The influence in difference of compatibilizers on the mechanical and rheological properties of LDPE/PLST blends

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Abstract. In this present study, low density polyethylene/plasticizer starch (LDPE/PLST) blends were prepared as a product to be used in disposable packaging (film applications), reducing the negative polymeric environmental effect. Because of their different molecular structures, LDPE blends with starch are fully immiscible; therefore, a compatibility agent is required. Three different polymer and/or copolymer: poly (vinyl alcohol) hydrolyzed 75% (PVOH), styrene-allyl alcohol copolymers (SAA) and polyethylene glycol (PEG) were selected as compatibilizers containing –OH groups. The effects of compatibilizer on the mechanical and rheological properties of LDPE/PLST blends were investigated and compared to LDPE/PLST without compatibilizer. The blends are also characterized by FTIR, which strongly indicates the existence of compatibilizers that can enhance phase interaction and promote compatibility in the blends of LDPE/PLST. Comparing to the blend without a compatibilizer, the tensile strengths of the blends containing PVOH and SAA increased significantly. The elongation at break results shows similar observation. The rheological measurement results suggested that the addition of a compatibilizer exhibited an increase in the shear stress and apparent viscosity comparing to the uncompatibilized blend except the blend with PEG which exhibited phase separation.

1. Introduction
Polyethylene is the highly and commercially used polymer in the world at present. The industrial demand for this polymer is still increasing, a result of the variety of applications based on its superior properties, such as high chemical and mechanical resistance, easy processability and low specific gravity, in addition to low manufacturing costs [1]. Several types of polyethylene, including different levels of density have been produced so far. One of the important types is low-density polyethylene (LDPE). It is a polymer containing long and short chain branches and is well known for its excellent melt characteristics and efficient processability [1]. These properties have contributed to the widespread use of LDPE in many industries, including films for agricultural and food packaging, creating many environmental issues associated with the disposal of plastic after using it. In the soil environment, LDPE is not degraded by microorganisms, which leads to their long-term survival [2].

This subject led researchers to be interested in improving LDPE's biodegradability or partial biodegradability by blending them with an inexpensive and abundant natural polymer like starch [3]. In the case of food packaging films (partially biodegradable) made from LDPE/starch blend, the presence of starch with content greater than 30% by weight has a negative influence on the mechanical properties of the blend [4]. As comparison, LDPE/starch film with starch content less than 20 %, the LDPE matrix dominates plastic deformation, resulting in less crazes and approximately equal to mechanical properties of LDPE films [4, 5]. In general, if these blends are deposited after use it in the environment, the addition of starch to the LDPE blend provides food for the soil microorganisms. The starch is consumed by soil microorganisms, the blend (film) loses its structural stability [6]. This
approach can contribute to deterioration in the mechanical properties, promoting the deterioration of other mechanisms and thus allowing the polymeric film blends to invade the bacteria and fungus that reside in the soil [7].

Several compatibilizers containing reactive groups able to form hydrogen bonds (H-bonds) with hydroxyl groups (–OH groups) of starch and interact with non-polar chain of LDPE, thus improve the compatibility of LDPE/starch blends [8-11]. Most of these compatibilizers have decreased the biodegradability of LPDE/starch blends and limited their use in humid environments. For this study, selected polymer and/or copolymer having -OH groups to study their compatibility LDPE with starch and its influence on the mechanical and rheological properties. Some of these compatibilizers has been widely used to prepare biodegradable blend with starch such as poly(vinyl alcohol) PVOH [12-14] and polyethylene glycol PEG [15].

2. Experimental part

2.1 Materials

Low density polyethylene LDPE (463) density=0.921 – 0.924, Melt Index= 0.28 – 0.38 was supplied by Petrochemical Company (SCPI), Basrah, Iraq. Starch (C₆H₁₀O₅)ₙ was supplied by Merck Company. Glycerol supplied by Fluka Company which was added as a plasticizer for starch in the amount of approximately 10% of the total weight of these blends to form plasticizer starch PLST.

2.2 Compatibilizers

The poly (vinyl alcohol) PVOH was prepared by the hydrolysis of poly (vinyl acetate), the degree of hydrolysis was 75%, molecular weight =2000. Styrene-allyl alcohol copolymer SAA, crystalline, allyl alcohol=33 mol % with molecular weight (Mw) average~ 1,600. Both copolymers were supplied by Aldrich Chemical Company. Polyethylene glycol PEG was supplied by BDH Company, waxy with average molecular weight = 1430-1570.

2.3 Blends preparation and characterization

Blends were prepared by mixing at 140°C, 40 rpm and mixing time of 10 min in a Brabender Plasticorder blender. The LDPE/PLST blends were prepared containing 70 wt% LDPE, 20 wt% PLST and 10 wt% compatibilizer. The blends were compressed and molded into sheets about 2 mm thick using 20×20 window frame molds in a hydraulic press. The window was placed between two steel sheets covered by aluminum foil. Then, the assembly was put into the hydraulic press and initially heated to 120 °C at pressure 5 tons for 3 min and for 10 min at a pressure 15 ton. Remove sheets from the press after cooling by water to room temperature. Dumbbell shaped specimens were cut from each sheet to mechanical properties tests.

All FTIR spectra was performed by using a Fourier transform infrared (FTIR)-8400S (Shimadzu, Japan). The mechanical properties measurement of tensile properties, such as tensile strength at yield and at break besides the elongation at break and break energy of the blends was performed using a tensile tester, according to ASTM D882. The evaluated rheological characteristics of all the blends were measured using a capillary rheometer (Instron model 3211). A wide range of cross-head speeds (0.06, 0.2, 0.6, 2.0 and 6.0 cm/min-1) is used for these measurements. The rheological data were recorded for all blends over shear rates of 5.43, 18.1, 54.3, 181, 543, and 1810 s⁻¹ at temperatures 150, 160, 170 and 180 °C. The data of shear stress, shear rate and the viscosity were calculated using manual capillary rheometer for 3211 Instron machine (10-364-1A).

3. Results and discussion

3.1. FTIR spectroscopy of blends

A significant and important research topic is the H-bond in polymer blends, it typically increases the miscibility of the blend. Compatibility and also miscibility can be promoted by the inter H-bonds among the components in the blend and has important effects on its properties. The introduction of H-bonds is a routine and successful way to achieve compatibility and changing the properties of the blends. In systems of polymer blends, a variety of experimental methods are used to characterize the H-bonds. FTIR spectroscopy is the most effective and commonly used technique among these methods for investigating the H-bond formation in polymer blends. So, the compatibility of LDPE/PLST blends with various compatibilizers was investigated by FTIR. Figure1 shows the FTIR spectra of PLST and
pure compatibilizers: PVOH, SAA and PEG. The complete assignment of the bands can be found in the other references [15-18]. In particular, FTIR showed that the H-bonds in LDPE/compatibilizer/PLST blends were essentially formed between the -OH groups of the sugar units in the starch and the -OH groups of compatibilizers. The interaction between starch and compatibilizer was possible via the -OH groups with a probability of interaction in the glucose ring with the ring oxygen O-5. Scheme 1 shows the H-bond interactions that presumably result among -OH groups of compatibilizer with functional groups of PLST [13].

In all blending spectra, the bands in the 3500-3600 cm\(^{-1}\) area were essential for evaluating the extent of the formation of H-bonds due to stretching of the --OH group. The reduction of the -OH peak frequency from 3600 cm\(^{-1}\) to lower wavelength and the broadening of this peak after blending provides details on the formation of H-bonding. The peak of the FTIR spectrum (figure 1) of PVOH at 1741 cm\(^{-1}\) was due to the carbonyl functional group belongs the residual acetate groups after poly(vinyl acetate) hydrolysis. H-bonding may also be strengthened by these groups, thereby increasing the compatibilization ability of the blend. In the blend, these carbonyl groups shifted from 1741 to 1734-1718 cm\(^{-1}\), suggesting new interactions between PVOH and PLST due to H-bond formation.

Scheme 1 The possible interaction between polymers containing -OH groups and functional groups in starch through H-bonding
Figure 1 FTIR spectra of (A) PVOH, (A1) SAA, (A2) PEG, (B) PLST, (C) LDPE/PVOH/PLST, (C1) LDPE/SAA/PLST, (C2) LDPE/PEG/PLST
3.2 Mechanical properties of the blends

It is well known, comparing to pure LDPE, most of the LDPE/starch blend appears lower values of tensile strength and break at break. The tensile strength of LDPE/starch blend has steadily decreased with increasing the percentage of starch in the blend. On the other hand, introducing 10% of starch into LDPE matrix, elongation at break decreasing significantly [19]. When stress force loads were applied to LDPE/starch blend and due to the weak of adhesion between LDPE and starch, it was not able to spread equally, therefore, mechanical properties of blend subsequently deteriorated [20]. Interfacial adhesion must be strong enough to ensure that the transfer of stress between the phases in order to enhance the mechanical properties of blends. Interfacial adhesion is typically improved either by chemical modification of the interfacial region or by the incorporation of third part of interface agents (compatibilizers).

In this study, we have attempted to enhance interfacial adhesion of LDPE/PLST blend with three different compatibilizers which were chosen based on their chemical structure. The influence of these compatibilizers has been assessed on the essential mechanical properties, which was represented to be tensile strength at yield and at break, elongation at break and break energy. The results are presented in figures 2, 3 and 4. In the blends, PVOH is a strong candidate for compatibility. It was containing –OH and unhydrolytic residual groups of poly(vinyl acetate), having H-bonding with the -OH groups of starch ensuring a good compatibility with PLST in the blends. Another important factor is the formation of a graft copolymer PVOH-g-LDPE from macroradical recombination which was generated at melt temperature [21, 22]. This factor probable acts as a reactive compatibilizer promoting increased interfacial adhesion among the blend polymers [23, 24], thus, improves the mechanical properties of the blend. Generally, different from the other compatibilized and uncompatibilized blends, it was observed that the blend with PVOH had a greater influence on the relative tensile strength improvement of the blend. The elongation at break results for blends compatibilized by PVOH was increased in the relative elongation at break of other blends. This is consistency with related findings on LDPE/EVOH/PLST blends [25, 26].

The second compatibilizer tried with LDPE/PLST blend was SAA, it is a random copolymer of polystyrene and poly (allyl alcohol) consist of the vinyl chains in the molecule and it can be compatible with the LDPE phase, while the polarity of the -OH groups and phenyl groups form H-bonding and dipole–dipole interaction, respectively, capable to interact with starch phase. The introduction of SAA copolymer improved the tensile strength of the LDPE/PLST blend, but the overall value, however, remains lower than LDPE/PVOH/PLST blend. Also, compared to the blend with PVOH, it shows a slight decline in tensile strength. At the same time, it reduces the elongation at break and there was significant difference compared to blends with PVOH. A possible explanation for this change, that the phenyl styrene groups presented in the compatibilizer SAA as it supports the toughness and rigidity of the blend.

Polyethylene glycol (PEG) was the third used compatibility agent, which is a low molecular weight linear polymer. It has ethylene groups possible theoretically able to miscible with LDPE hydrophobic chains, and –OH groups in the terminal chains interact with –OH groups in starch. Incorporation PEG in LDPE/PLST blend induces partial miscibility with starch phase while miscibility with LDPE chains led to phase separation due to the ethylene groups in backbone of the PEG immiscible with the LDPE as referred in literatures [25, 27]. Therefore, the results show the deteriorated significantly mechanical properties of blend with PEG as compatibilizer.
Figure 2 Tensile strength at yield and at break of the blends

Figure 3 Elongation at break of the blends

Figure 4 Break energy of the blends
3.3 Rheological properties of the blends

The flow curves of LDPE/PLST blends containing PVOH, SAA and PEG were measured at 150 °C which presented to be typical temperature for standard processing conditions as shown in figure 5. The shear stress increase along with shear rate for all LDPE/PLST blends with and without compatibilizer confirming pseudoplastic non-Newton melt fluids of blends, analogous to most polymeric melts and the relation shear stress with shear rate attached to the power law [28]. In addition, the non-Newtonian index (n) values of LDPE/PLST blends which was calculated from the slope of the fitted lines which were less than one, confirming that the blends were pseudoplastic [29].

The shear stress of LDPE/PVOH/PLST blend is more than shear stress LDPE/SAA/PLST blend and LDPE/PLST blends without compatibilizer. While LDPE/PEG/PLST blend appeared lower value of shear stress compared to the other blends. However, adding PEG to the LDPE/PLST blend exhibited plasticization effect and enhanced the melt fluidity of blend. Figure 6 shows the result of viscosity versus shear rate of LDPE/PLST blends compatibilized by 10wt% compatibilizer. Noticing that the viscosity of LDPE/PLST blends decreases with increasing shear rate, those results reflecting another indicator of a typical feature of pseudoplastic non-Newton melt fluids.

The viscosity result of blend with PEG is the lowest value while the viscosity result of blend with PVOH is the highest. The highest value of melt viscosity may be explained by the fact that the PVOH was used for this investigation containing –OH and carboxyl groups (vinyl acetate groups) and capable to form H-bonding with starch hydroxyls (as explained above), the intermolecular and interlayer forces of blend fluids were increased thus the viscosity of melt was also increased.

The blend with SAA shows lower values of viscosity comparing to the viscosity of blend with PVOH. However, the viscosity of blend with SAA was higher than the viscosity of blend without compatibilizer and with PEG as a result of the substantial destruction of phenyl rigid groups acting on the PLST and LDPE.PEG had a low molecular weight, so at the processing temperature, the PEG melt had a low viscosity and melt strength. It was expected, due to immiscibly LDPE and PEG and lubricates nature of PEG caused interlayer slippages of the LDPE melt. Therefore, PEG acts only as a plasticizer, reducing the viscosity.

The effect of temperature on melt viscosity for all blends is shown in figure 7. With increasing the temperature, the viscosity of all blends increased except blends with PEG. In the melt state processing, a number of branch points in LDPE with loosely connected tertiary hydrogen's in the polymer molecule can forms free radicals [21]. At the same time, when the temperature reached about 150 °C, the macromolecules of partially hydrolyzed PVOH (which content acetate groups about 25%) degraded by double bonds formation. Furthermore, releasing acetic acid catalyzed the degradation reactions [22, 24]. The macroradicals was generated in the blend melt, causes crosslink between LDPE and PVOH, probably, due to mutual reactions between the tertiary carbon radicals of LDPE and the double bonds of the PVOH activated during melt blending. Therefore, those blends exhibited high viscosity with evaluated temperature. Blend with SAA, exhibits viscosity higher than blend without compatibilizer at a fixed temperature. When the temperature goes up to 180°C, the viscosity of LDPE/SAA/PLST increases sharply. This result attributed to effect polystyrene structure which has high viscosity [30].
**Figure 5** Flow curves of blends at 150 °C

**Figure 6** Viscosity versus shear rate of blends at 150 °C

**Figure 7** Effect of temperatures on viscosity of blends
4. Conclusion
The influences of the three kinds of compatibilizers on the properties of LDPE/PLST blends was a study. Blends with and without compatibilizer was prepared in the melt state using Brabender Plasticorder. The compatibility of blends was characterized by FTIR, mechanical and rheological analyses. FTIR measurement shows all compatibilizers which are able to form H-bonds with –OH groups of starch. Regarding to the results of mechanical properties, PVOH demonstrated better tensile strength results as a compatibilizer among others. Also, using PVOH and SAA as a compatibilizer, the elongation at break values of the LDPE/PLST blends was improved compared to the blend without compatibilizer. Rheological results of the various LDPE/PLST blends showed increase the shear stress and viscosity along with shear rate. The viscosity of the blends was highly influenced by the temperature. Viscosity was increased along with the temperature when increased from 150 to 180 °C. From the results, it was also concluded that adding PEG to the LDPE/PLST blend shows a negative effect on the mechanical and rheological properties due to immiscibility with LDPE caused the phase separation of blend.

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