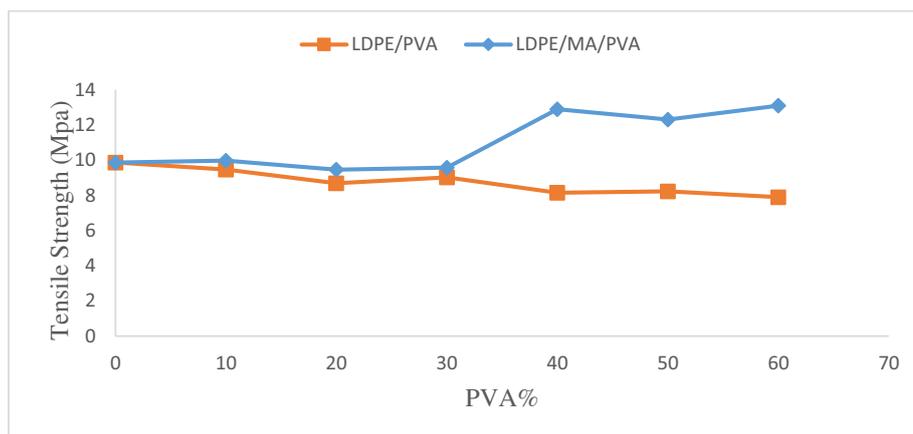


Figure 1. Effect of PVA content on the tensile strength of LDPE/PVA with and without maleic acid.

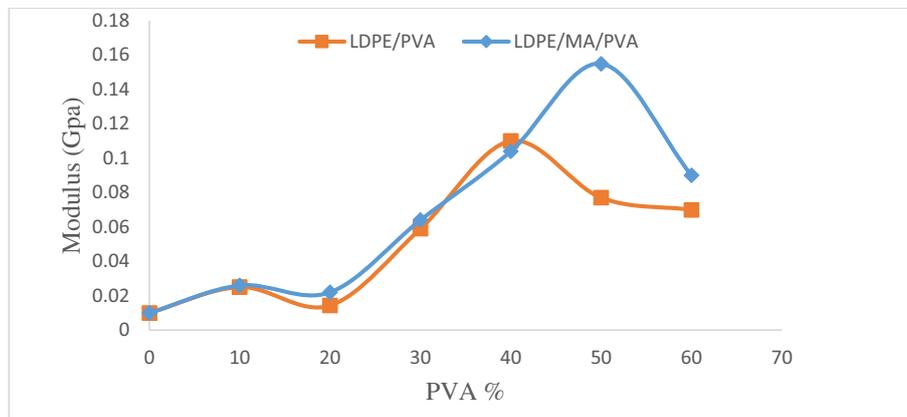


Figure 2. Variation of Young's modulus with PVA content in LDPE/PVA blends with and without maleic acid.

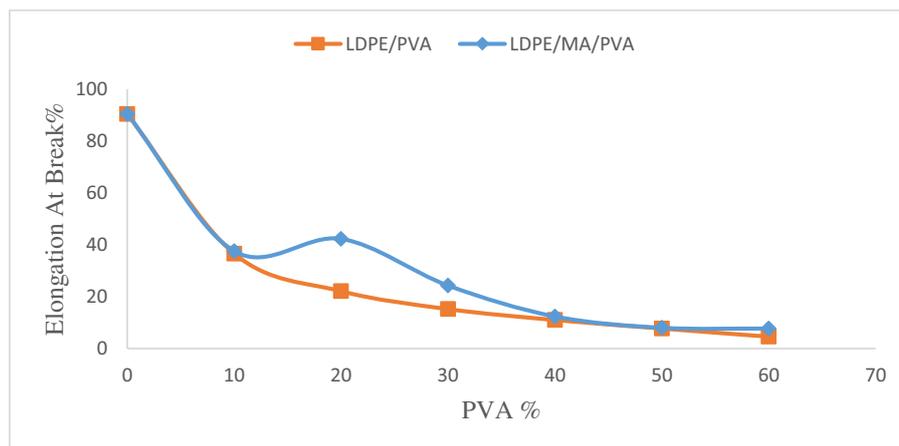


Figure 3. Variation of elongation at break with PVA content in LDPE/PVA blends with and without maleic acid.

4.2. Hardness test

Figure 4 shows the hardness of LDPE/PVA blends with and without the addition of maleic acid. For blends of LDPE/PVA it can be shown that the hardness decreases with the increase in PVA content due to the minimal hardness of PVA [12], as well as the agglomerating effects that weaken the secondary bonds between LDPE chains. As maleic acid is added to the blend, the hardness is increased due to the link formation between LDPE and PVA, which improves the interfacial adhesion and dispersion of PVA agglomerates into the LDPE matrix.

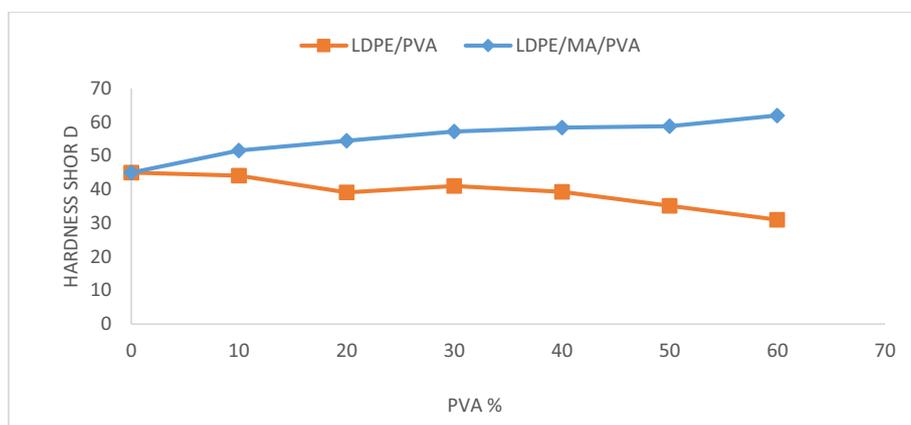


Figure 4. Hardness of LDPE/PVA with and without maleic acid.

4.3. Density test

Figure 5 shows the density of LDPE/PVA blends with and without maleic acid. The density of LDPE/PVA blends is increased with increasing PVA content due to the higher density of PVA, which fills the voids between LDPE chains. For blends with maleic acid, the density is further increased with PVA content due to link formation between the LDPE and PVA, which reduces the volume of cavities and restricts the chains' motion.

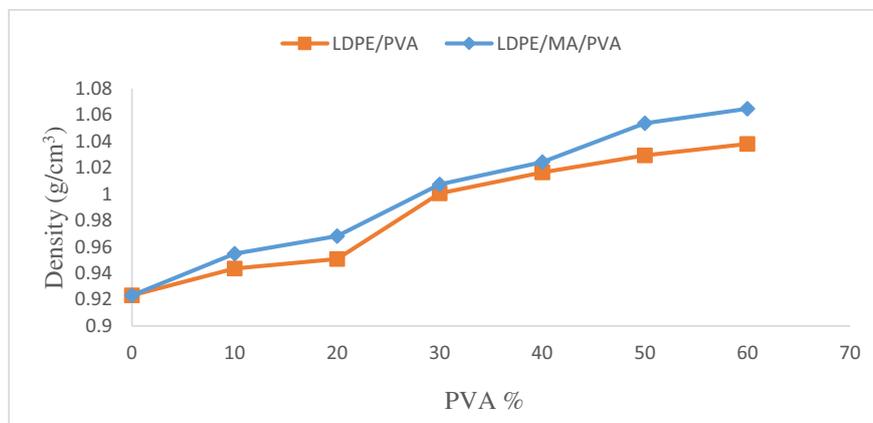


Figure 5. Density of LDPE/PVA blends with and without maleic acid.

4.4. FTIR analysis results

The changes in intensity, seen as shifts in peaks, recorded by Fourier transform spectroscopy (FTIR) are shown in Table 5; these were derived from Figure 6. FTIR for LDPE shows many bands, such as the bands at $2,939\text{ cm}^{-1}$ and $2,850\text{ cm}^{-1}$ for CH_2 stretching, the band at $1,463\text{ cm}^{-1}$ for CH_2 bending, and the band at 721 cm^{-1} for CH_2 rocking. For a blend of LDPE/PVA, the band values of LDPE are shifted, with the bands at $2,939\text{ cm}^{-1}$ and $2,850\text{ cm}^{-1}$ shifting to $29,20\text{ cm}^{-1}$ and $2,852\text{ cm}^{-1}$ respectively, with an additional band at $3,327\text{ cm}^{-1}$ for OH-stretching vibrations. The other bands remain unchanged.

As maleic acid is added to this mix, the same band values as in LDPE/PVA appear, and bands with ester bonds also appear at $1,033\text{ cm}^{-1}$, $1,097\text{ cm}^{-1}$ and $1,257\text{ cm}^{-1}$, along with a (C=O) carbonyl bond from the maleic acid's links with LDPE at $1,728\text{ cm}^{-1}$. The band at 842 cm^{-1} is for tertiary carbon. The FTIR analysis thus shows that that chemical reactions occur due to maleic acid addition.

Table 5. the absorption bands of IR spectrum characteristic of LDPE and blends.

Type of bond	LDPE standard[13]	LDPE exp.	LDPE/PVA	Maleic acid
CH₂ stretching	2919	2939	2920	2918
	2851	2850	2852	2850
CH₂ bending	1473	1463	1463	1465
CH₂ rocking	720-731	721	721	719

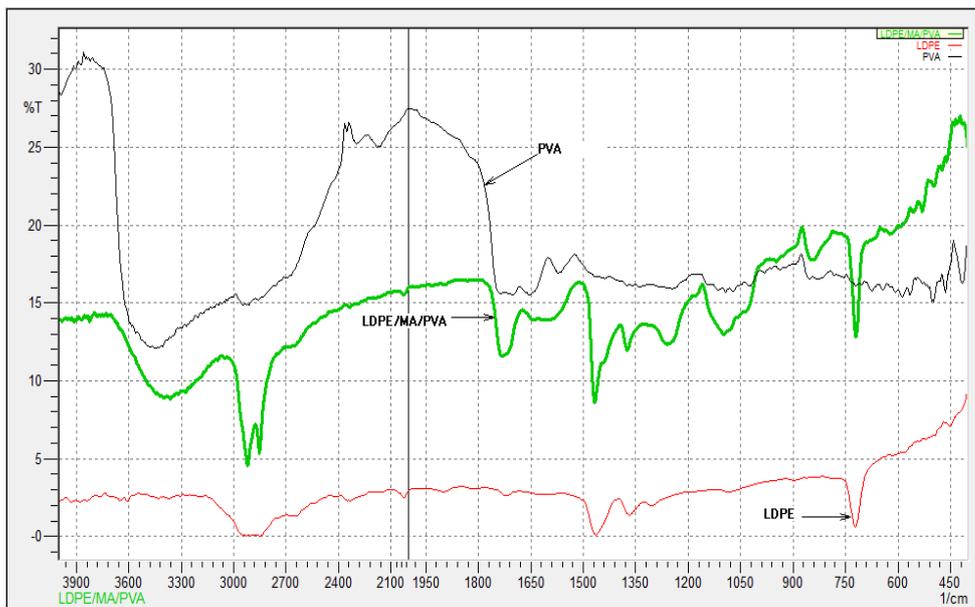


Figure 6. FTIR spectrum for LDPE, PVA, and blended polymers with maleic acid.

4.5. Morphology Test

The surface morphology of LDPE and blend samples were examined using digital microscopy, which can be used as an indicative test for polymer blend compatibility. It was observed that LDPE had a smooth and uniform phase without any discontinuity on the surface, as seen in Fig. 7 (a). As PVA was added, the surface morphology of the blend became less uniform, exhibiting voids due to the agglomeration of PVA particles and

phase separation between the LDPE and PVA, which had adverse effects on the mechanical properties, as seen in Fig. 7 (b, c).

The addition of maleic acid offered an improvement in surface morphology; images from the digital microscope show a uniform dispersion of PVA agglomerates into the LDPE matrix in these cases. This is attributed to the coupling agent effect, which improves the compatibility and miscibility of LDPE and PVA, as shown in Fig. 7 (d, e).

4.6. Scanning Electron Microscope (SEM) test

Scanning electron micrographs of the melts mixed by twin-screw extruder of pure polymer and blends of LDPE and PVA are shown in Figure 8. The PVA agglomeration and incompatibility of the blend can be identified from these micrographs. The LDPE/PVA blend shows an irregular and rough surface that indicates the presence of various holes on the surface, which suggest that miscibility and compatibility are poor, as shown in Fig. 8 (c, d). SEM images of the blend with maleic acid show that the LDPE covers the PVA agglomerates and a more interconnected rough surface is produced in this case.

This surface is believed to be a cross-linked material resulting from the reaction of maleic acid with both LDPE and PVA. This creates good interaction and adhesion between the two polymers due to maleic acid increasing the adhesion through wetting and reducing the surface tension between LDPE and PVA; this result is in agreement with [14] and [11], as shown in figure 8 (e, f).

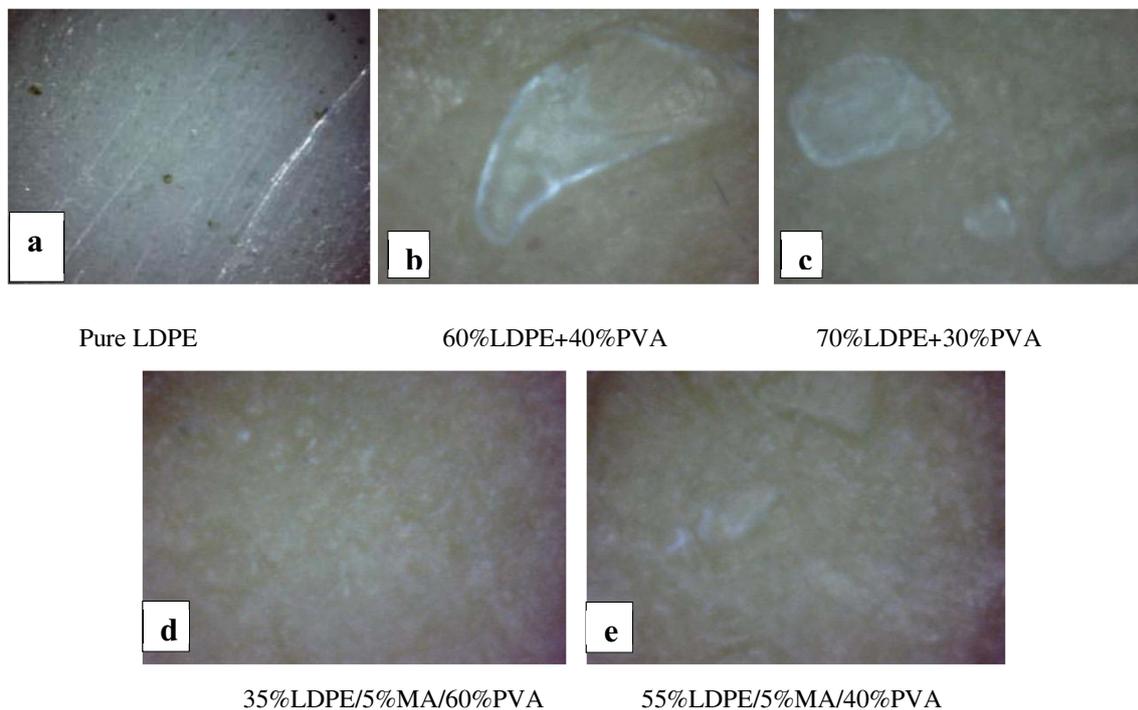


Figure 7. Digital microscope images of LDPE/PVA blends with and without maleic acid.

4.7. DSC test results

DSC was used to investigate the miscibility between LDPE and PVA with maleic acid additions. The peak melting temperature was taken as indicative of the compatibility of the blends. From figure 9 (a, b), the DSC peak melting temperature of LDPE is seen to be 117.66 °C, while for PVA it is 190.19 °C. For LDPE/PVA blends, the DSC thermo-gram peaks are slightly shifted to a lower value due to the phase separation between PVA agglomerates and the LDPE matrix, as shown in figure 9 (c) [15]. The addition of maleic acid causes a decrease in the melting temperature of LDPE by 1 °C and PVA by 12 °C; this behaviour is due to esterification and the grafts formed by these additives, which prevent crystal packing and chain arrangements, as shown in Figure 9 (d). The melting enthalpy and degree of crystallinity decreased from 96.93 J/g to 34.18 J/g and from 69.24 to 24.41%, respectively, due to maleic acid addition. These behaviours are believed to be due to the formation of links between these additives and LDPE and PVA, which hinder the order arrangement of chains, in agreement with [16].

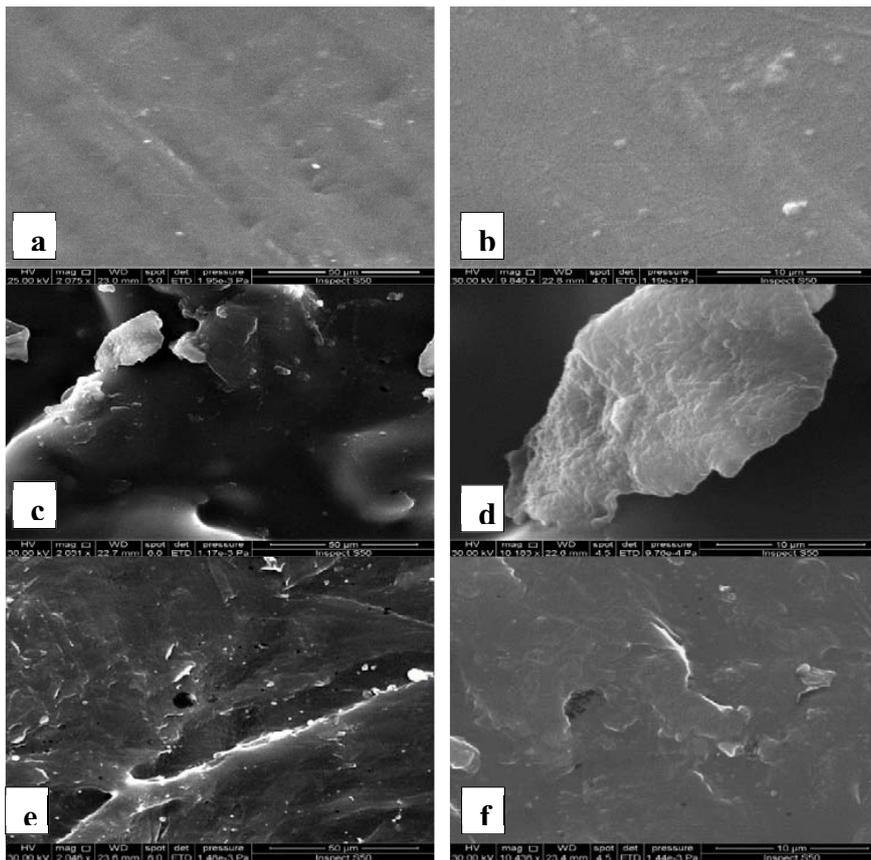


Figure 8. SEM images for: 1) LDPE (a, b). 2) 70%LDPE/30% PVA(c, d). 3) 65%LDPE/5% MA/30%PVA (e, f).

Conclusions

The following conclusions can be drawn from this work:

- The compatibility of LDPE/PVA blends is enhanced by adding maleic acid, as shown by the depression of the melting temperatures of LDPE and PVA.
- Tensile properties such as tensile strength, elongation-at-break, and Young's modulus in the LDPE/PVA blends are improved by the incorporation of maleic acid.
- The SEM micrographs of the blends show that maleic acid improved the adhesion between the PVA dispersed phase and the LDPE matrix.

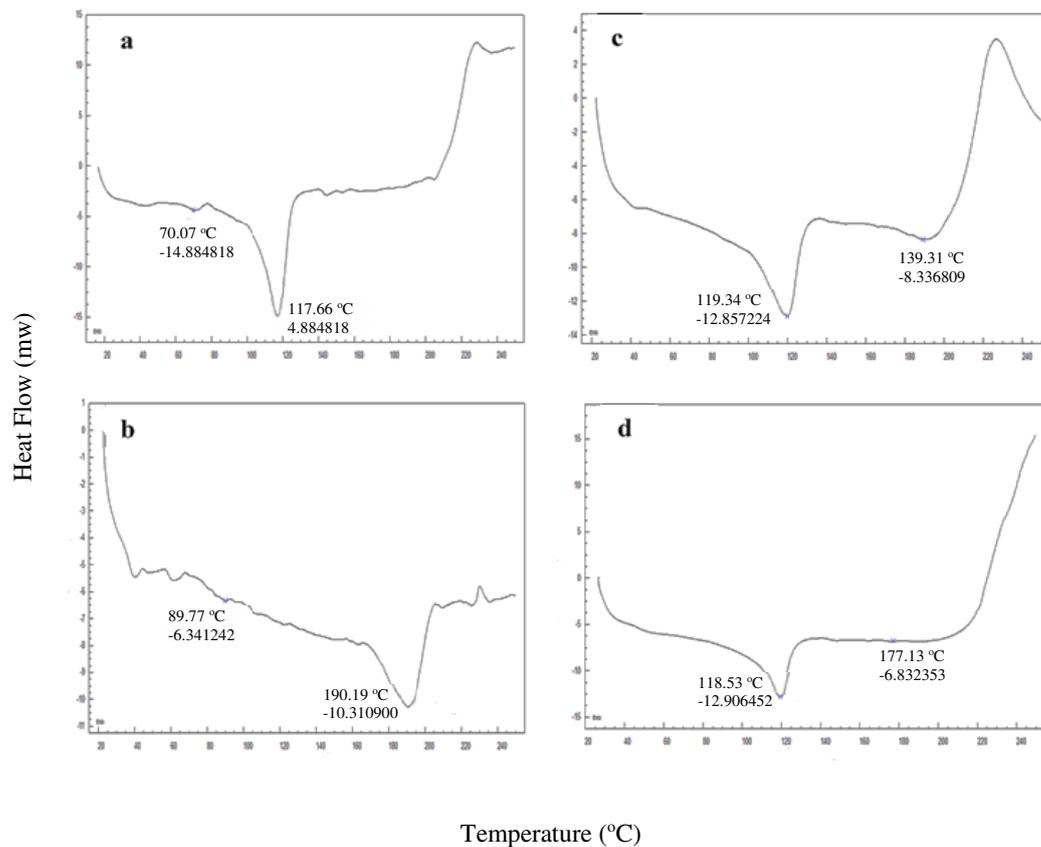


Figure 9. DSC curves for a) LDPE, b) PVA, c) LDPE/PVA, d) LDPE/MA/PVA.

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