

PREPARATION AND PROPERTIES OF BIODEGRADABLE STARCH/CLAY NANOCOMPOSITE

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Introduction

Pollution due to plastics is a result of the slow rate of disappearance of the synthetic polymers from the environment because of their production via chemical synthesis so that enzymes or microorganisms that degrade or utilize them have not evolved yet. Whereas, the biological polymers, due to their synthesis via the enzymatic route, degrade rapidly in the biological medium. Among the natural biodegradable polymers, starch obtained from various botanical sources, is the most abundant, renewable, and inexpensive biopolymer. However, starch by itself is not suitable for the production of materials due to moisture susceptibility, brittleness, and processing difficulties.

Native starch granules swell when they absorb water through hydrogen bonding with their free hydroxyl groups, but they still retain their order. However, when these swollen starch granules are heated, hydrogen bonding between adjacent glucose units is disrupted and the crystallinity is destroyed. This process is called gelatinization. Addition of a plasticizer such as glycerol or sorbitol can further improve the ductility of GS.¹ Plasticized GS is known as thermoplastic starch (TPS) and is capable of flow. However, poor water resistance and low strength are limiting factors for the materials prepared only from TPS, thus it is often blended with other polymers. The melt blending of TPS has been studied with polyethylene²⁻⁴ and biodegradable polyesters such as polycaprolactone,⁵ polylactic acid⁶ and results indicated that addition of such plasticizers considerably improves mechanical properties when compared with native starch. Even so, starch films had poorer mechanical properties than synthetic polymers and the tensile properties of these blends decreased significantly as TPS content increased. Recent research has indicated that the small addition of inorganic fillers such as organically modified clay particles increased the mechanical properties of TPS⁷

In this study, we mainly focused on the improvement of the physical and mechanical properties of starch by making an organic-inorganic hybrid nanocomposite with pristine clay and starch.

Experimental

Materials. Native corn starch was provided Cargill, Turkey. Natural Na⁺ montmorillonite was supplied by Nanocore, USA. Analytical grade dimethyl sulfoxide (dmsO), glycerol, ethyl acetate, acetic acid, acethyl chloride, and sodium hydroxide were used as received.

Measurements. After the samples are efficiently dried, X-ray diffraction (XRD) experiments were performed using a Bruker AXS-D8 diffractometer with CuK_α radiation, operating at 40kV and 40 mA. Thermal behaviors of the samples were determined by using a Netsch 449C thermogravimetric analyzer (TGA) at the temperature range of 25 to 900°C with a heating rate of 10°C/min. in N₂/O₂ atmosphere. For the morphology observations Leo G34-Supra 35VP scanning electron microscope (SEM) operating with an accelerating voltage of 10kV was used after the samples are fractured in liquid nitrogen and coated with thin carbon film to avoid charge built up due to their low conductivity.

Preparation of Starch/Clay Nanocomposites. The starch/clay ratios with 100/0, 95/5, 93/7, 86/14, 83/17, 81/19, and 77/23 (w/w) were prepared. The clay was dispersed in distilled water, producing a gel that was added to a starch solution prepared by dissolving starch in 90% dmsO solution. For TPS production, this suspension was heated to boiling point for 30 min with continuous stirring to gelatinize the starch granules. Glycerol (20% w/w, clay hybrids relative to starch on dry basis) was added to the hot solution as a plasticizer. All the solutions were put into the ultrasonicator and stirred for different time scale. The solutions were then poured on to acetone to precipitate the resultant polymer/clay composites, followed by the solvent evaporation to dryness at 65 °C and ground to powder. Glycerol-plasticized and unplasticized starch/clay composite films were prepared from starch/clay solutions by casting.

Results and Discussion

Solvent Effect. Different solvents (water, ethyl acetate, water /acetic acid, acethyl chloride, water/ sodium hydroxide, dimethyl sulfoxide) have been tried in order to find the suitable solvent system for the nanocomposite formation. Dispersion occurred when water was used as a solvent and starch completely dissolved in dmsO (90% v/v).

Figure 1 represents that the interplanar basal spacing in pure Na⁺ montmorillonite is 11.40 Å and it remained almost unchanged in starch/clay hybrids when distilled water was used as a solvent. Starch molecules intercalated between the clay galleries only slightly in TPS/clay hybrid. On the contrary, the disappearance of the first basal peak of clay in XRD pattern of starch/clay hybrids showed that exfoliation of the clay layers occurred in unplasticized starch matrix when 90% dmsO was used as a solvent. This observation was attributed to the formation of stable dispersion by dissolving starch completely in dmsO solution so that the strong intermolecular hydrogen bonding between starch molecules that hold them in a big granule sizes decreased and starch-clay interactions improved. In TPS/clay composite samples, intercalation occurred with the d spacing of 16.23 Å.

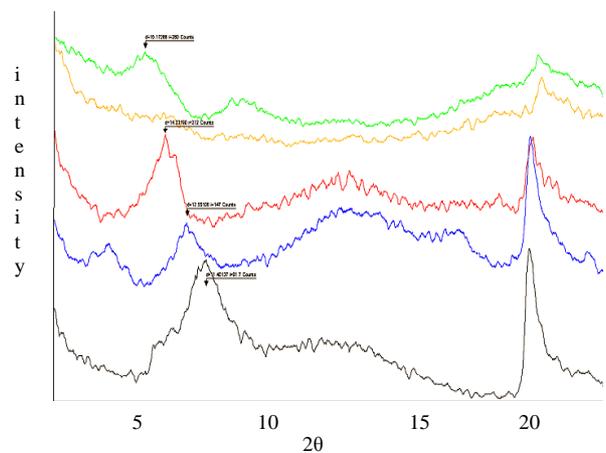


Figure 1. XRD pattern of a) Na⁺ montmorillonite b,c) starch/clay,TPS/clay (in water) d,e)starch/clay, TPS/clay (in DMSO).

Dependency on Concentration and Reaction Time. The effect of reaction time and solid concentration (on the basis of starch) on the clay dispersion were investigated. As illustrated in Table I, it is possible to obtain an intercalated nanocomposite in a very short time of reaction like 3 hours which normally requires much longer time (at least 2 days) when water is used as a solvent. The dispersibility of the clay particles in starch matrix was found to be starch content dependent since the amount of starch dissolved in dmsO solution is limited by the viscosity. Since dmsO is not as cheap as water, the maximum amount of starch dissolved in it for the desired morphology of the nanocomposite is important. XRD results showed that exfoliation occurred up to 13.5 g starch (for 2 days stirring) beyond which intercalation occurred. This observation however was found to be reaction time dependent that it is possible to increase the distance between the clay layers or exfoliate them completely by increasing the stirring time.

Table I. Effect of Starch Concentration and Reaction Time

Starch conc. g/100mL dmsO	8.5	9.0	9.0	9.0	10.5	13.5	13.5	15.0
Stirring time (hours)	3	3	24	48	48	48	168	48
Nanocomp.	Int.	Int.	Int.	Exf.	Exf.	Int.	Exf.	None

Dynamic Mechanical Analysis. Figure 2 shows the variation of loss modulus with temperature for the nanocomposite with and without the glycerol addition. The TPS nanocomposite film showed small frequency

relaxation about -60°C that can be attributed to the partial miscibility of glycerol and starch (pure glycerol has a glass transition of -78 °C). Second relaxation at the vicinity of 40°C is most probably resulting from the loss of moisture during the heating process, leading to a sample contraction, as the water is lost. This contraction makes the films more rigid so E' increases. The film without glycerol exhibited the lower contraction showing more rigidity.

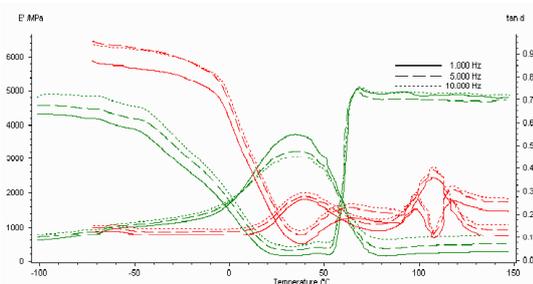


Figure 2. Loss modulus versus temperature a) starch/mmt, b) TPS/mmt hybrid.

Mechanical Properties. The tensile properties of TPS, TPS/mmt and unplasticized starch/mmt composite films are given in Table II. The unplasticized starch/clay film exhibited higher modulus and lower elongation at break compared to glycerol added composite film indicating the plasticizing effect of glycerol unit on the brittleness of the composite film.

Table II. Tensile Properties of Composite Films.

Sample	Tensile Stress at Break (MPa)	Tensile Strain at Break (%)	Young's Modulus (MPa)
TPS film	1.75	188.80	192.89
TPS/mmt film	3.98	56.00	362.00
Starch/mmt film	6.35	11.00	571.00

Thermal Properties. The thermal decomposition of starch followed generally a three-step. The first one attributed to the water loss, the second one corresponds to the starch (and glycerol in TPS) decomposition, and the third one to oxidation of partially decomposed starch. Pure clay exhibited one degradation step corresponds to the clay dehydroxylation at around 750°C. The starch molecules with hydroxyl groups degraded almost completely and rapidly. The presence of clay into the starch/clay and TPS/clay hybrids, however, prevented the mass loss at high temperatures and leading to hydroxyl groups of starch less susceptible to degradation by forming a heat-barrier. This behavior is especially effective after 300°C.

The large difference between the clay content and residual mass in TPS sample was attributable to the fact that the intercalation of the glycerol molecules between the clay layers makes the clay more susceptible to degradation due to the presence of easily degradable hydroxyl groups. The mass loss in the exfoliated composites was a little bit lower than expected which can be explained by the better heat barrier properties of clay structure when it is homogeneously distributed in the starch matrix.

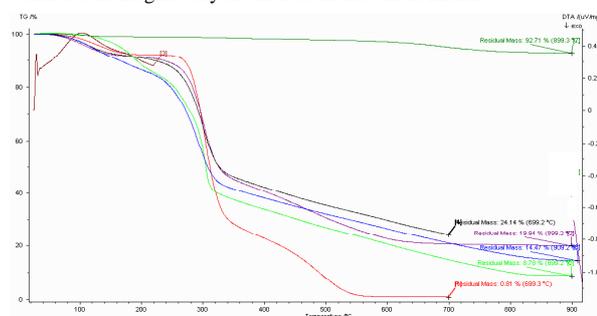


Figure 3. TGA thermograms of pure starch, mmt and nanocomposites.

Table III. Residual mass of the samples with different clay content.

Residual Mass (%)	Sample	Clay Content (%)
92.71	Pure clay	100.0
19.94	Starch/clay/ water	23.0
24.14	Starch/clay/dms0 (exf.)	23.0
14.47	TPS/clay in dms0 (int.)	23.0
8.78	Starch/clay/ dms0(int.)	11.8
0.81	Pure starch	0.0

Morphology of Nanocomposite Films. The morphology of the exfoliated and intercalated films are presented in Figure 4. All the composite films exhibited a homogeneous distribution of clay particles on the starch matrix. The size of the clay particles in the nanocomposite films are in the range of approximately 150-600 nm.

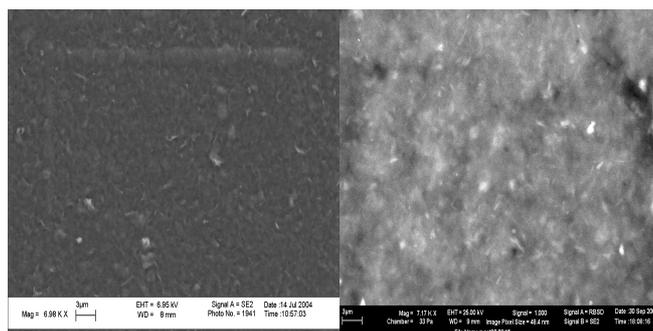


Figure 4. SEM images of exfoliated (left) and intercalated (right) films.

Conclusions

Unplasticized and plasticized starch/clay hybrids were prepared in a new solvent system which provides easy dispersibility of clay particles in starch matrix. The morphology of the nanocomposites was found to be both starch content and reaction time dependent that is by adjusting these parameters, it is possible to obtain the desired form of the nanocomposite. The presence of clay particles makes the film more brittle but the presence of glycerol in TPS/clay hybrid acts as a plasticizer and increase the percent elongation at break compared to unplasticized one. Due to the homogeneously distributed nature of the clay layers in the matrix, exfoliated morphology of the nanocomposite was found to be more stable to high temperatures. The investigation of the physical and biodegradable tests of the nanocomposite films are in progress. Future work includes the blending of this nanocomposites with polyethylene in twin screw extruder in order to provide the heat sealability and flexibility to the films for the packaging application.

Acknowledgements. Financial support given by Sabanci University Research Foundation is gratefully acknowledged. The authors also thank the contribution of Baran Inceoglu from Alcan Rotopak Istanbul in conducting the tensile experiments.

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SYNTHESIS AND PROCESSING OF BIODEGRADABLE LDPE/STARCH-CLAY NANOCOMPOSITES

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The environmental pollution from consumed plastics becomes very serious due to the increasing usage of the synthetic plastics, especially ones used in the packaging materials. With tighter environmental regulations and increasing waste disposal costs, plastic manufacturers are forced to seek solutions or alternatives. One of the challenging ideas in this aspect is the production and usage of biodegradable polymers with the goal of replacing non-biodegradable plastics. Among the natural biodegradable polymers, starches from various botanical sources are the most abundant, renewable, and inexpensive natural biopolymers.

However, biodegradable plastics from starch cannot compete with conventional petroleum-based plastics because starch alone is brittle and sensitive to water. Therefore, starch must be combined with other materials, like synthetic polymers, to produce satisfactory plastic.¹⁻¹⁰ Using starch to partially replace synthetic plastics will not only reduce the dependence on petroleum but also reduce plastic waste. One major problem with granular starch composites, on the other hand, is their limited processibility, due to the big particle size, which make it difficult to produce blown thin film for packaging application. In general, the addition of granular starch to polyolefin results in a severe reduction of tensile strength and elongation at break.¹¹⁻¹² The main problem associated with the use of starch as filler is its hydrophilic nature and consequent incompatibility with the hydrophobic polymers. One of the alternative approaches to bring compatibility between starch and the polymer matrix is by modification of the starch. Native starch granules swell when they absorb water through hydrogen bonding with their free hydroxyl groups, but they still retain their order and crystallinity. However, when these swollen starch granules are heated, hydrogen bonding between adjacent glucose units is disrupted and the crystallinity is destroyed. This process is called gelatinization. The processing of starch and water in a heated extruder is an efficient way to obtain gelatinized starch (GS) since the high shear that can be generated in the extruder disrupts the starch granules. Addition of a plasticizer such as glycerol can further improve the ductility of GS. Plasticized GS is known as thermoplastic starch (TPS) and is capable of flow. However, poor water resistance and low strength are limiting factors for the materials prepared only from TPS, thus it is often blended with other polymers. Yet, starch films had poorer mechanical properties than synthetic polymers and the tensile properties of these blends decreased significantly as TPS content increased. In the last few years, increased interest has focused on the use of starch together with polymers containing reactive groups. Such polymers are styrene-maleic anhydride (SMA) copolymer and ethylene propylene-g-maleic anhydride copolymer (EPMA).^{2,3,13}

Polymers differ in the rate or form of degradation. While biological polymers degrade very rapidly in the biological medium, synthetic ones disappear from the environment very slowly because of their production by chemical synthesis so that enzymes or microorganisms that degrade them have not evolved. However, recent studies have shown that when natural biopolymer is included in the synthetic one, the degradation rate of the synthetic polymer is also increasing. Microbes first create pores on consumption of the biopolymer and increase the surface area of the composite. Increased surface area enhances oxygen-based reactions, which could increase synthetic polymer chain oxidation. Creating oxidized polymer chain ends in a degraded composite will make synthetic polymer susceptible to biotic reactions.¹⁴⁻¹⁷

The purpose of this project is to increase the rate of degradation of one of the most commonly used commodity polymers, polyethylene without deteriorating its mechanical and optical properties. Two major processes for the natural source addition to plastics are considered. One is based on the use of native starch and the other one is based on the use of thermoplastic starch (TPS) as an integral part of the polymeric structure. In order to decrease the moisture sensitivity and enhance the mechanical properties, primarily experiments include the preparation of the starch/clay nanocomposite to be used as a filler material in the main matrix.

Experimental

Materials. LDPE was kindly supplied by Alcan Rotopak A.Ş., Istanbul. Aldrich grade maleic anhydride was used. Native corn starch was provided Cargill, Turkey. Natural Na⁺ montmorillonite (MMT) was supplied by Nanocore, USA. Analytical grade dimethyl sulfoxide (dms), glycerol and formamide were used as received.

Measurements. After the samples were efficiently dried, X-ray diffraction (XRD) experiments were conducted using a Bruker AXS-D8 diffractometer with CuK_α radiation, operating at 40kV and 40 mA. For the morphology observations Leo G34-Supra 35VP scanning electron microscope (SEM) operating with an accelerating voltage of 10kV was used after the samples were fractured in liquid nitrogen and coated with thin carbon film to avoid charge built up due to their low conductivity. 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 UV-3150 spectrophotometer. The tensile tests were performed on Zwick/Roell tensile tester at a cross speed of 50mm/min. according to ASTM D 882-91.

Preparation of Starch/MMT Nanocomposites. To obtain Starch/MMT hybrid with the ratio of 1/12.5 (w/w), starch was first dissolved in 90% dms solution and kept in sonicator for two hours. The clay was then dispersed in distilled water, producing a gel that was added to a starch solution and the mixture was stirred at room temperature. It was then poured onto acetone to precipitate the resultant product. The solvent was evaporated to dryness at 65 °C and the product was grounded to powder.

Melt Grafting of Maleic Anhydride. The grafting reaction of maleic anhydride on LDPE was carried out in a twin screw extruder (Leistritz, screw diameter:27mm, L/D:44). Maleic anhydride, benzoyl peroxide and styrene were premixed with LDPE before feeding into the extruder. The blend was extruded at a constant rotating speed of 100 rpm with barrel temperature profile of 130-170 °C. The product was then dissolved in the hot xylene followed by precipitation in acetone. After drying, it was analyzed by FTIR.

Preparation of LDPE/MAGPE/Starch and LDPE/MAGPE/TPS Blends. LDPE/PEgMA mixture with 64/16 w/w ratio was melt blended with starch (20%) in a twin screw extruder with a barrel temperatures between 150-180 °C and screw speed of 100 rpm. For the blend containing TPS, formamide and glycerol were premixed with starch and kept overnight before the mixture was charged into the extruder. The extruded samples were palletized and then hot pressed to obtain sheet films.

Preparation of LDPE/PEgMA /Starch-Clay and LDPE/ PEgMA /TPS-Clay Nanocomposite. LDPE/PEgMA (64/16 w/w) mixture and starch/clay nanocomposite (20% of total weight) were fed into a twin-screw extruder operating at a proper rotating speed and with a barrel temperature profile of 150-200°C. For the TPS production, starch/clay nanocomposite was mixed with glycerol and formamide before extrusion.

Results and Discussion

Wide-angle x-ray diffraction has provided the information about the degree of delamination of the Na⁺-MMT layers in Starch/MMT hybrid. It was observed that the clay galleries were intercalated by starch molecules with interlayer basal spacing of 17 Å. (Figure 1.)

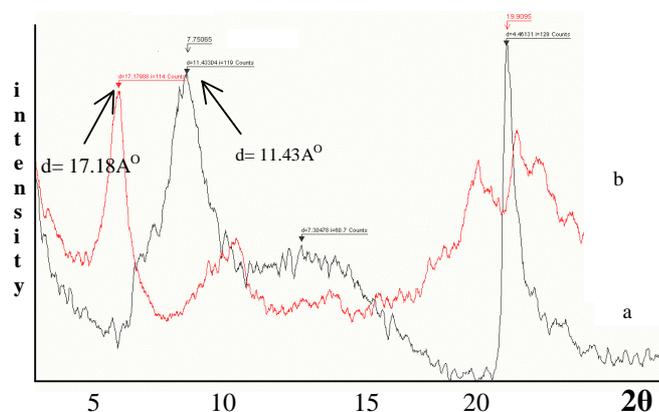


Figure 1. XRD pattern of a) MMT , b) Starch/MMT.

In order to provide the compatibility between starch and LDPE, maleic anhydride was grafted onto polyethylene molecules. MA-g-PE exhibited peak at 1737 cm^{-1} that was assigned to the (C=O) group of carboxylic acid (Figure 2). It can be assumed that most of the grafted maleic anhydride in the sample is in the form of carboxylic acid which provides the active site for the starch binding. The graft degree of MA was found to be 2.13% that was determined from the ratio of peak areas at 2900 cm^{-1} and 1737 cm^{-1} .

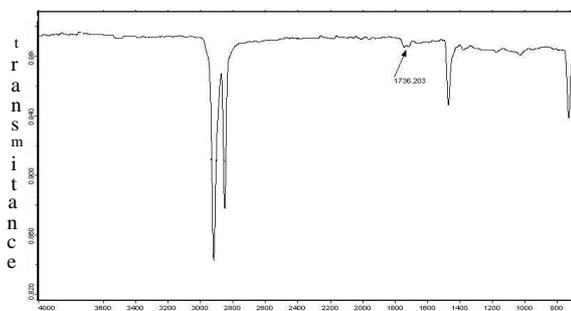


Figure 2. FTIR spectrum of MAGPE.

The effect of maleic anhydride grafting on the morphology of the samples is seen in SEM images (Figure 3). The big granules of starch molecules on the orders of $500\text{-}600\mu\text{m}$ and the poor interfacial adhesion between cornstarch and LDPE matrix indicates that the starch acted as a physical filler in LDPE/Starch blends (Figure 3a) as also suggested by many other authors.² By the addition of MAGPE (25%w/w), starch granule size were significantly reduced to the maximum size of $20\mu\text{m}$ which was further decreased after TPS formation with glycerol and formamide. The disappearance of LDPE/Starch interface distinction after using MAGPE as a compatibilizer also suggests the improved adhesion between filler and the matrix. In addition, FTIR spectrum results has proved the chemical bond interaction between the hydroxyl groups in starch and carboxylic groups in maleic anhydride with the peak appearing at around 1740 cm^{-1} which is due to C=O group of ester linkage (Figure 4).

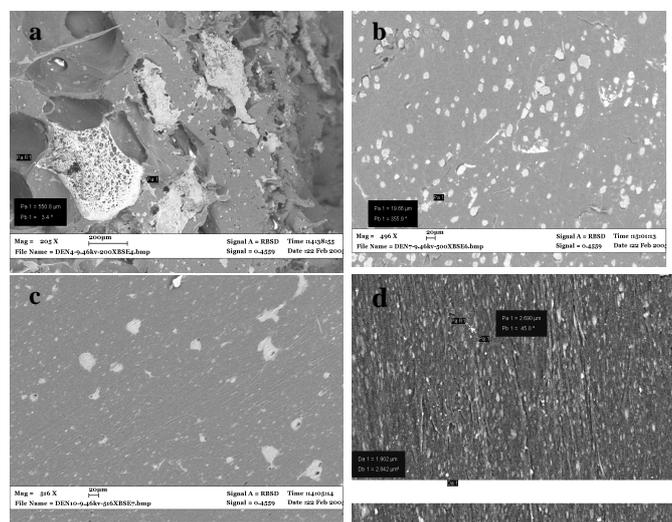


Figure 3. SEM images of Starch/LDPE (a), Starch/MAGPE/PE (b), TPS/MAGPE/PE (c) and LDPE/MAGPE/Starch-MMT(d).

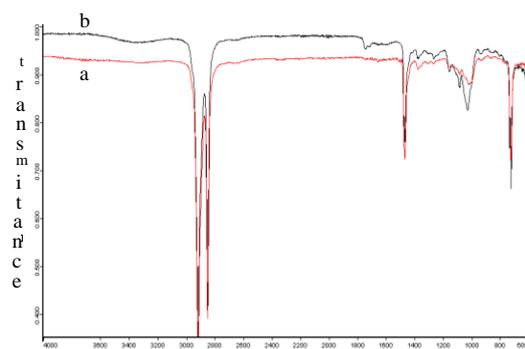


Figure 4. FTIR spectra of (a) LDPE/Starch, (b) LDPE/PEgMA/Starch.

The homogeneous dispersion of the Starch/MMT hybrids on the LDPE matrix providing nanocomposite structure depends on the interaction between the polymer, silicate layers and the starch molecules intercalated between the silicate layers. The strong chemical interaction between the hydroxyl end groups of starch and carboxylic acid groups of maleic anhydride as well as the predispersion of silicate layers in starch in nanoscale ranges provided more homogeneous dispersion of starch/clay hybrid as compared to dispersion of raw starch in LDPE/MAGPE blend. The starch granule size decreased significantly in the final product as seen in SEM image in Figure 3d, with the addition of small amount of clay particles (1.4 w/w). Film clarity also improved and much more transparent film was obtained in LDPE-MAGPE/Starch-MMT film than all the other film samples suggesting the nanostructure of the former product (Figure 5).



Figure 5. Optical appearance of (left) LDPE/PEgMA/ST-MMT, (right)LDPE/ Starch films.

The tensile properties of various polymer sheet films are presented in Table I. As expected, the addition of starch significantly decreased the tensile strength and elongation properties of polyethylene. Using MAGPE as a compatibilizer, however, led to obtain a better tensile strength yet elongation values of the films were still insufficient for many applications. In order to improve the flexibility of the films, strong intermolecular interaction between starch molecules were broken with glycerol and formamide during extrusion process so that starch has been plasticized and melt mixed with LDPE matrix resulting in more homogeneous mixture with less distinct interfacials and better elongation values as compared to pristine starch containing blend. The better distribution of starch molecules after plasticization is also seen in SEM image. Incorporation of small amount of clay particles in the form of Starch/MMT hybrid followed by plasticization of starch improved both the tensile strength and elongation properties much more significantly than all the other trials. Unexpected high elongation behavior of sample 6 can be attributed to three different mechanism. First of all, it is obvious that plasticizing the starch molecules increases the interfacial adhesion between LDPE matrix, starch and clay layers. This increased interfacial adhesion improved the nanoscale reinforcing of the composite and led to the higher elongation as well as higher tensile strength even higher than that of pristine LDPE. Second effective mechanism in the improvement of flexibility with MMT can be due to the modified crystalline structure of the final composite because clay is probably inhibiting the crystallinity and thus increasing the chain mobility. Lastly, presence of MMT may inhibit the evaporation of plasticizer during extrusion process so that it increases the effect of TPS on the elongation properties.

Table I. Mechanical Properties of the composite films.

Sample No	Sample	Tensile Strength (Mpa)	Strain @ Break (%)	Young' Modulus (Mpa)
1	LDPE	9.72	>500	107.96
2	PE / ST	6.59	22.39	123.83
3	PE-PEgMA/ ST	8.88	24.75	151.54
4	PE-PEgMA/ TPS	8.31	55.21	125.50
5	PE-PEgMA/ ST-MMT	8.79	31.47	159.31
6	PE-PEgMA/ TPS-MMT	10.58	125.23	137.62

Biodegradation rate of starch containing films were investigated 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. In order to determine total amount of glucose in starch granules, raw starch film was also incubated in enzyme solution. Figure 6 presents the biodegradation rate of starch in 20%starch containing composite films. All the films exhibited the similar trend in starch degradation rate at the beginning and the presence of MMT did not inhibit the degradation rate until about 45% starch content has been digested after which degradation rate started to slow down. This behavior is most probably due to the easy attachment of enzyme to starch molecules on the surface but the diffusion to the underlayer starch molecules would be more difficult and thus slowly due to the presence of silicate layers.

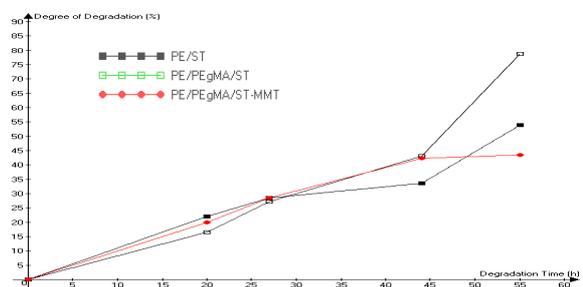


Figure 6. Biodegradation rates of starch in 20% starch containing films.

SEM images were also taken from the degraded composite films after 55 hours of incubation and formation of pores in starch granules were observed in all the film surfaces (Figure7).

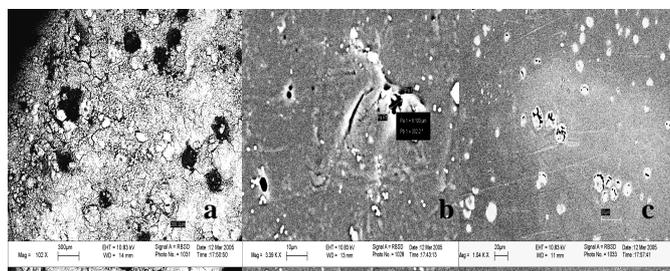


Figure 7. SEM images of degraded (a) LDPE/Starch, (b) LDPE/MAGPE/Starch and (c) LDPE/MAGPE/Starch-MMT composite films.

Conclusions.

In the present study, starch was incorporated into LDPE matrix in order to make it biodegradable, at least partially. However, adding starch deteriorated the mechanical properties as well as the physical appearance of polyethylene film in a great extent that could be solved by addition of 25% MagPE as a compatibilizer. The starch granule size and the presence of distinct interfacials were found to greatly influence the mechanical properties. The interfacial adhesion between starch and the matrix polymer was improved by addition of plasticizers which in turn increased the flexibility of films. The effect of using small amount of MMT in predispersed form was much more pronounced in the improvement of tensile properties and physical appearance due to the stress distributing and uniform dispersion behaviours of nanostructure. All the composite films exhibited the pores on the surface of film samples due to degradation of starch granules. Presence of clay particles slowly inhibited the degradation degree only at high exposure time to enzyme solution most probably due to small diffusion rate of enzymes to the underlayer of starch surfaces.

Acknowledgements. Financial support given by Sabanci University Research Foundation is gratefully acknowledged.

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