

# INVESTIGATION OF THE PHYSICAL-MECHANICAL AND BIODEGRADABLE PROPERTIES OF NANO-BIOCOMPOSITE PREPARED FROM MIXTURE OF STARCH, LLDPE, HDPE AND NANOCCLAY

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## Abstract

*In this study a novel nanobiodegradable composite based on Corn Starch /High density polyethylene (HDPE) / Linear low density polyethylene(LLDPE) and Nanoclay cloisite 30B were prepared by melt mixing. Three kind of copolymers such as: ethylene-vinyl alcohol (EVOH), ethylene vinyl acetate (EVA) and polyethylene grafted maleic anhydride (PE-g-MA) were used as a compatibilizers in HDPE/LLDPE/Starch composites. In comparing the effect of the above compatibilizers, the mechanical properties of the biocomposites showed that the tensile strength, Young's modulus and elongation at break increase when a polyethylene-g-maleic anhydride(PE-g-MA) copolymer was used as compatibilizer. In addition 3% wt of nano clay in the composites , the results showed good dispersion of the nano particles cloisite 30B .Also a combination of intercalated and nearly exfoliated structure was obtained in the sample by microstructure study of X-ray diffraction and transmission electron microscope(TEM) analysis. Biodegradation studied in activated sludge samples were tested by weight loss methods and scanning electron microscope( SEM) observed holes and cracks on the surfaces can be considered as signs of the samples biodegradation.*

## 1. Introduction

Polyethylene is widely used as a packaging material because of its good mechanical properties and low cost. However, these qualities have been over shadowed by its highly nonbiodegradable nature, leading to waste-disposal problems, particularly in short-term packaging application. It has been estimated that nearly 2% of all plastics ultimately reach the environment, leading to acute pollution problems[1]. Environmental problems associated with the disposal of plastics and the need for environmental-friendly products has resulted in the significant use of Starch is a low cost, biodegradable material, which makes it an attractive option for manufacturing sustainable products. The incorporation of starch into some synthetic thermoplastics can enhance its environmental degradation .The use of starch in blends to enhance the biodegradability of conventional plastics has been reported by many researchers. Starch is a highly hydrophilic macromolecule, while

polyethylene is non-polar and hydrophobic [2]. Since then, many studies have been focused on increasing the compatibility and mechanical properties of the PE/starch blend system[3, 4]. In order to improve the compatibility of the blends, starch can be blended with PE using a compatibilizer. The most common compatibilizers are poly (ethylene-co-acrylic acid) (EAA), poly(ethylene-co-vinyl alcohol) (EVOH), poly(ethylene-g-maleic anhydride) (PE-g- MA) copolymers[5, 6]. In addition, for food packaging, important characteristics include mechanical properties such as tensile strength and elongation at break (%E) [7], So it is well known that incorporation of nanoparticles in polymer matrices and blends provides a powerful and flexible tool to develop composite materials with desired physical and mechanical properties[3]. On the other hand , reaching the desired level of mechanical performance still requires further reinforcement by addition of nanofillers for instance, as it was done with the development of bio-based nanocomposites dedicated to packaging applications [8].

In this paper the effect of three kind of compatiblizers: EVOH,EVA and PE-g-MA on the mechanical properties of LLDPE/HDPE/Starch composites were investigated. Then adding 3%wt of nanoclay Cloisite 30B to the composite with a good compatiblizer. Finally, the mechanical, morphological and biodegradable properties of the prepared specimen nano biocomposite were examined.

## **2. Experimental**

### *2.1. Materials*

The high density polyethelene (HDPE), B5429, (MFI=0.3 gr/10 min, density = 0.954 gr/cm<sup>3</sup>), supplied by Sabic Co. The linear low density polyethylene (LLDPE), LL0209AA (MFI=0.9 gr/10 min, density = 0.90 gr/cm<sup>3</sup>), was obtain from from Arak Petrochemical Co. Iran, Corn starch, which consisted of 25 wt% amylose and 75 wt% amylopectin, was obtained from Glucosan Co., Iran, The glycerol was purchased from Dr. Mujalli Co., Iran. PE-g-MA with 1.5 wt% maleic anhydride with a melt flow index of 2 g/10 min was provided by Grankin Co. Iran, ethylene-vinyl alcohol (EVOH), EVAL-E195B were provided Kuraray Co. and ethylene vinyl acetate (EVA), VS430 supplied by Lotte Chemical Corporation were used as compatibilizer. The clays were sodium montmorillonite modified with quaternary ammonium salt, polar modified nanoclay (Cloisite®30B, Southern Clay Products Co., USA – further named C30B) as reinforcement.

### *2.2. Preparation of HDPE/LLDPE/Starch composites*

For evaluation the effect of three compatiblizer(EVOH, EVA, PE-g-MA) on the composites Each compatibilizers were used separately The twelve blends of HDPE/St with 0, 10, 20, 30 %wt of LLDPE and constant percentage of compatibilizers are depicted in table 1, also LLDPE/HDPE blend as a reference sample (Sample code 13) is presented in mentioned table . The level of glycerol in the blends was 36 wt% based on the native corn starch as a plasticizer. After dried the materials in an oven at 70 °C for 24hr. The composite were mixed together using Brabender Internal Mixer at 150 °C for 5 min with 60 rpm Composite films were formed by using compression molding (Toyosiki press, Tokyo, Japan) at 160 °C and pressure of 25 MPa.

Sample . Code	LLDPE (wt%)	HDPE (wt%)	Starch (wt%)	EVOH (wt%)	EVA (wt%)	PE-g-MA (wt%)
1	0	64	30	6	0	0
2	10	54	30	6	0	0
3	20	44	30	6	0	0
4	30	34	30	6	0	0
5	0	64	30	0	6	0
6	10	54	30	0	6	0
7	20	44	30	0	6	0
8	30	34	30	0	6	0
9	0	64	30	0	0	6
10	10	54	30	0	0	6
11	20	44	30	0	0	6
12	30	34	30	0	0	6
13	30	70	0	0	0	0

**Table 1.** Component composition of the samples.

### 2.3. Preparation of HDPE/LLDPE/Starch/C30B nano biocomposites

For improving mechanical properties of bio composite nano clay (Cloisite 30B) was used as reinforcement at 3wt% level on blend with exhibited the best mechanical properties. The blend composition are depicted in Table 2.

Sample . Code	LLDPE (wt%)	HDPE (wt%)	Starch (wt%)	PE-g-MA (wt%)	C30B (wt%)
14	30	31	30	6	3

**Table 2.** Component composition of the sample.

### 2.4. Tensile properties

Tensile tests were done according to the ASTM-D882 method using a Comotech Testing machines Co., LTD with a 5 kN cell at a crosshead speed of 50 mm/min. At least 5 dumbbells of each sample were tested and their mean values were reported.

### 2.5. X-ray diffraction (XRD)

A Philips X’pert -X-ray Diffraction with Cu K $\alpha$  radiation ( $\lambda=1.78$  °A) at a generator voltage of 40 kV and a current of 40 mA was used. The data were collected between 1° and 12° at ambient temperature with a scanning speed of 0.02°/s and step size of 0.02°.

### 2.6. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) observations were performed with a Philips EM 208 transmission electron microscope operating at 120 keV. Ultra-thin sections of the samples for TEM analysis were prepared by ultra cryomicrotomy using a diamond knife. The polymer’s latent ability to degrade selectively in the electron beam causes the contrast between the phases in the system The Starch is more electronegative (due to its polar groups)

and absorbs electrons more easily. Thus the Starch domains form lighter regions than the HDPE phase[9].

### 2.7. Scanning electron microscopy (SEM)

Scanning electron microscopy, SEM, (Philips XL30) images were also used to study the phase morphology of the samples. The samples were sputter-coated with a thin layer of gold.

### 2.8. biodegradable test

Activated sludge from a municipal wastewater treatment plant (Khatam polymer Company) was used to evaluate the polymer biodegradability.

## 3. Results and discussion

### 3.1. Tensile properties

The tensile properties of LLDPE/HDPE/Starch blend with three kinds of compatibilizer (EVOH, EVA and PE-g-MA) are shown in Table 3. In comparing the mechanical properties of all prepared composites it showed that the composite of LL/HD/St/PE-MA samples had higher tensile strength and elongation at break than the LL/HD/St/EVOH and LL/HD/St/EVA series. But the Young modulus of LL/HD/St/MA samples had lower than the LL/HD/St/EVOH series that can be attributed to the increase in the polymer chain flexibility after addition of the MA-g-PE compatibilizer [10]. The composite of LLD/HD/ST/MA (30/34/30/6) %wt (sample code 12) was selected as the suitable composite [11].

Sample Code.	Sample	Wt%	Tensile Strength(MPa)	Young Modulus(MPa)	Elongation at Break(%)
1	LLD/HD/ST/ EVOH	(0/64/30/6)	13.14	630	8.83
2		(10/54/30/6)	11.94	520	11.01
3		(20/44/30/6)	10.53	430	11.39
4		(30/34/30/6)	8.24	325	14.51
5	LLD/HD/ST/ EVA	(0/64/30/6)	10.56	320	74.16
6		(10/54/30/6)	8.98	300	136.32
7		(20/44/30/6)	7.75	281	182.11
8		(30/34/30/6)	6.22	241	217.41
9	LLD/HD/ST/ PE-g-MA	(0/64/30/6)	18.22	472	130.47
10		(10/54/30/6)	14.23	382	168.60
11		(20/44/30/6)	12.53	327	241.30
12		(30/34/30/6)	11.80	312	310.21

**Table 3.** Effect of compatibilizer type on Tensile Strength and Young Modulus and Elongation at Break.

The effects of nanoclay on the ultimate mechanical properties of the samples were also investigated. Young modulus, tensile strength and elongation at break are compared sample code 12,14,13 in table 4. The tensile strength and elongation at break of the nanocomposites depend on many factors, including the aspect ratio of the filler, the degree of dispersion of the filler in the matrix resin and the adhesion at the filler-matrix interface [12]. Therefore the tensile strength, elongation at break and young modulus of the sample code 14 was superior

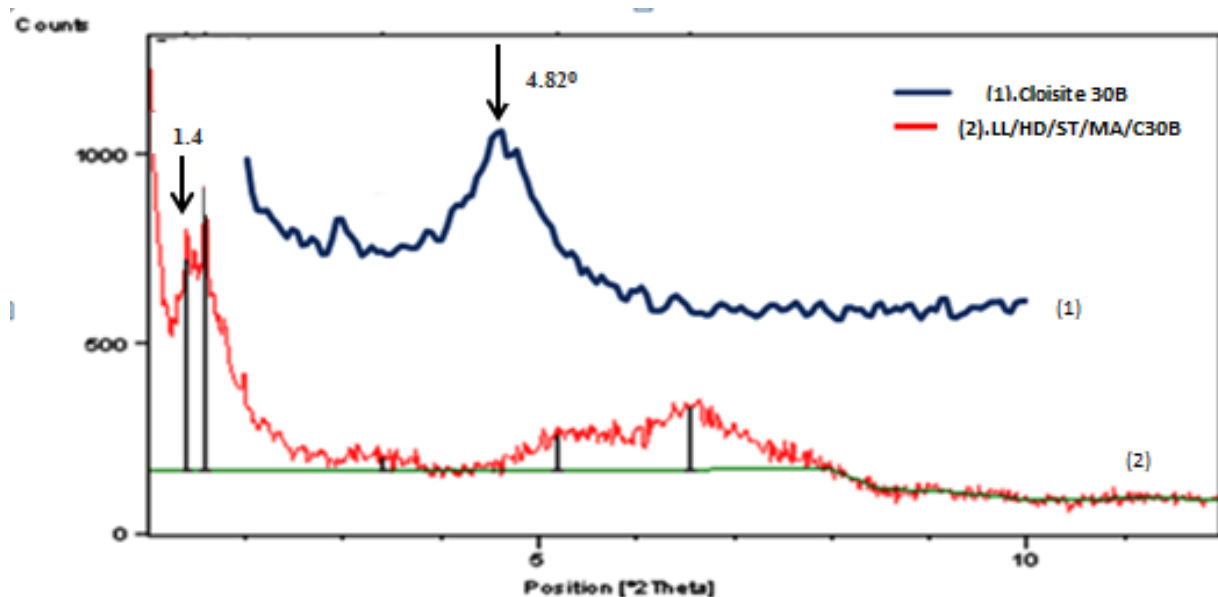
to sample code 12 ones due to the finer dispersion of clay layers with higher aspect ratios in the former (as mentioned earlier). It can also be seen from Table 4 that the addition of the organoclay increased the tensile strength. However, owing to the stiffening effect of the organoclay material, the elongation at break decreased as the organoclay content increased in both systems, Moreover, the addition of Cloisite C30B was able to increase the interfacial adhesion between the starch and HDPE phases by decreasing their electrostatic repulsion[3].

Sample Code.	Sample	Wt%	Tensile Strength(MPa)	Young Modulus(MPa)	Elongation at Break(%)
12	LLD/HD/ST/PE-g-MA	(30/34/30/6)	11.80	312	310.21
14	LLD/HD/ST/PE-g-MA/C30B	(30/31/30/6/3)	12.65	833	546.92
13	LLD/HD	(70/30)	20.21	600	677.40

**Table 4 .**Effect of clay on Tensile Strength and Young Modulus and Elongation at Break.

### 3.2. XRD

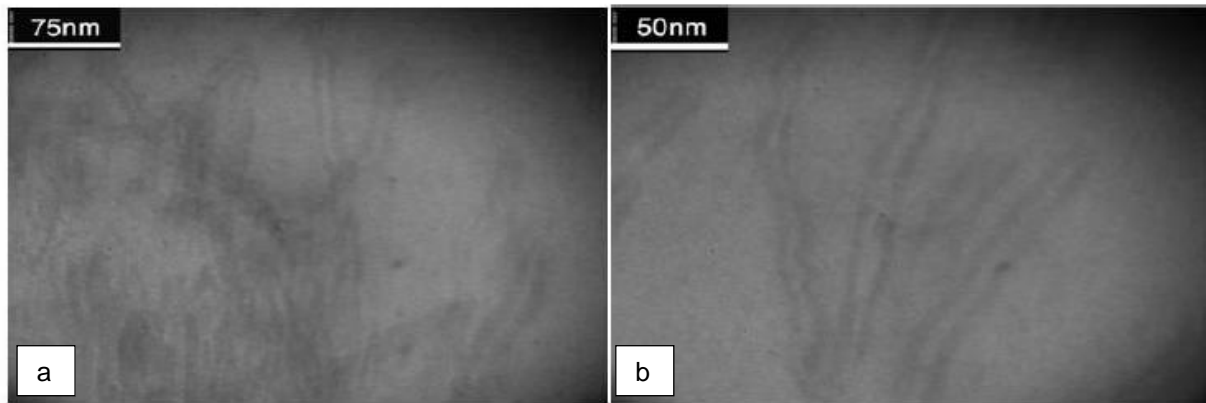
The XRD studies provided information on the intercalation and exfoliation processes in clay-polymer composites. Based on XRD analysis Figure1, the space gallery was determined using the Bragg law for the organoclays and the blends containing nanoclay. A decrease in the degree of coherent layer stacking of the clay would lead to a peak broadening and an intensity decrease in the XRD The primary (*d*001) diffraction peaks of neat C30B are located around  $2\theta = 4.82^\circ$ , which give interlayer spacing (*d*-spacing) of 1.8 nm. Upon addition of C30B clays into LLD/HD/ST/PE-g-MA blend, the XRD peak shifts to lower angles around  $2\theta = 1.40$  indicating an increase in interlayer spacing due to polymer intercalation within clay platelets In fact blend enter the gallery, the platelet is even pushed apart from the stacks of clay particles (partial exfoliated). This will cause XRD peak shift to the left side(confirmed by TEM imaging, Figure 2). The average distance between the platelets then becomes about 7.29 nm instead of 1.85 nm before intercalation. The maleic anhydride of the PP-g-MA compatibilizer can interact with both the polar organo-modified clay (C30B) and the starch phase of the matrix according to the chemical reactions presented in Figure1 [8].



**Figure 1.** XRD patterns of (1) original nanoclay Cloisite 30B, (2) blend of LLD/HD/ST/PE-g-MA/C30B (30,31,30,6,3 wt).

### 3.3. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy TEM images provide further evidence for the occurrence of intercalation and exfoliation processes. TEM allows a qualitative understanding of the internal structure, spatial distribution, and dispersion of nanoparticles within the polymer matrix through direct visualization [7] TEM micrographs of LLD/HD/ST/PE-g-MA/C30B (30/31/30/6/3 %wt) composite are presented in Fig2. TEM result corresponded well with XRD pattern. Composites exhibited a multilayered nanostructure and mixed intercalation and partially exfoliation of the clay platelets within the polymer matrix were observed.



**Figure 2.** TEM images of LLD/HD/ST/PE-g-MA/C30B (30,31,30,6,3 %wt) (a) lower (b) and higher magnifications.

### 3.4. Biodegradation

As one of the main objectives of this research, we studied the effect of the organoclay on biodegradation of the prepared systems. Table 5 shows the final weight losses of the selected samples in the biodegradation test. These loss of weights correspond directly to the extent of biodegradation by the activated sludge. The LLD/HD, as an essentially non-biodegradable material, exhibited only 0.09 wt% of weight loss while the LLD/HD/ST/PE-g-MA (30/31/30/6%wt) and LLD/HD/ST/PE-g-MA/C30B (30/31/30/6/3 %wt) samples showed 9.88 and 20.01 wt% loss of weights, respectively. It can also be observed that addition of 3 %wt of the organoclay to the LLD/HD/ST/PE-g-MA sample resulted in weight loss increasing from 9.88 to 20.01 wt%, respectively[13]

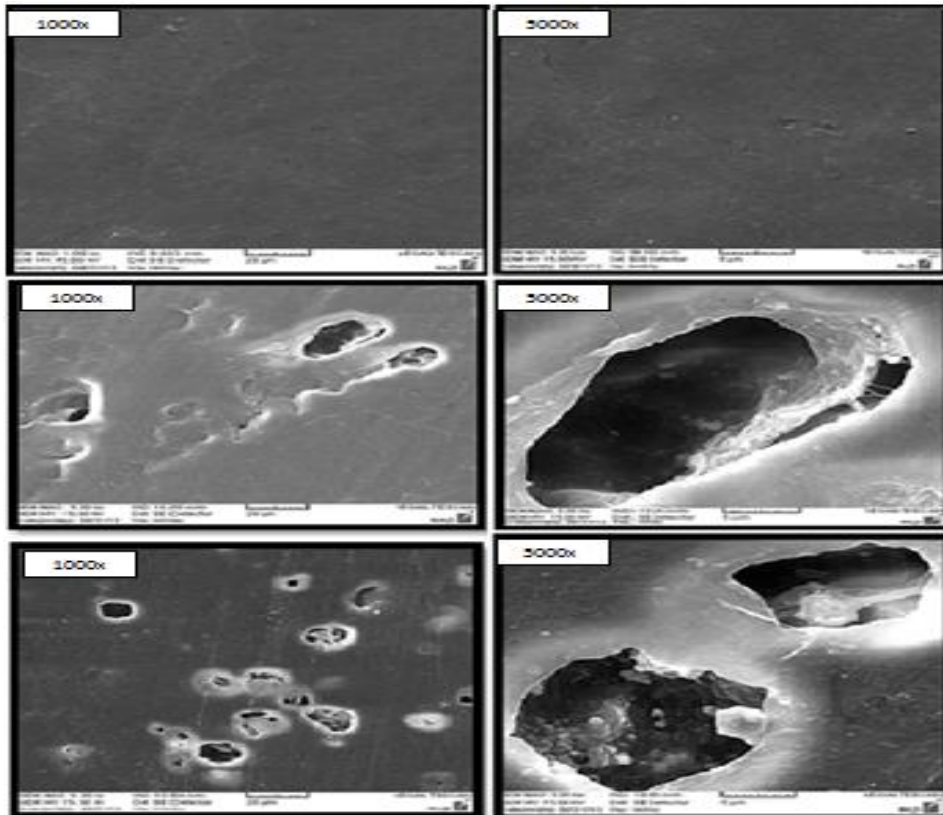
	Samples	Weight loss (wt%)
12	LLD/HD/ST/PE-g-MA	0.09
13	LLD/HD	9.88
14	LLD/HD/ST/PE-g-MA/C30B	20.01

**Table 5** Final weight losses of the selected samples after three months of biodegradation by the activated sludge.

### 3.5. SEM

The SEM images of the samples after 2 month of biodegradation are shown in figure 3. The holes and cracks of the sample surface are the signs of biodegradation As can be seen in the figures, the LLD/HD (30,70%wt) sample has very smooth surfaces which implies to non-biodegradation. At 30 wt% of starch in LLD/HD/ST/PE-g-MA sample, there are large holes that shows the starch domains consumed with the bacteria. In the case of nanocomposite, the

SEM micrographs show that the cracks and holes enlarged in comparison with sample code 12. This observation confirms the biodegradation results from weight loss tests. As discussed in the previous section, the nanoclay provides appropriate condition for the bacteria growth and accelerates the biodegradation progress [14]



**Figure3.** SEM micrographs (with different magnifications) of (a) LLD/HD, (b) LLD/HD/ST/PE-g-MA and (c) LLD/HD/ST/PE-g-MA /C30B samples after two months of exposing to the active sludge.

#### 4. Conclusions

The mechanical properties, morphology, as well as biodegradability, of nanocomposites based on HDPE, LLDPE and TPS were studied. The combination of high elongation at break, young module and tensile strength was obtained in the samples containing PE-g-MA as a compatibilizer in LLDPE/HDPE/Starch/PE-g-MA (30,34,30,6 %wt) in comparison with EVA and EVOH compatibilizer at the same level. The ability of the organoclay in enhancing the mechanical properties and biodegradability of the blends LLDPE/HDPE/Starch/PE-g-MA/C30B (30,34,30,6/3% wt) was higher than LLDPE/HDPE/Starch/PE-g-MA (30,34,30,6 % wt). Moreover, a nanocomposite of intercalated and nearly exfoliated.

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