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Miscibility improvement of LDPE/PVA blends by using silane-coupling agent

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Abstract

Mixing two polymers usually results in an immiscible system, characterized by a coarse, easy to alter morphology, and poor adhesion between the phases. These blends have large size domains of dispersed phase and poor adhesion between them. Therefore, miscibility of polymer blend must be improved by using suitable additives such as compatibilizer. In this study 5% of silane 3-(trimethoxysilyl)propyl methacrylate is used as compatibilizer to improve the miscibility and compatibility of LDPE/PVA blends. The samples were prepared by using a twin screw extruder. LDPE and PVA have been mixed with different weight proportion. Several tests were carried out to identify the compatibility and miscibility of the blends such as tensile properties, hardness, density, Fourier transforms infrared FTIR, digital microscope, scanning electron microscopy SEM and differential scanning calorimetry DSC. Result show that tensile strength, young modulus, elongation at break, density and hardness is increased with silane addition to the blends. SEM and digital microscope shows an improvement in the miscibility due to the better interaction between the two polymers as silane is added.

Keyword: LDPE, PVA, Silane, Miscibility, Compatibilizer, Coupling agent, Blend.

الخلاصة

خلط اثنين من البوليمرات عادة ما ينتج خليط بوليمري غير ممتزج، يتميز بالخشونة، سهولة تغير الشكل وضعف الترابط بين الطورين. إضافة الى كبر حجم الطور المشتت كبير وضعيف الارتباط بالطور الاخر. لذا فان الامتزاجية للبوليمرات يجب ان يتم تحسينها باستخدام مضافات مناسبة مثل محسن التوافقية. في هذه الدراسة تم استخدام السيلان كمحسن للتوافقية والامتزاجية بين البولي اثيلين واطئ الكثافة و بولي فنيل الكحول. تم تحضير العينات باستخدام الباثق ثنائي اللولب حيث تم خلط نسب مختلفة من البولي اثيلين و بولي فنيل الكحول وبإضافة ٥% من مادة السيلان. عدة اختبارات أجريت لتحديد تأثير محسن التوافق على خصائص هذه الخلائط وامتزاجيتها مثل اختبار الشد والصلادة والكثافة والاشعة تحت الحمراء والتحليل الحراري التفاضلي و الفحص بالمجهر الالكتروني الماسح والمجهر الرقمي و أظهرت النتائج زيادة متانة الشد ومعامل يونك، الاستطالة عند القطع والصلادة والكثافة بإضافة السيلان اما نتائج المجهر الالكتروني الماسح والمجهر الرقمي فقد أظهرت حدوث تحسن في امتزاجية البوليمرين.

الكلمات المفتاحية:– بولي اثيلين واطئ الكثافة ، بولي فنيل الكحول ، السيلان، الامتزاجية ، محسن التوافقية ، عامل الربط، خليط .

Introduction

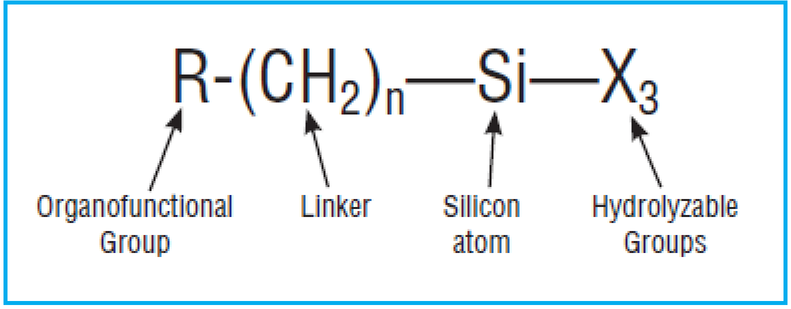
In recent years, there is an increasing interest to produce polymeric materials with improved properties by blending two or more polymers(El Sayed, Diab, and El-Mallawany 2013).

Low density polyethylene (LDPE) has light-weight, good impact resistance, extremely high flexibility, no moisture absorption and has high chemical and corrosion-resistivity. It is used mainly for the blown and cast film, extrusion products as well as coatings, rotational and injection molding (Chrissafis and Bikiaris ,2011).

Poly (vinyl alcohol) PVA is a non-toxic, synthetic polymer, soluble in water, somewhat soluble in ethanol, however insoluble in other organic solvents. PVA has a moderately simple chemical structure with a pendant hydroxyl group. (Saxena, 2004;Hassan and Peppas, 2000;Silva *et.al.*, 2008)

Polymer blend represents a very important field in processing of new materials, which have better properties in comparison with the constituent polymers. They are significant also from ecological and economical viewpoint. High molecular weight polymers show low entropy of mixing (Cimmino,1992), so that, most polymer blends show immiscible systems, whose properties are not only a function of the blend composition but also depend crucially on the degree of dispersion phase particle size, and phase interaction between the components of the blend. Also by controlling the morphology of polymer blend leads to practicability of controlling the polymer blend properties (SHAZIA , 2015). Many polymer pairs are not only immiscible but also incompatible. It means that they show high interfacial tension that leads to rough phase structure, poor adhesion at the interface, and therefore poor mechanical properties. Compatibility arises from thermodynamic interaction between the blend constituents, which is a function of their physical and chemical structure (Ibrahim and Kadum , 2010). The main reasons lead to creating incompatible systems that can be summarized as: absence of any specific interaction between their blend constituents, dissimilarity in their structure, and broad differences in their viscosities. Therefore, the control of the dispersion and interfacial adhesion between phases of a multiphase polymer system is critical in order to create useful polymer mixtures (Eastwood *et.al.*, 2005).

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Encounters between dissimilar materials often involve at least one member that's siliceous or has surface chemistry with siliceous properties; silicates, aluminates, borates, etc., are the principal components of the earth's crust. Interfaces involving such materials have become a dynamic area of chemistry in which surfaces have been modified in order to generate desired heterogeneous environments or to incorporate the bulk properties of different phases into a uniform composite structure.



The general formula for a silane coupling agent typically shows the two classes of functionality. X is a hydrolysable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. The R group is a nonhydrolyzable organic radical that may posses a functionality that imparts desired characteristics. The final result of reacting an organosilane with a substrate ranges from altering the wetting or adhesion characteristics of the substrate, utilizing the substrate to catalyze chemical transformations at the heterogeneous interface, ordering the interfacial region, and modifying its partition characteristics. Significantly, it includes the ability to effect a covalent bond between organic and inorganic materials. Most of the widely used organosilanes have one organic substituent and three hydrolyzable substituents. In the vast majority of surface treatment applications, the alkoxy groups of the trialkoxysilanes are hydrolyzed to form silanol-containing species. Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally, during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. Although described sequentially, these reactions can occur simultaneously after the initial hydrolysis step. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either in condensed or free form. The R group remains available for covalent reaction or physical interaction with other phases.(Annalese, 2014).

Experimental Part

Materials

LDPE was obtained from Amir Kabir Petrochemical Company as pellets, Iran, with properties as shown in table1, PVA was obtained from Yonghui chemical Holdings Limited Company, China PVA with properties as shown in table 2,3-(trimethoxysilyl) propyl methacrylate (TMS) was obtained from Shijiazhuang Lemandou Chemical Co., Ltd. China, with density of 1.045 g/ml and molecular weight of 248.35.

Table 1: Properties of LDPE

Properties	Unit	Value
Density	g/cm^3	0.923
MFR(190^{o}C/2.16Kg)	g/10min	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

Mixing procedure

According to table 3 of materials, LDPE, PVA and silane were mixed together in dry condition at room temperature. Forming process for the mixed materials was carried out using a twin-screw extruder model (SLJ-30A) at a rotating speed of 35 rpm. The temperatures used for zones 1 and 2 were 135 and 150˚C respectively. At the end of the extrusion, the melt passes between two cylinders to form a sheet. The blend sheets of 2 mm thick are then cut according to ASTM-D.

Table 3: Polymeric blends components

PVA/LDPE%	Silane %
0/100	-
10/90	5
20/80	5
30/70	5
40/60	5
50/50	5
60/40	5

TESTS

Tensile test was performed by using the electronic universal testing machine (model WDW 5 E) according to (ASTM D638-IV). This test conducted at a cross head speed of 10 mm/min. Shor D hardness test carried out using (TH 210 FJ) device according to ASTM D 2240. An average of three readings have to be taken in different locations and at different points for each sample .

Density test was performed using high precision density tester type GP-120 S, based on ASTM D-792. The specimen is weighed in air and immersed in distilled water by applying Archimedes law.

Fourier transforms spectrophotometer (FTIR) was carried out using (IR Affinity-1) which is made in (Kyoto Japan) using the KBr powder

Differential scanning calorimetry (DSC) measurement was carried out by using DSC i-series (CW-05G) instrument with nitrogen atmosphere. The sample was heated from (25 – 250) °C with sample weight of 10± 0.5 mg.

Scanning electron microscope (SEM) was carried out using INSPECT (S50). The sample was cut into small pieces (1x1 cm) and sputtered with gold

Digital microscope the used Digital microscope (model AM4815T Dino-Lite Edge) which is made in (Kyoto Japan), with a magnification rate of (20x-220x).

Results and Discussion

Tensile Properties

Figure 1 shows the effect of PVA amount on the tensile strength of PVA/LDPE blends with and without silane. The tensile strength of blend PVA/LDPE decreases as PVA content increases. This reduction in tensile strength is due to the poor interfacial adhesion between LDPE and PVA with different polarities that causes poor stress transfer between matrix LDPE and dispersed phase PVA. Due to the strong intramolecular hydrogen bonds between hydroxyl groups, PVA formed agglomerates that results in the poor dispersion in LDPE at high PVA content. That is mean the interaction between PVA-PVA molecules is more favorable than PVA-PE(Vidya, 2012). As silane is added to PVA/LDPE blends the tensile strength is raised when compared with PVA/LDPE without addition. This increment is due to the ability of silane to form links and better interaction between PVA-PVA and PVA-LDPE, which reduces the cavities and restrict the chain motion. The modulus of elasticity for blend with silane increased with PVA increasing due to the cross-linking and better interaction between LDPE and PVA as shown in figure 2. The presence of silane slightly improve the elongation at break at 30% of PVA content while the other remain the same for PVA/LDPE only. This is due to the ability of silane to improve PVA dispersion and enhance the interaction between LDPE and PVA as shown in figure 3, this agreement with(Razif, 2012).

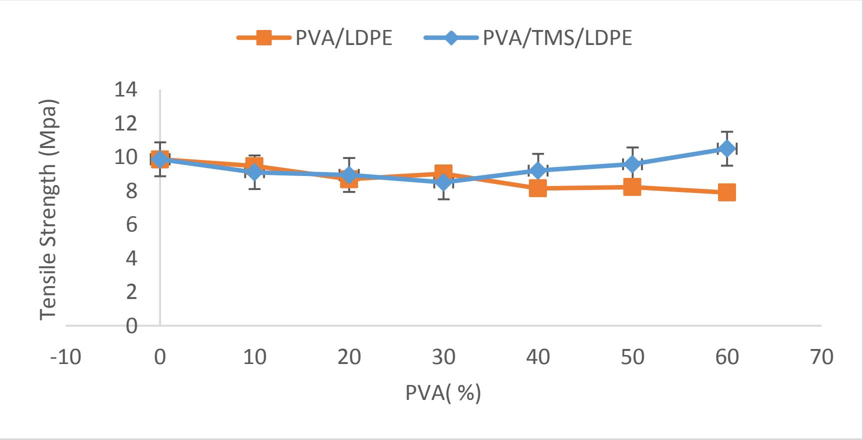


Fig 1: Effect of PVA amount on the tensile strength of PVA/LDPE with and without silane.

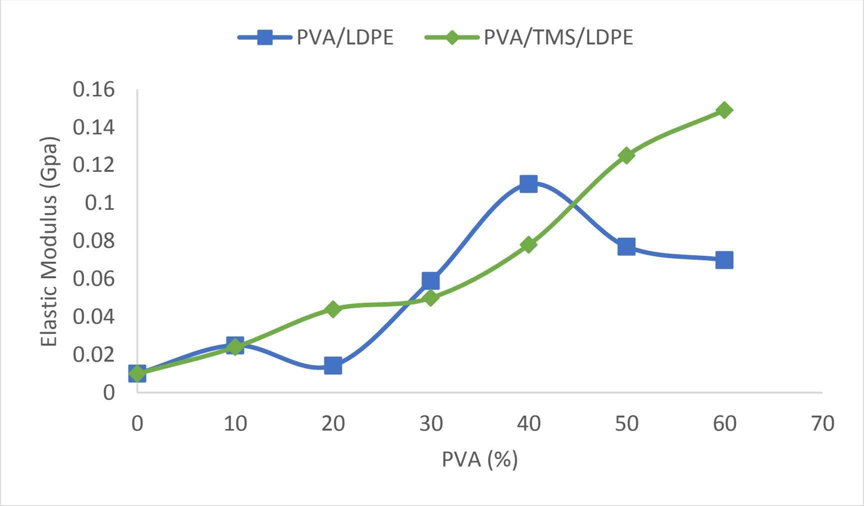


Fig 2: Variation of Young modulus with PVA amount in PVA/LDPE blend with and without silane.

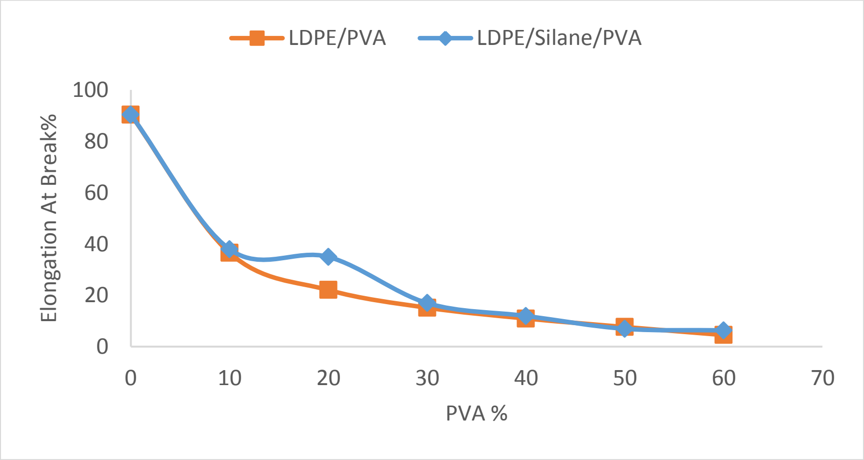


Fig 3: Variation of elongation at break with PVA amount in LDPE/PVA blend with and without silane.

Hardness Test

It is well known that the hardness depends on the resistance to penetration at the outer surface and there are different ways to represent the hardness guide. Figure 4 shows the hardness (shore D) of PVA/LDPE blend with and without silane addition. For the neat blend its shown that the hardness decreased as PVA amount increased due to the minimum hardness of PVA (Mishra *et.al.*, 2006), as well as to the agglomerating effects, which weaken the secondary bonds between LDPE chains. As silane is added to the blend, the hardness increased due to the links formation between LDPE and PVA, which improve the interfacial adhesion and dispersion of PVA agglomerates into LDPE matrix.

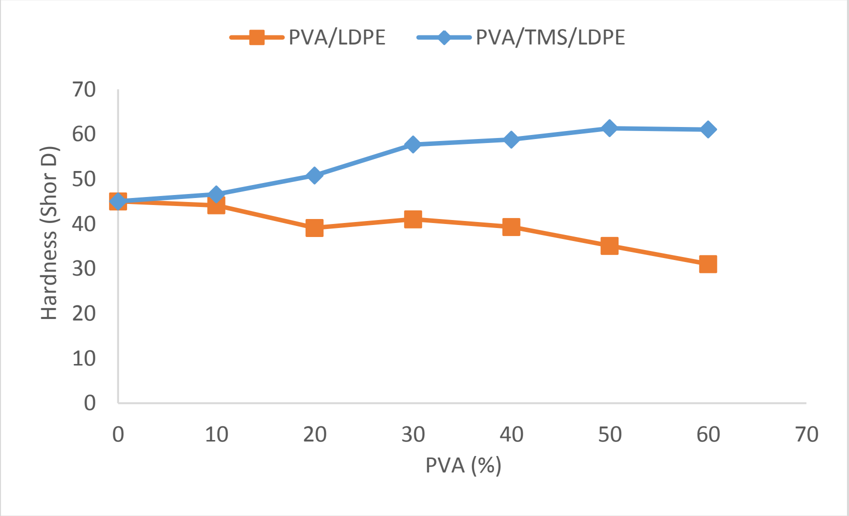


Fig.4: Hardness of PVA/LDPE with and without silane.

Density Test

Figure 5 shows the density of PVA/LDPE blends with and without silane. From table 1 and table 2 the densities of LDPE, PVA and silane are 0.923, 1.19 and 1.045 respectively. The density of PVA/LDPE blend is increased with increasing PVA content due to the higher density of PVA, which fill the voids between LDPE chains. For blends with silane, the density increases with PVA amount this is due to the links formation between LDPE and PVA, which reduces the voids and cavities so restrict the chain motion.

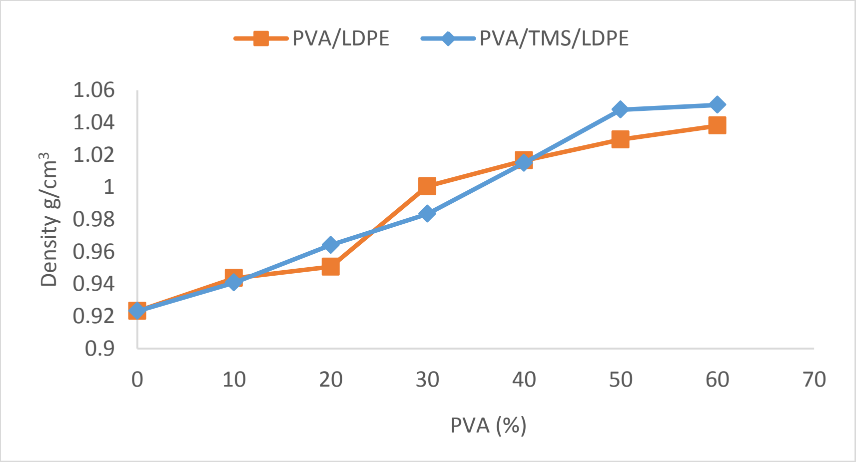


Fig.5: density of PVA/LDPE blend with and without silane.

FTIR analysis results

FTIR was used to identify the change in chemical structure for polymeric blend with different composition through band values. The change in intensity or shifting of peaks recorded by FTIR are shown in table 4, which were derived from figure 6. FTIR spectrum for LDPE shows many bands such as the bands at 2939 cm^{-1} and 2850 cm^{-1} for –CH_2- stretching, bands at 1463 cm^{-1} for CH_2 bending and the band at 721 cm^{-1} for CH_2 rocking. For blend of PVA/LDPE the band values of LDPE shifted, bands of 2939 cm^{-1} and 2850 cm^{-1} shifted to 2920 cm^{-1} and 2852 cm^{-1} respectively with an additional band at 3327 cm^{-1} for –OH- stretching vibration, while the other remain unchanged .

With the addition of silane for blends bands at 1265 cm^{-1} for (Si-CH$_2$) , 1093 cm^{-1} for (Si-O-C) and 848 cm^{-1} for (Si-O-Si). The other bands of PVA/LDPE blend are also appear with some shifting.

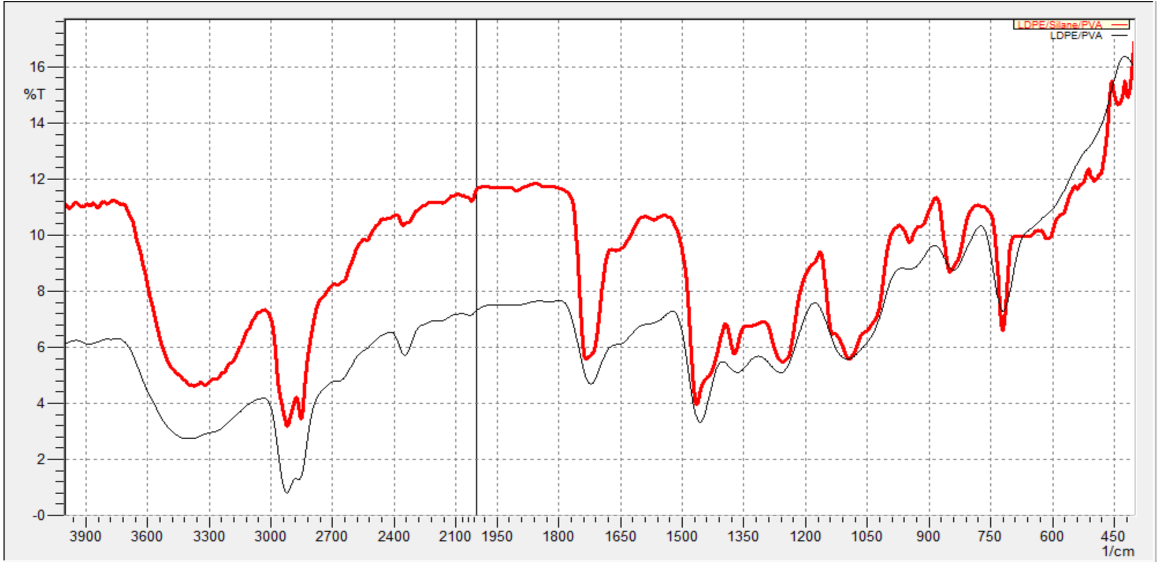


Fig. 6: FTIR spectrum for LDPE, PVA and blend polymers with silane.

Table 4: the absorption bands of IR spectrum characteristic of LDPE and blends.

Type of bond	**LDPE standard**(Gulmine *et.al.*, 2002)	**LDPE exp.**	**PVA/LDPE**	**PVA/TMS/LDPE**
CH$_2$ stretching	**2919** **2851**	**2939** **2850**	**2920** **2852**	**2920** **2850**
CH$_2$ bending	**1473**	**1463**	**1463**	**1463**
CH$_2$ rocking	**720-731**	**721**	**721**	**721**

Morphology Tests

Surface morphologies of LDPE and blend samples were performed by using both digital microscope (Figure 7) and SEM (Figure 8). It can be seen from Fig.7 (a) that LDPE has smooth and uniform phase without any discontinuity in the surface. As PVA added the surface morphology of blend become less uniform exhibit some voids due to agglomeration of PVA particle and phase separation between LDPE and PVA which adverse effect on the mechanical properties Fig.7 (b, c).

By the addition of silane an improvement in surface morphology occurs, images of digital microscope shows a good adhesion and uniform dispersion of PVA agglomerates into LDPE matrix. This is attributed to the coupling agent effect, which improve the compatibility and miscibility of LDPE and PVA, as shown in Fig. 7 (d, e).

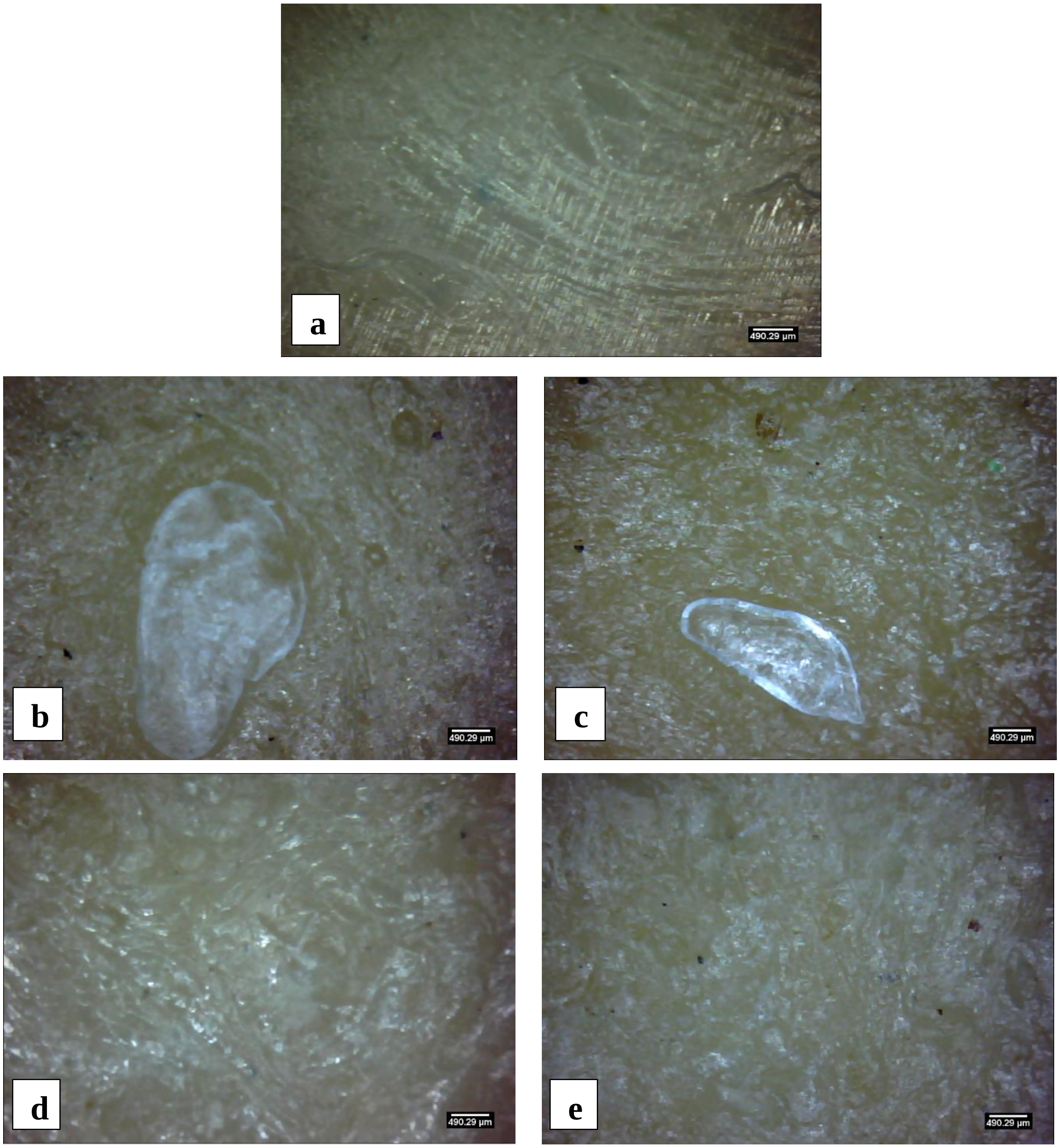


Fig.7: Digital microscope images for: a)pure LDPE, b)30%PVA+70%LDPE, c)40%PVA+60%LDPE,d)50%PVA/5%TMS/45%LDPE,e)60%PVA/5%TMS/35% LDPE

Figure 8 shows SEM micrographs for pure LDPE and uncompatibilized and compatibilized blends. PVA agglomeration and incompatibility of blend was identified from Fig.8 c and Fig.8 d micrographs where there irregular and rough surface which indicate the presence of different holes on the surface. This means the miscibility and compatibility is poor between the blend components. SEM images of compatibilized blend show that LDPE covers PVA agglomerates and an interconnected rough surface is produced as shown in fig.8 (e, f).

This means a good interaction and adhesion between the two polymers, due to the effect of silane increases the adhesion and reducing the surface tension between LDPE and PVA. This agreed with (Brandalise *et.al.*, 2009; Razif , 2012) .

DSC Test Results

DSC was used to investigate the miscibility between LDPE and PVA with silane addition. The peak melting temperature is taken as indicative for the compatibility of the blends. From figure 9 (a, b), the DSC peak melting temperature of LDPE is 117.66 ºC and for PVA is 190.19 ºC. For PVA/LDPE blend, DSC thermograph peaks shifted slightly to a lower value due to the phase separation between PVA agglomerates and LDPE matrix as shown in figure 9(c) (Taylor *et.al.*, 2009). This figure, also, showed that there are two melting points, which proved that there is a phase separation and the blend is immiscible. The addition of silane causes a decrease in melting temperature of both LDPE and PVA by 5 ^{o}C this behavior is due to the grafts formed by silane addition, this prevent crystal packing and chain arrenegment, as shown in Fig.9 (d) . The melting enthalpy and degree of crystallinity decreased from 96.93 J/g to 44.47 J/g and 69.24 % to 34.96 % respectively by silane addition. This behavior is believed due to the formation of links between silane and LDPE and PVA which hinder the order arrangement of chains, this agreement with (Bengtsson and Oksman , 2006).

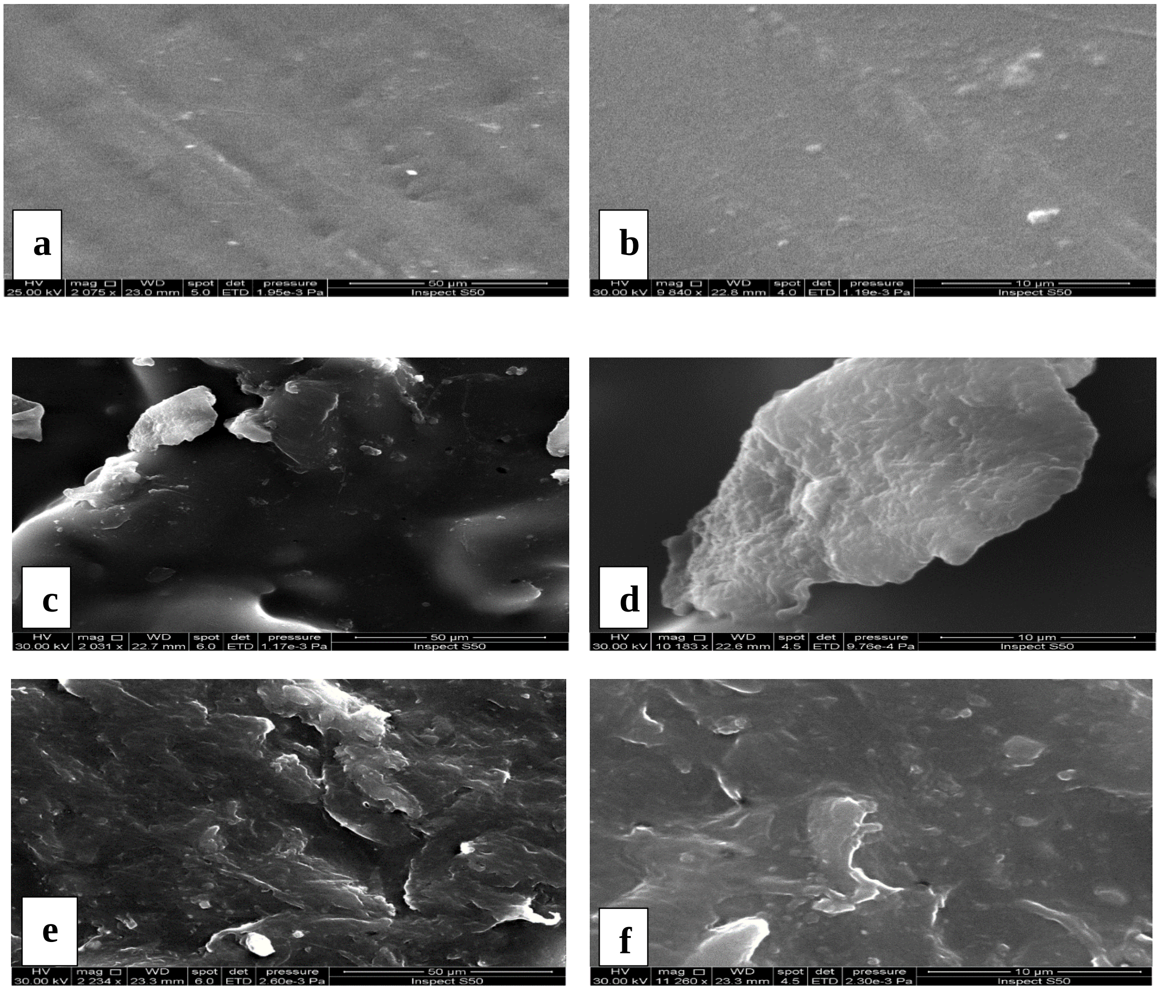


Fig.8: SEM images of pure LDPE (a, b), uncompatibilized polymer blends(c, d) and compatibilized blends (e, f).

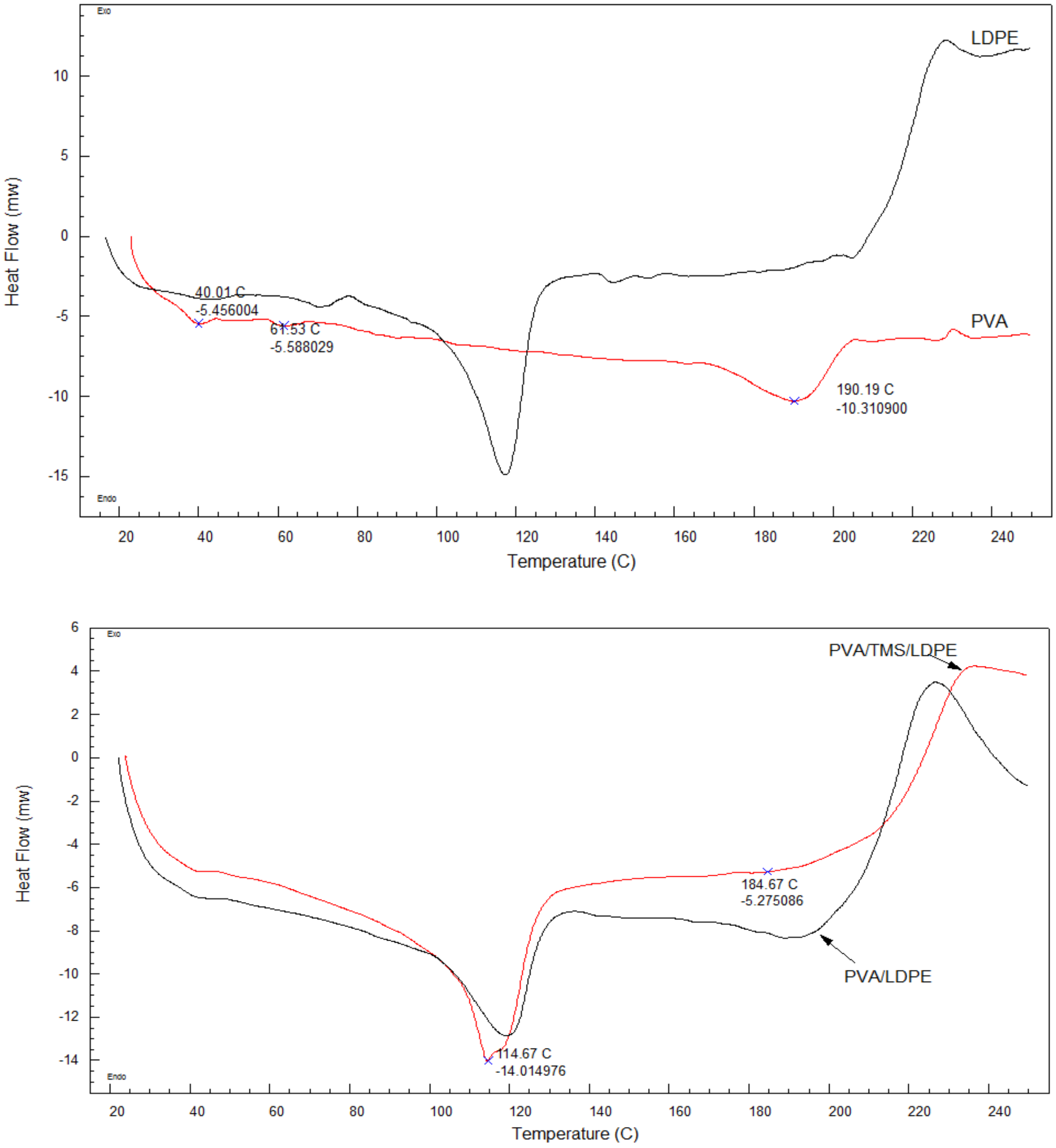


Fig.9: DSC curves for: LDPE, PVA, PVA/LDPE, d)PVA/TMS/LDPE

Table 5: DSC data for pure and blends with and without silane

samples	LDPE T_m (^oC)	PVA T_m (^oC)	Crystallinity %	Enthalpy ΔH(J/g)
LDPE	**117.66**	**-------**	**69.24**	**96.93**
PVA	**-------**	**190.19**		
LDPE/PVA	**119.34**	**189.31**	**34.3**	**60.6**
LDPE/S/PVA	**114.67**	**184.67**	**31.76**	**44.47**

Conclusion

1- The addition of 5% of silane improves the compatibility between PVA/LDPE blend.

2- The tensile properties such as tensile strength, elongation at break and young modulus of PVA/LDPE blend were improved by silane addition.

3- DSC curves shows that the miscibility of PVA/LDPE is enhanced by melting temperature depression while crystallinity and melting enthalpy were decreased with silane addition.

4- Morphology tests show that silane improves the dispersion and adhesion of PVA in LDPE matrix.

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