Transparent Low-Density Polyethylene/Starch Nanocomposite Films

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ABSTRACT: Low-density polyethylene (LDPE)/starch nanocomposite films were prepared by melt extrusion process. The first step includes the preparation of starch–clay nanocomposite by solution intercalation method. The resultant product was then melt mixed with the main matrix, which is LDPE. Maleic anhydride-grafted polyethylene (MAgPE), produced by reactive extrusion, was used as a compatibilizer between starch and LDPE phases. The effects of using compatibilizer, clay, and plasticizers on physico-mechanical properties were investigated. The results indicated that the initial intercalation reaction of clay layers with starch molecules, the conversion of starch into thermoplastic starch (TPS) by plasticizers, and using MAgPE as a compatibilizer provided uniform distribution of both starch particles and clay layers, without any need of alkyl ammonium treatment, in LDPE matrix. The nanocomposite films exhibited better tensile properties compared to clay-free ones. In addition, the transparency of LDPE film did not significantly change in the presence of TPS and clay particles. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1907–1914, 2013

INTRODUCTION

Environmental concerns related to the accumulation of plastic waste and the huge consumption of nonrenewable resources for the production of plastics have increased the interest in the use of biodegradable materials in place of the synthetic ones. There is an especially great demand for making packaging materials degradable, because the packaging sector is the largest single user of plastics.[1] Unfortunately, biodegradable polymers from natural sources cannot compete with conventional petroleum-based plastics because of their poor mechanical and gas barrier properties. They are also very difficult to be processed because of the strong hydrogen bonds between the chains, which causes degradation before melting. Therefore, plasticizers are commonly used to decrease the melting point and to make the natural polymers thermoplastic.[2–5] However, the resultant product has moisture sensitivity, poor mechanical properties, and additionally it loses plasticizer over time resulting in a very fragile product.[6–10] In recent years, researchers have focused on the production of thermoplastic biopolymer–clay nanocomposites using solution and melt intercalation techniques.[11–16] Compared to clay-free composites, stiffness, tensile strength, and water resistance properties of the nanocomposites were reported to be better. However, their low melt strength and poor elongation properties make them difficult to be used in the film applications.[17,18]

One of the most convenient way to reduce the usage of synthetic plastics is to blend them with renewable ones. Using a proportion of biopolymers in synthetic polymers would not only reduce the dependence on petroleum products but also reduce the amount of plastic waste. Here, the most critical question is: What happens to the degradation mechanism of synthetic polymers after the addition of biopolymer? Previous studies have shown that when biopolymer is mixed with synthetic one, the degradation rate of the synthetic polymer increases.[19–23] It was suggested that microbes first create pores by consumption of biopolymer and thereby increase the surface area of the composite. Increased surface area enhances oxygen-based reactions, which could increase synthetic polymer chain oxidation. Because this is the slowest step in the degradation mechanism of synthetic polymers, any factor which increases the oxidation tendency of polymers also controls the degradation process of plastics. Hence, creating oxidized polymer chain ends in a degraded composite will make a synthetic polymer susceptible to biotic reactions.

In the family of renewable based polymeric materials, starch has been considered as one of the most promising materials for the future because it is readily available and may form cost effective end products. As a synthetic counterpart, LDPE is a good candidate, as it is the most commonly used packaging material. There are many studies in the literature related to the addition of starch into polyethylene.[24–36] However, in most of them, it

was reported that the properties of polyethylene has begun to deteriorate with the incorporation of biopolymer. The deterioration is most commonly seen in gloss, transparency, tensile elongation, tensile strength, tear strength, and gas barrier properties.[24–29] The main problem associated with the use of biopolymer as a filler is its hydrophilic nature and consequent incompatibility with the hydrophobic polymers. Recently, increased interest has focused on the use of biopolymers together with polymers containing reactive groups (e.g., maleic anhydride, glycidyl methacrylate, and hydroxyl) as compatibilizers due to the better dispersion of biopolymers in the polymer blends containing functional groups.[30–36] However, the problem in poor mechanical properties in the blends could not be completely solved by the addition of these compatibilizers.

The main purpose of this study is to prepare starch-containing LDPE films with good physical and mechanical properties. For this purpose, the effects of using compatibilizer, reinforcing filler, and plasticizer on these properties were investigated. Na^+-montmorillonite (Na^+mmt) type of clay was used as a reinforcing filler. To provide compatibility between LDPE and starch, MAgPE was first prepared and then incorporated into the formula. The resultant nanocomposite film having intercalated clay layers, plasticized starch phase and compatibilizer exhibited superior physico-mechanical properties.

EXPERIMENTAL

Materials

Exxon Mobil LD156 BW grade LDPE with MFI value of 0.75 g/10 min and melting point of 113°C was kindly supplied by Alcan Packaging, Istanbul. The native corn starch with diameter of between 5 to 20 μm was provided by Cargill, Turkey. It was dried in a vacuum oven at 80°C for 4 h before use. G-105 PGN polymer grade Na^+mmt with cation exchange capacity (cec) of 120 meq/100 g was obtained from Nanocor, USA. The clay was dried in a vacuum oven at 120°C for 2 h before use. Aldrich grade maleic anhydride, analytical grade dimethyl sulfoxide (dmso), glycerol, and formamide were used as received. Styrene monomer was purified by passing through glass column filled with alumina, and then dried with anhydrous magnesium sulfate ($MgSO_4$). Benzoyl peroxide was obtained from Aldrich with 75% purity and used as received.

Methods

Preparation of LDPE/Starch Blend. LDPE/starch blend containing 20 wt % of starch was prepared in a corotating twin-screw extruder (Leistritz Micro 27-GL 44D, D = 27 mm, L/D = 44) operating at a melt temperature of 170°C (the temperature along the screw was increased from 155 to 175°C) and screw speed of 120 rpm. LDPE and starch were fed into the first zone of the extruder from the feeders.

Preparation of Maleic Anhydride-Grafted Polyethylene (MAgPE). The maleic anhydride (1.5 wt %, based on polymer matrix), benzoyl peroxide (0.15 wt %, based on polymer matrix), and purified styrene (1.5 wt %, based on polymer matrix) were premixed with LDPE before feeding into the twin-screw extruder. The mixture was extruded at a screw speed of 100 rpm and melt temperature of 170°C.

To determine the efficiency of grafting reaction, 5 g of the product was refluxed in 200 mL of hot xylene for 2 h and then the solution was poured into the acetone to precipitate the pure product. The precipitate was washed several times with acetone to remove unreacted maleic anhydride monomers and dried in an oven at 80°C. The presence of maleic anhydride that had been grafted onto polyethylene chains was checked with Fourier transform infrared spectroscopy (FTIR) analysis.

The degree of grafting was determined by titration method. The pure product (0.4 g) was dissolved in hot toluene and then several drops of water were added to this solution to hydrolyze the anhydride groups into carboxylic acid groups. After adding thymol blue as an indicator, the solution was titrated with 0.05N KOH solution until the formation of stable blue color. The amount of carboxylic acid was then calculated by eq. (1) and converted into maleic anhydride content:

$$\text{Carboxylic acid content (weight \%)} = (45 \times N \times V) \times 100/M \tag{1}$$

where N is the normality of KOH solution (mol/L), V is the volume of consumed KOH solution (L), M is the amount of polymer sample used in titration method (g), and 45 is the molecular weight of single carboxylic acid group (g/mol).

Preparation of Starch–Plasticizer Mixture. The formamide and glycerol, in an amount of 30 wt % (based on starch) from each one, were heated to 60°C, separately. The starch powders were then manually mixed with these plasticizers until the formation of completely wetted particles and the mixture was kept overnight in sealed PE bags to allow the starch particles to swell with plasticizer before the extrusion process.

Preparation of LDPE/MAgPE/Starch and LDPE/MAgPE/TPS Blends. To prepare LDPE/MAgPE/starch blend, LDPE (60 wt %), MAgPE (20 wt %), and starch (20 wt %) were blended in a corotating twin-screw extruder operating at a melt temperature of 170°C and screw speed of 120 rpm. For the blend containing TPS, the starch-plasticizer mixture was melt blended with LDPE and MAgPE under the same conditions used to prepare LDPE/MAgPE/starch blend.

Preparation of Starch–clay Nanocomposite and Its Mixture with Plasticizer. The starch–7.5 wt % clay nanocomposite was prepared by solution intercalation method. The starch was first dissolved in 90% (vol %) dmso solution and kept in an ultrasonic bath for 2 h to obtain a clear solution. The clay was then dispersed in distilled water at room temperature, producing a gel that was added into the starch solution and the mixture was stirred at room temperature for 24 h. The product was then precipitated in acetone, filtered, and washed several times with acetone. Finally, it was dried at 65°C in an oven and ground into the powder.

For the mixture of starch–clay and plasticizer, powdered form of starch–clay nanocomposite was mixed with formamide and glycerol in the same way as described in "Preparation of Starch–Plasticizer Mixture" section.

Preparation of LDPE/MAgPE /TPS-Clay Nanocomposites. The samples of LDPE, MAgPE, and starch–clay nanocomposite
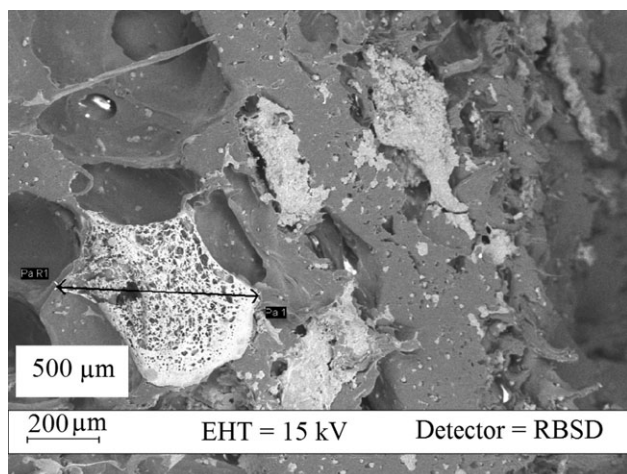
Figure 1. SEM image of LDPE/starch composite.

Figure 2. FTIR spectrum of (a) LDPE and (b) MAgPE.

premixed with plasticizers at the composition of 60 wt %, 20 wt %, and 20 wt %, respectively, were melt blended in a corotating twin screw operating at a melt temperature of 170°C and screw speed of 120 rpm.

Compression molding. The neat LDPE granules and the samples obtained by extrusion process were first melted in Scientific LRM-S-110 two-roll mills at a temperature of 170°C and then hot pressed into the films using Scientific LP-S-50 at a pressure of 100 bar. The thickness of the films was measured as 400 μm.

Characterization methods. The compatibility between LDPE and starch in the composite films was evaluated by FTIR measurement (wave resolution is 2 cm^{-1} and the accumulation number is 20) using Bruker Equinox 55 spectrometer, over the wavenumber range 600–4000 cm^{-1}. The distance between the clay layers were measured by X-ray diffraction (XRD) analysis conducted using a Bruker AXS-D8 diffractometer with CuKα radiation (wavelengh of 1.542 Å), operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded in an angular range of 2–30° (2θ) at room temperature. A Leo G34-Supra 35VP scanning electron microscope (SEM) was used for the surface morphology observation of the film samples after they were coated with thin carbon film to avoid charge built up. Transmission electron microscopy (TEM) images were obtained using a JEM–1230 model of JEOL, Japan. The thin sections (about 40 nm) were cut from the film samples at −140°C using EM FC6 model ultra cyro-microtome (Leica, Swiss) were then subjected to TEM analysis. The transmission of UV–vis light through the films was detected using Shimadzu UV-3150 spectrophotometer. Biodegradation degree was evaluated by calculating the amount of glucose that was evolved due to the degradation of starch molecules by AG-Amiloglucosidase. Glucose amount was calculated from the absorbance measurement conducted on Shimadzu UV-3150 spectrophotometer at a specific wavelenght of 550 nm. The tensile tests were performed at room temperature using a Zwick/Roell (model Z100, BT1-FB100TN) machine at a cross speed of 50 mm/min according to ASTM D 882-02 standard. The test specimens were conditioned at room temperature (23 ± 2°C) and 50 ± 5% relative humidity for 48 h before the test.
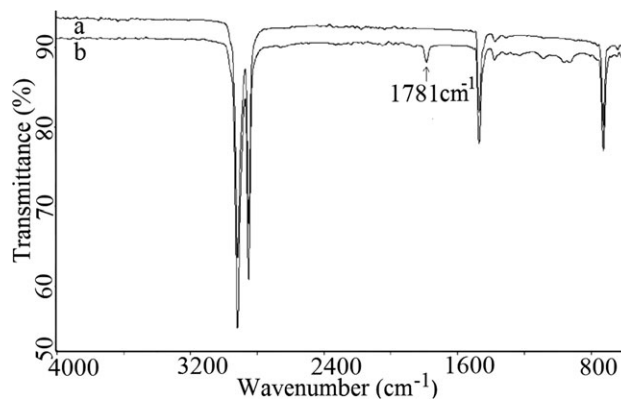
RESULTS AND DISCUSSION

The first stage of the composite preparation includes simply mixing of starch powders with LDPE matrix in a corotating twin-screw extruder. SEM analysis of this composite shows that starch (bright particles in Figure 1) acted as a physical filler through the formation of large particles, in the order of 500–600 μm. Moreover, the presence of voids indicates poor interfacial adhesion between starch particles and LDPE matrix, which is caused by the chemical incompatibility between the two phases.[25–28,31]

To provide compatibility between starch and LDPE, maleic anhydride was grafted into polyethylene chains. Figure 2 shows FTIR spectrum of MAgPE that was taken after purification in xylene. The peak at 1781 cm^{-1} is assigned to the stretching vibrations of carbonyl groups (—C═O) in maleic anhydride, showing the success of the grafting reaction. The amount of maleic anhydride that is grafted into LDPE chains was found to be 1.0 wt % (based on LDPE content) from eq. (1).

The effect of using compatibilizer on the morphology of LDPE/starch composite can be seen in SEM image (Figure 3). After the addition of MAgPE, the size of the starch particles drastically reduced to a maximum size of about 20 μm and the voids
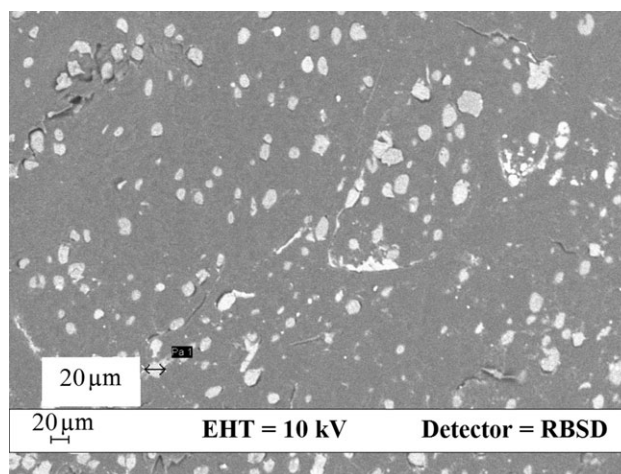

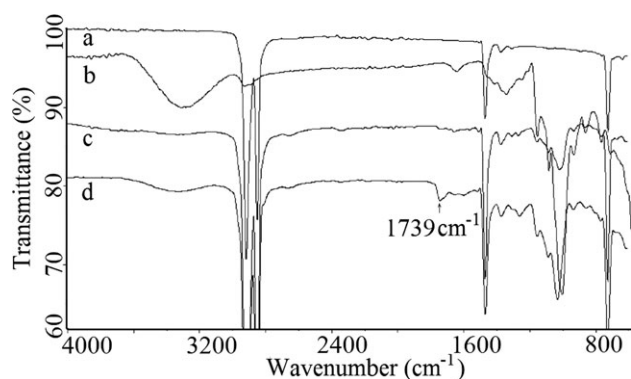**Figure 3.** SEM image of LDPE/MAgPE/starch composite.

Figure 4. FTIR spectra of (a) LDPE, (b) starch, (c) LDPE/starch, and (d) LDPE/MAgPE/starch.

Figure 6. XRD pattern of (a) clay (Na$^+$ MMT) and (b) starch–clay nanocomposite.

between the two phases disappeared. The compatibility between starch and LDPE phases was also evaluated by FTIR analysis. The spectrum of LDPE/MAgPE/starch composite film verifies the efficiency of compatibilizer in providing strong interfacial adhesion through the formation of ester linkage between ─OH of starch molecules and ─C═O groups of MAgPE (Figure 4). In FTIR spectrum, the peak observed at 1739 cm^{-1} corresponds to ─C═O groups of this ester linkage. The absence of peak at 1781 cm^{-1} indicates that all the cyclic maleic anhydride groups in compatibilizer were opened up and reacted with the hydroxyl groups in starch molecules. On the other hand, for LDPE/starch composite sample, FTIR spectrum exhibited only the characteristic peaks of the individual polymer components.

The mixture of formamide and glycerol was then used as a plasticizer to convert granular starch into TPS during extrusion process. The improved starch dispersion in LDPE/MAgPE/TPS sample is apparent in SEM micrograph (see Figure 5). Even though plasticizer provides better starch dispersion by the disruption of long range interaction between the polymer chains, it causes the reduction in tensile strength and modulus of the material. The reinforcing effect of nano-additive, in this case, would play an important role in regaining/enhancing the mechanical strength as well as the stiffness while maintaining the
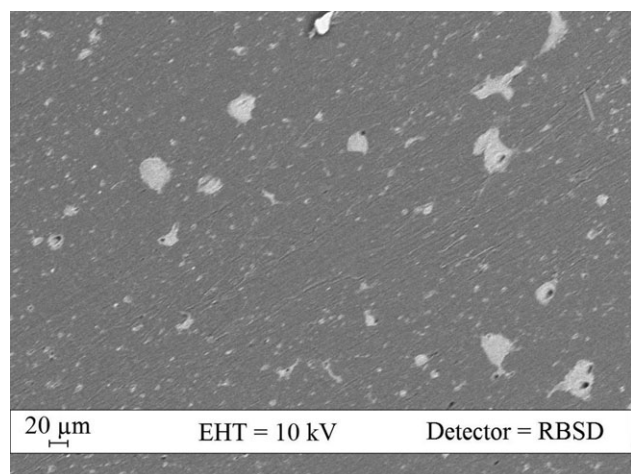
high elongation of the matrix. The only requirement to observe these effects is to provide homogeneous, nanoscale dispersion of the filler.[37] In this study, natural clay (Na$^+$mmt) has been used as a reinforcing filler, as it is easily available and much cheaper than organo-modified clay. The hydrophilic character of natural clay makes it compatible only with polar polymers.[38] Therefore, it has been initially dispersed in starch phase and then in LDPE matrix. The separation extent of clay layers in starch–clay sample was investigated using XRD. Figure 6 reveals that d_{001} basal spacing of clay increased from 1.14 to 1.79 nm after dispersing in starch, indicating the formation of intercalated nanocomposite structure.[39]

Figure 7(a and b) show SEM images of LDPE/MAgPE/TPS-clay, where the starch phase appears gray and the clay particles are bright. There is a good compatibility between starch and LDPE matrix. The majority of the clay particles appear to reside in starch phase because of their chemical compatibility with starch molecules. This may provide an additional moisture barrier to the composite film because starch is normally permeable to the environmental moisture and this limits the use of such composite films in packaging applications requiring low water vapor transmission rate. The morphology of LDPE/MAgPE/TPS-clay sample was further studied with TEM analysis and the related image is given in Figure 8. Similar to what was observed in SEM analysis, TEM analysis also revealed that the sample is free of agglomerated clay particles, clay layers dispersed at nanoscale were easily observed. Moreover, TEM analysis provided better vision about the location of clay layers that they were found to be mainly concentrated in TPS phase and then at the interface between LDPE and TPS phases. Besides, few of the layers were also encountered at LDPE matrix.

Film transparency is another tool to get information about the particle size of the dispersed particles. If the particle sizes are larger than the wavelength of the light, the film appears translucent or opaque. Figure 9 represents the light transmission rate of the films at selected wavelengths from 200 to 900 nm, measured by UV-Vis spectrophotometer. The transparency of polyethylene film was not significantly reduced by the addition of TPS–clay hybrids, indicating the homogeneous dispersion of clay layers as well as starch particles inside the matrix. The LDPE film containing starch and compatibilizer (LDPE/MAgPE/
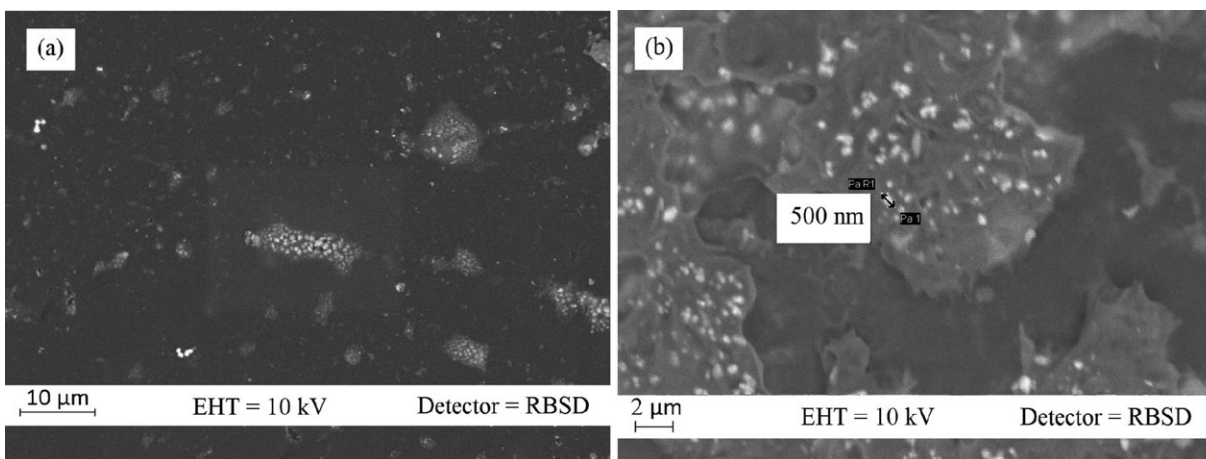

Figure 5. SEM image of LDPE/MAgPE/TPS composite.

Figure 7. SEM images of LDPE/MAgPE/TPS-clay at (a) low magnification and (b) high magnification.

Starch), on the other hand, exhibited much poorer optical transparency because of the presence of large starch particles. The transparency of the samples was also evaluated by inserting a text under the films and taking the pictures with a digital camera. Figure 10 represents that the texts under LDPE and nanocomposite films are easily readable, whereas the text under LDPE/MAgPE/starch film is barely perceptible.

The tensile properties of various polymer sheet films are presented in Table I. It was observed that the mechanical properties, especially the tensile strength and the elongation at break, of LDPE film significantly decreased with the addition of starch particles. The reduction in tensile strength is around 32% and that in elongation at break is more than 95%. The poor mechanical strength of LDPE/starch composite is assigned to the phase separation between the two components due to their different polarities. Therefore, starch particles act as physical fillers, leading to the formation of defects in the interface and the mechanical rupture occurs easily from these defects during the tensile test. After using MAgPE as a compatibilizer, the tensile strength of LDPE/starch sample increased, which illustrates the improved adhesion between starch and LDPE phases. However, no significant increase was observed in elongation at break property with the addition of compatibilizer because of the presence of rigid starch particles and incomplete phase homogeneity. To improve the film flexibility, strong intermolecular interactions between starch molecules were broken up with formamide and glycerol during the extrusion process, so that starch was plasticized and melt mixed with LDPE matrix. This process provided more uniform distribution of starch particles as observed in SEM picture of the sample (Figure 5), and increased the elongation at break property but the tensile strength as well as the modulus decreased by the incorporation of plasticizers. The similar effect of plasticizer on mechanical properties of LDPE/starch blends was also noted by Sailaja and Chanda.[40] On the other hand, the presence of TPS–clay nanocomposite in LDPE matrix improved both the tensile strength and the elongation properties much more significantly than all the other trials. The tensile strength increased to 10.6 MPa, which is higher than the tensile strength of LDPE itself, and percent elongation increased to around 125%. The significant change in tensile properties with the addition of TPS–clay nanocomposite can be explained by different mechanisms. First of all, the plasticizers disrupted both intermolecular and intramolecular H-bonds and provided homogeneous distribution of starch molecules in the polymeric matrix. Thus, clay layers that had been
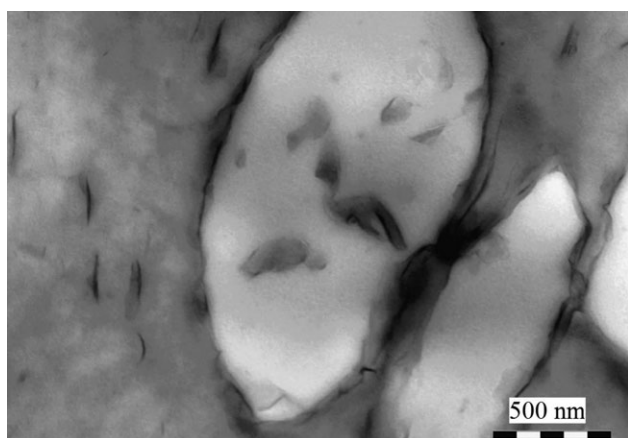

Figure 8. TEM image of LDPE/MAgPE/TPS-clay (black particles represent clay layers, white particles represent TPS phases, and the gray areas represent LDPE matrix).
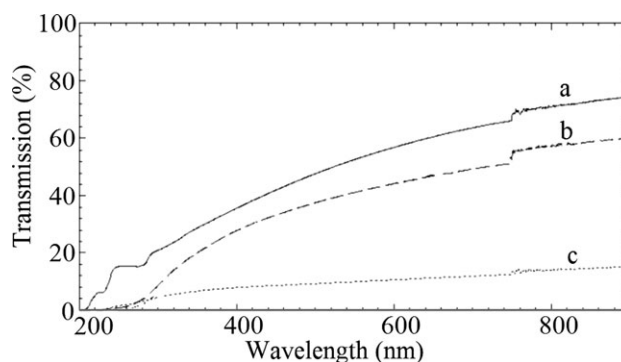

Figure 9. UV-Vis transmission spectra of (a) LDPE, (b) LDPE/MAgPE/TPS-clay, and (c) LDPE/MAgPE/starch.
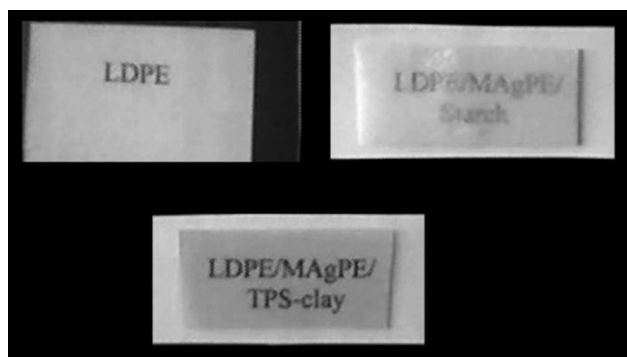
Figure 10. Transparency of the films captured by digital camera.

Table II. The Degree of Starch Degradation in Films After 3 Days of Enzyme Incubation

Sample	Degree of starch degradation (wt %)		
	24 h	48 h	72 h
LDPE/starch	37.8	65.4	73.7
LDPE/MAgPE/starch	27.0	31.0	34.7
LDPE/MAgPE/TPS	18.4	19.3	20.9
LDPE/MAgPE/TPS-clay	18.2	18.8	26.4

intercalated with starch molecules were also uniformly dispersed in the matrix. This improved dispersion increased the nanoscale reinforcing effect of clay and resulted in better tensile properties in nanocomposite film compared to other samples. Second, clay helps to keep plasticizers inside the matrix due to its barrier properties and its polar structure, which enables it to interact strongly with formamide and glycerol. The similar behavior has also been reported by number of other authors in the literature.[12,14,41] Finally, clay may inhibit the recrystallization process of starch molecules in TPS, which normally occurs due to the evaporation of plasticizer and causes the embrittlement of the TPS materials in time.[14] The increase in the plasticizer efficiency by the presence of clay also explains why the elastic modulus of LDPE/MAgPE/TPS-clay sample is almost the same with that of LDPE/MAgPE/TPS, even though it has a rigid inorganic additive.

The tensile toughness of the film samples was calculated by determining the area under stress–strain curves and the results are given in Table I. LDPE film did not exhibit a specific fracture point, thus the area under the stress–strain curve for this sample was calculated till 500% strain value. All the other samples had specific fracture points; hence, the area under the curves for these samples were measured till the fracture point. It has been observed that LDPE/starch film compatibilized with MAgPE exhibited toughness value that is 90% larger than uncompatibilized one. The improvement in toughness is much higher for the sample containing both compatibilizer and plasticizer. As the tensile strength values are very close for LDPE/MAgPE/starch and LDPE/MAgPE/TPS samples, this increase in toughness is due to increase in strain at break with plasticizer. The most drastic enhancement with 1060% increase in toughness value (compared to that of LDPE/starch) is realized in LDPE/MAgPE/TPS-clay film sample due to its superior tensile

strength and elongation at break properties. It can be suggested that such improvement in toughness will also provide high impact resistance to the film samples.

The biodegradation rate of starch-containing films was studied using AG-Amiloglucosidase that digests both amylose and amylopectin chains and results in the liberation of glucose molecules. The amount of glucose molecules evolved was calculated from the absorbance values of the enzyme solutions at specific wavelength. To determine the total amount of glucose in starch particles, pure starch was also incubated in enzyme solution.[42] Table II presents the amount of starch content that was degraded into glycose molecules after the film samples were incubated in enzyme solution for 3 days. The data were taken in every 24 h. The noticeable differences in starch degradation rate of clay-free samples reveals that; as biopolymer disperse more homogeneously in LDPE matrix, the rate of its degradation decreases. There are two possible reasons for this behavior. First of all, the finer the dispersion the better the interfacial adhesion so the slower the enzyme diffusion from the LDPE-starch or LDPE-TPS interfaces.[20] Second, the big starch particles can uptake more water molecules and hence more enzyme can be activated on starch surface. Even though the dispersion of starch is much finer in the nanocomposite sample, biodegradation rate is similar to that observed in LDPE/MAgPE/TPS sample. This behavior can be explained by the tendency of clay particles to absorb or interact with water molecules leading to the faster activation of enzyme. The effect of clay on starch degradation rate can be seen more clearly in data taken after 72 h of incubation. The improved biodegradability of polycaprolactone and polylactic acid nanocomposites with clay was also reported previously in compost environment.[43,44] The morphology of the degraded films after biodegradation test is shown in Figure 11. The black holes in SEM images show the degraded

Table I. Tensile Properties of the Samples

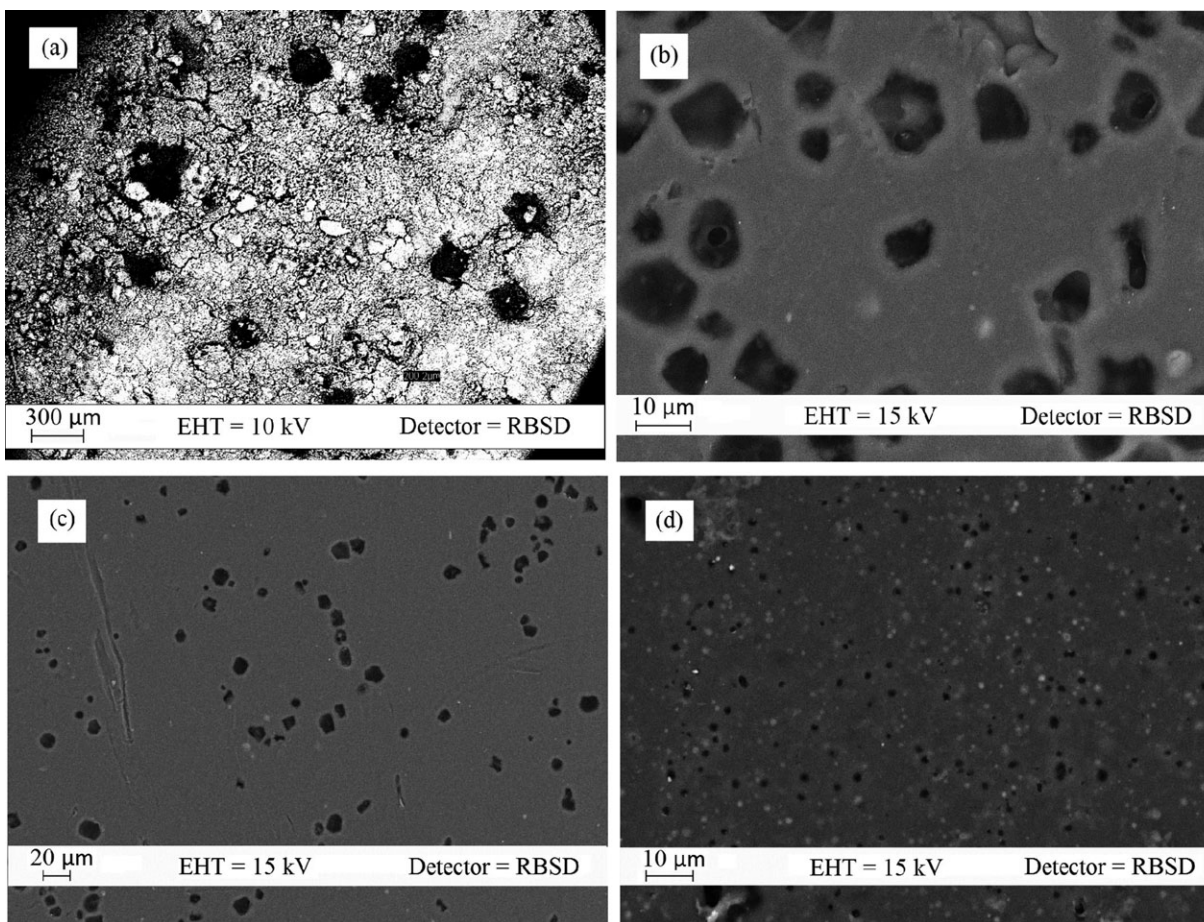| Sample	Tensile strength (MPa)	Strain at break (%)	Young's modulus (MPa)	Toughness (MPa)
LDPE	9.7 ± 0.3	>500	107.9 ± 3.3	>42.8
LDPE/starch	6.6 ± 0.1	22.4 ± 2.0	123.8 ± 13.4	1.0 ± 0.1
LDPE/MagPE/starch	8.9 ± 0.2	24.8 ± 3.0	151.5 ± 5.9	1.9 ± 0.2
LDPE/MagPE/TPS	8.3 ± 0.1	55.2 ± 5.1	125.5 ± 5.8	4.1 ± 0.4
LDPE/MagPE/TPS-clay	10.6 ± 0.2	125.2 ± 6.0	137.6 ± 5.8	11.6 ± 0.8

Figure 11. SEM images of degraded (a) LDPE/starch, (b) LDPE/MAgPE/starch, (c) LDPE/MAgPE/TPS, and (d) LDPE/MAgPE/TPS-clay films after incubation in enzyme solution.

starch particles by the action of enzyme. As it is clearly seen in the images, all the film samples exhibited a porous structure due to the digestion of starch molecules. Because of the porous structure, the higher surface area with enhanced accessibility of LDPE to oxygen and microorganisms was created on the film samples. This means that LDPE phase became more accessible to oxidative and hence biotic reactions in soil environment after the removal of dispersed starch phase.

CONCLUSIONS

This study demonstrated the preparation of starch containing LDPE nanocomposite films using a novel approach. Starch–clay nanocomposite was first prepared by solution intercalation method and then it was blended with LDPE in the melt state via twin-screw extruder. MAgPE, prepared by reactive extrusion, was used as a compatibilizer between LDPE and starch phases, while the mixture of glycerol and formamide was used as a plasticizer to convert a granular starch into a thermoplastic. To compare the effects of different components on morphology and physico-mechanical properties, compatibilized and uncompatibilized composites as well as plasticized and unplasticized starch formulations were studied. The results showed that the addition of starch solely into LDPE matrix resulted in the deterioration of mechanical properties as well as the physical appearance of polyethylene film

due to the incompatibility between the two phases. The uses of compatibilizer and plasticizer decreased the size of the starch dispersed phase and hence resulted in a better tensile properties compared to LDPE/starch composite. To further enhance the tensile properties, intercalated starch–clay nanocomposite was used. LDPE film including TPS/clay nanocomposite exhibited the most remarkable enhancement in all the properties; namely tensile strength, strain at break, tensile toughness, and transparency. The main reason for these improvements was related to the uniform distribution of both starch and clay particles as well as the effect of clay in inhibiting the evaporation of plasticizer during and after the extrusion process. In biodegradation test, starch molecules in all the samples degraded in the presence of enzymes, resulted in a porous structure of LDPE matrix, which became more susceptible to oxidative and hence biotic reactions.

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