

## Physical and Thermal Mechanical Properties of Corn Starch/LDPE Composites

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**ABSTRACT:** The potential of biodegradable polymers has long been recognized. In this work, composites of low density polyethylene (LDPE) and low density polyethylene/thermoplastic starch (LDPE/TPS) at different ratios of TPS (40%-60% w/w) were prepared in internal mixer. Polyethylene-grafted maleic anhydride (PE-g-MA) at 3 wt % was used as coupling agent. Chemical reactions between functional groups of composite components were studied and confirmed by Fourier transforms infrared (FTIR) spectroscopy. The morphology of film surfaces was studied using scanning electron microscopy. The physical, mechanical, and dynamic-mechanical thermal analyses of LDPE/TPS composites were evaluated. The FTIR results showed transmission peak at  $1642\text{ cm}^{-1}$ , which is the result of chemical reaction between the hydroxyl groups of starch and anhydride groups of coupling agent. This verifies the presence of the carboxylate group due to the formation of ester bonding. The results showed that the water absorption and density of composite films increased by increasing the starch content in LDPE/TPS composites. The tensile strength and elongation at break decreased by increasing the starch level in the composites, but the young's modulus increased. The morphological studies showed that the biodegradability of composites increased by increasing the starch content and the results was confirmed by weight loss in burying the samples in wet soil during time intervals. The dynamic mechanical thermal analyzer thermograms showed that there are two relaxation temperature peaks. The amplitude of peaks increased by increasing the starch content from 40 to 60% probably due to increasing amorphous phase of composite. The starch was uniformly distributed throughout the LDPE polymer matrix and compatible and biodegradable composites were formed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** low-density polyethylene; thermoplastic starch; DMTA; physical properties; biodegradable composite

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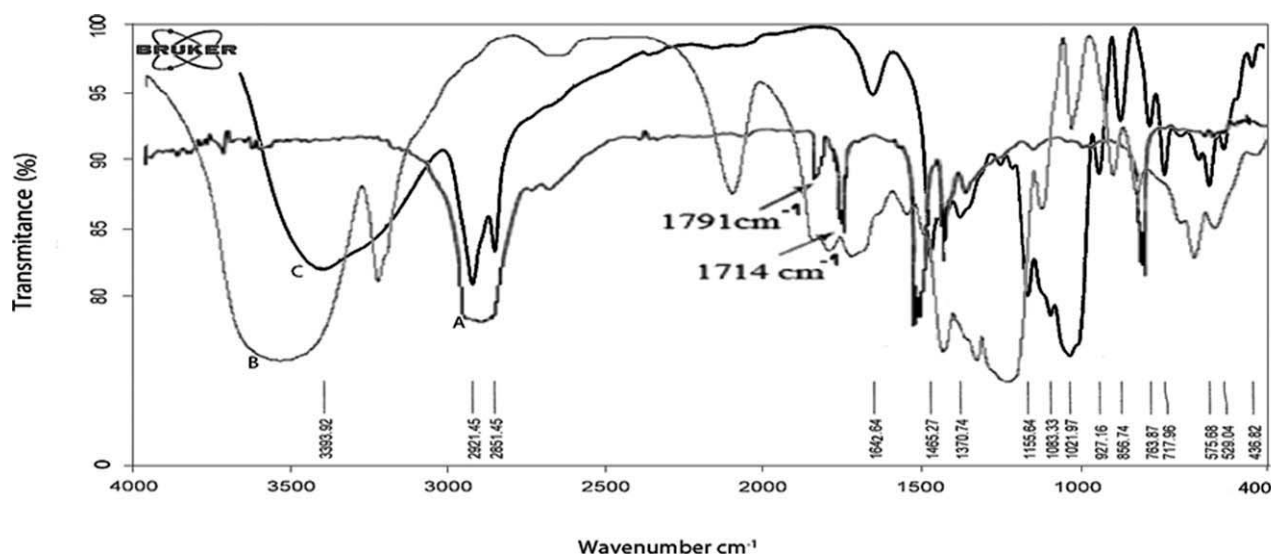
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### INTRODUCTION

Composites are materials composed of a mixture of two or more phases.<sup>1,2</sup> Composites are increasingly replacing metals in many applications, especially in particular engineering, where the main advantage is weight reduction with improved mechanical properties. Biodegradable polymers are materials that can be degraded by micro-organisms and enzymes. The use of such polymers provides an approach to the problem of plastic waste. Biodegradable polymers can also be used for medical applications such as implants, sutures and in drug release, and for agricultural applications such as mulch and agrochemicals.<sup>3–7</sup> Polymers that are biologically degraded contain functional groups that are susceptible to enzymatic hydrolysis and oxidation. Polyesters, polyvinyl alcohol, and polyvinylethanoate are examples of such materials. Biodegradable polymers need to be designed to

have a certain lifetime and then have degradation triggered by, for instance, exposure to ultraviolet radiation.

Starch is an important productive polysaccharide in plants. Because of its low cost availability as a renewable resource, biodegradable, and innocuous degradation products, it has already been widely researched.<sup>8,9</sup> Starch is not a true thermoplastic but in the presence of plasticizer at high temperature and under shear, it can readily melt and flow, similar to most conventional synthetic thermoplastic polymers.<sup>10</sup> Plasticizers increase starch flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular space. The main plasticizer used in thermoplastic starch is glycerol.<sup>8,11,12</sup> The proportion of plasticizer and its chemical nature strongly influence physical properties of TPS.<sup>12,13,14</sup> One approach to reinforce plasticized starch is to composite TPS with synthetic



**Figure 1.** FTIR spectra of (a) pure PE-g-MA, (b) corn starch, and (c) LDPE/TPS composite from 400 to 4000  $\text{cm}^{-1}$ .

polymers.<sup>15</sup> However, TPS and synthetic polymers tend to separate from each other due to incompatible chemical structures.

According to the previous works,<sup>16–18</sup> different factors such as weight percent of composite components, plasticizer, coupling agent, and starch types were studied. Also, other author researchers applied different processing methods to prepare biodegradable composites.<sup>19–21</sup> This article describes the preparation of thermoplastic starch by premixing corn starch with glycerol (30 wt % of starch) and reinforcing with synthetic polymer such as low density polyethylene (LDPE). Maleic anhydride-grafted-polyethylene (PE-g-MA) was introduced into the low density polyethylene/thermoplastic starch (LDPE/TPS) samples as coupling agent to prepare biodegradable LDPE/TPS films and improvement of phase compatibility.

## EXPERIMENTAL

### Materials

All raw materials were obtained from local marked made in Iran as follows:

Corn starch containing 30 wt % amylose and 70 wt % amylopectin was obtained from Glocozan Co. (Ghazvin, Iran) Extra pure grade of Glycerol was purchased from Dr. Mojalali Co.

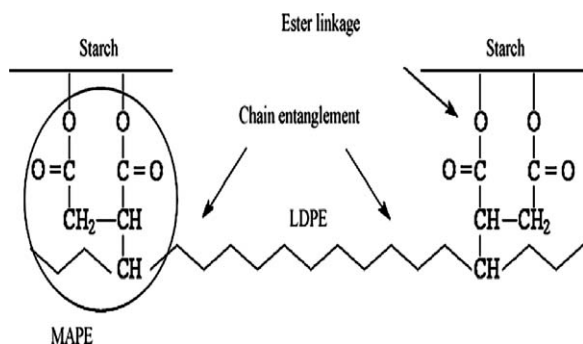
(Tehran, Iran) LDPE (LF0200) with MFI of 2 g/10 min (at 190°C) was obtained from Arak Petrochemical Co. (Arak, Iran) PE-g-MA (Karaband ELH) as coupling agent was obtained from Grankin Co. (Teharn, Iran), containing 1.7 mol % anhydride groups with MFI of 0.6 g/10 min (at 190°C).

### Sample Preparation

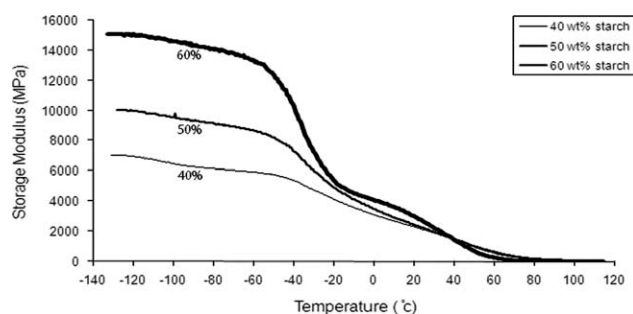
Corn starch was premixed with glycerol (30 wt % of starch). The composites of LDPE/TPS were prepared using 40, 50, 60, and 100 wt % of LDPE. The 3 wt % of PE-g-MA coupling agent was added in all samples. Haake–Buchler Reomixer (HBISYS 90) was used for mixing processes. The working temperature was set up at 120°C, and the speed of screw was set at 60 rpm for 10 min to obtain a homogenous material. Polymers fed into the mixer are subdivided or melted under shear stress by the rotating rotors and mixed with filler. After the mixture passes through a dispersive mixing step and a distributive mixing step, the homogenous mixture is discharged from the mixer. After processing, the samples were hot pressed to obtain 300- $\mu\text{m}$  thickness films.

### Dynamic Mechanical Thermal Analyzer Analysis

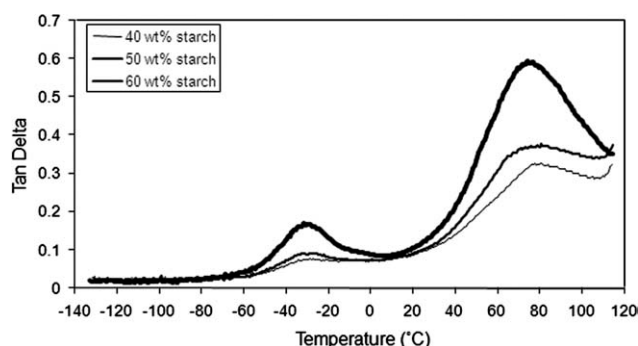
Dynamic mechanical thermal properties were measured using a dynamic mechanical thermal analyzer (DMTA), model DMTA-PL, over a temperature range of  $-130$  up to  $120^\circ\text{C}$  at 1 Hz and



**Figure 2.** Schematic interaction between starch and maleic anhydride.



**Figure 3.** Storage modulus of LDPE/TPS composites containing 40, 50, and 60% of starch.



**Figure 4.**  $\tan \delta$  of LDPE/TPS composites containing 40, 50, and 60% of starch.

a heating rate of  $5^{\circ}\text{C}/\text{min}$ . The measurement was carried out using the dual cantilever bending mode.

## PHYSICAL PROPERTIES

### Water Absorption

The composite films were immersed in boiling distilled water for 2 h, according to the ASTM D570-98 method. The films were taken out and wiped to measure the water absorption in weight percent. The percentage of water absorption was calculated as following:<sup>22,23</sup>

$$\text{waterabsorption} = W_2 - W_1 / W_1 \times 100 \quad (1)$$

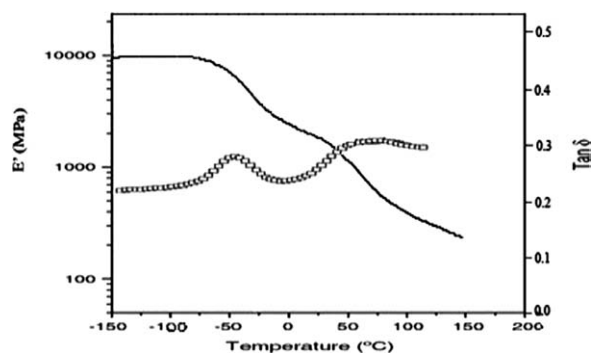
where  $W_2$  and  $W_1$  are the weight of wet and dry films, respectively.

### Density

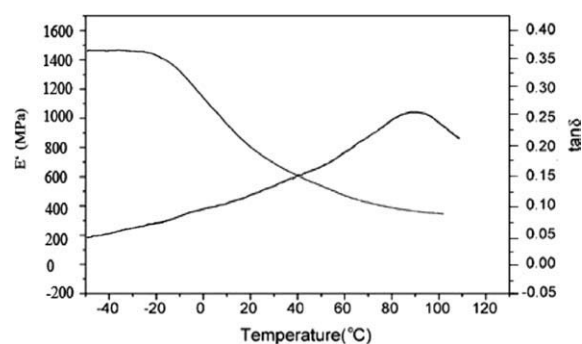
Density measurements were carried out according to the ASTM D792-00 method using the kite densitometer.

### Mechanical Properties

Modulus, tensile strength, and elongation at break of composite films were measured on an instron mechanical tester model 1067 MTS. The samples, previously conditioned at 30% of relative humidity at  $23^{\circ}\text{C}$  for 48 h, in a closed chamber containing a saturated  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution in distilled water were tested according to ASTM D638 method, using a crosshead speed of  $10 \text{ mm}/\text{min}$ . Four measurements of each composition were tested and the average value was taken.



**Figure 5.** Storage modulus and  $\tan \delta$  behavior of TPS.



**Figure 6.** Storage modulus and  $\tan \delta$  curve of pure LDPE.

### Scanning Electron Microscopy

The composite film surfaces were observed with a scanning electron microscope (Vega Tescan model). The scanning electron microscopy (SEM) was operated at  $23^{\circ}\text{C}$ , 37% of RH and 20 kV of voltage. All surfaces were coated with gold to avoid charging under the electron beam. All the composite film micrographs were reported after burring in wet soil condition.

### Fourier Transforms Infrared Spectroscopy

Infrared spectroscopy is a popular method for characterizing polymers.<sup>24,25</sup> It was used to investigate the reaction between starch and maleic anhydride. Fourier transforms infrared (FTIR) spectra of LDPE/TPS composites were recorded on a FTIR Bruker spectrometer, Tensor 27 model, using KBr disk technique in a spectral range of  $400\text{--}4000 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### FTIR Spectroscopy

FTIR spectra of pure PE-g-MA, Corn starch, and LDPE/TPS composites were characterized and confirmed in the range of  $400\text{--}4000 \text{ cm}^{-1}$  (Figure 1). The FTIR spectrum of pure PE-g-MA copolymer shows two main peaks at region of  $1714$  and  $1791 \text{ cm}^{-1}$ , which is related to symmetry and asymmetry maleic anhydride groups, respectively.<sup>26,27</sup> According to corn starch spectrum, the bands at region of  $3200\text{--}3400$  and  $2850\text{--}2900 \text{ cm}^{-1}$  are attributed to O-H stretching and  $\text{CH}_2$  stretching vibrations. The bands at domains  $1600\text{--}1700$ ,  $1300\text{--}1450$ , and  $850\text{--}900 \text{ cm}^{-1}$  representing the  $\text{--C--C--}$  stretching, O-H bending and  $\text{--C--C--}$  bending, respectively.<sup>27,28</sup>

In the FTIR spectrum of LDPE/TPS composite at  $400\text{--}4000 \text{ cm}^{-1}$  two main transmission peaks of  $1791$  and  $1714 \text{ cm}^{-1}$  related to anhydride ring of coupling agent disappeared and a broad peak at  $1642 \text{ cm}^{-1}$  is formed. The formed band at region of  $1642 \text{ cm}^{-1}$  is attributed to formation of ester groups, which is the result of reaction between the hydroxyl group of starch and anhydride groups of coupling agent. The ester bond formation at regions of  $1642 \text{ cm}^{-1}$  and  $1000$  to  $1200 \text{ cm}^{-1}$  is indicative of breakage of anhydride ring and binding of starch with LDPE. As already mentioned, the peak position at  $1642 \text{ cm}^{-1}$  is the result of resonance between the carbonyl group and non-paired electrons on oxygen which cause the ester group to appear at lower wave numbers.<sup>23,26</sup> The LDPE/TPS composite also includes two peaks at  $1465$  and  $850\text{--}950 \text{ cm}^{-1}$ , which are

**Table I.** Physico-Mechanical Properties of LDPE/TPS Films

Composition of LDPE/TPS (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Water absorption (%)	Density (g/cc)
100/0	11.6	691	171	0.005	0.9202
60/40	9.6	13.3	317	2.81	1.0854
50/50	8.5	5.42	433	6.41	1.1501
40/60	6.8	4.5	590	10.08	1.2027
0/100	2.3	4.3	579	96.61	1.4301

representative of the  $-\text{CH}_3$  and  $\text{C}-\text{C}$  bending vibrations, respectively.<sup>29,30</sup>

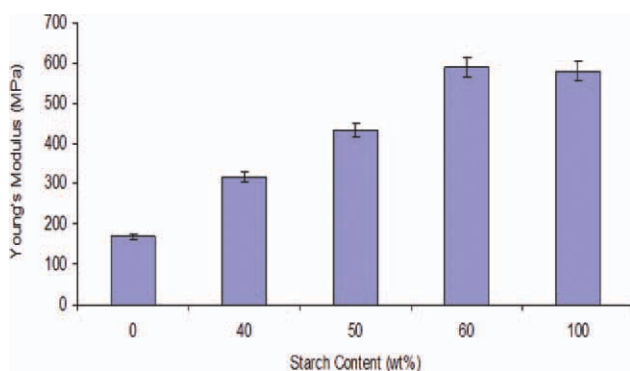
Figure 2 depicts breakage of anhydride functional groups, related to coupling agent and bonding formation with starch due to interaction between carboxylate and hydroxyl groups. Therefore, the coupling agent caused starch linkage to LDPE matrix by chemical bondings.<sup>13,22,28</sup>

### Dynamic Mechanical Thermal Analysis

The thermal properties of LDPE/TPS composites containing 40–60% of starch and constant content of compatibilizer were studied using DMTA technique (Figures 3 and 4). Previous studies have shown that unplasticized starch presents a unique  $\alpha$  relaxation or  $T_g$  at around  $50^\circ\text{C}$ .<sup>31,32</sup> Pure glycerol (plasticizer) has a glass transition temperature of  $-78^\circ\text{C}$ .<sup>33</sup> As shown in Figure 5, plasticized starch by means of glycerol is a heterogenous mixture. The storage modulus and  $\tan \delta$  thermograms shows a phase separation which results in glycerol-rich domains and starch-rich domains.<sup>34,35</sup> This can be attributed to presence of two phases that originated from the partial miscibility of glycerol and starch.<sup>10,36</sup>

Munaro et al. showed that the pure LDPE has three transition relaxation peaks. The thermo-grams (Figure 6) shows that the  $E''$  decreased slowly followed by the appearance of a shoulder at about  $-10$  to  $0^\circ\text{C}$  and a significant peak at about  $80^\circ\text{C}$  are attributed to  $\beta$  relaxation which has the properties of glass transition temperature and  $\alpha$ -transition peak, respectively.<sup>37,38</sup>

In LDPE/TPS composite sample (Figure 3), the higher the starch content, the higher is the storage modulus. The reason can be attributed to stiffness of the starch and rigidity character



**Figure 7.** Young's modulus of LDPE/TPS composite films. [Color figure can be viewed in the online issue, which is available at [www.wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

of starch in comparison with the PE structure. In composite containing starch which possesses  $-\text{OH}$  groups have tendency for inter and intra-molecular hydrogen bonds would restrict the chain movements.

According to (Figure 4), the thermograms of the  $\tan \delta$  of composites distinctly exhibit two relaxation peaks.<sup>22,39</sup> The higher temperature peak situated at about  $80^\circ\text{C}$  with slightly shift to lower temperatures is an overlap of LDPE  $\alpha$ -transition and glass transition temperature of TPS, even though a significant growth in amplitude at higher amount of TPS in composites is seen. Although the peak amplitude of the lower temperature peak situated nearly at  $-30$  to  $-40^\circ\text{C}$  is increased with increasing the glycerol content in composite, but the position does not change.<sup>40</sup>

The shift of the higher temperature peak is indicative of compatibility between starch and LDPE in composite. As it is well known that starch is a semi crystalline mixture, the significant growth in amplitude of the higher peak by changing the starch content from 40 to 60% is probably related to increasing amorphous phase of composite. This indicates that the energy dissipation ability is increased with incorporation of more starch amounts to the composite, due to amorphous character of starch. This is because at constant weight percent of coupling agent, the loss modulus is increased by increasing the composite TPS content leading to improvement of elastic behavior of LDPE/TPS composite.<sup>38,40</sup>

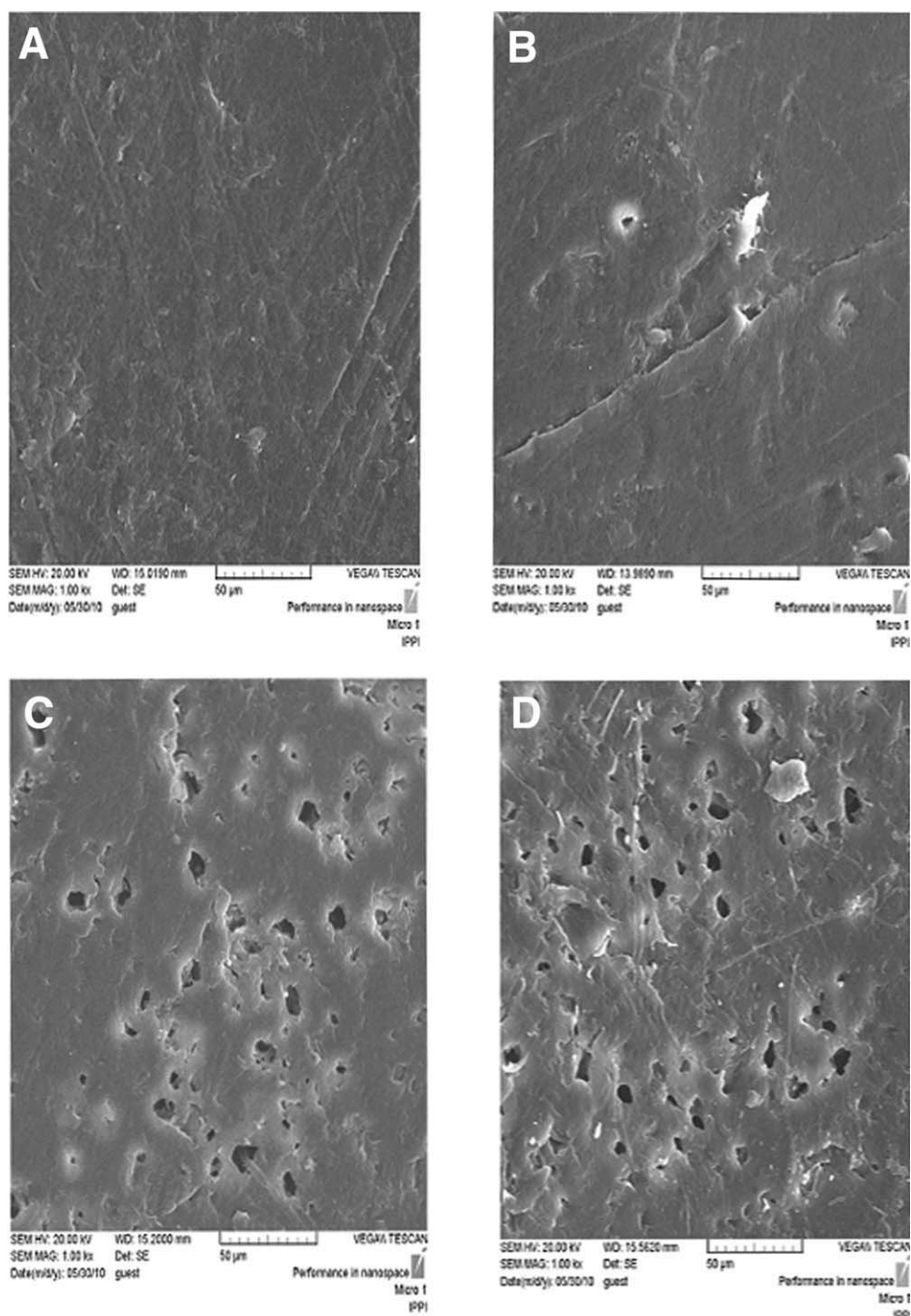
## PHYSICAL PROPERTIES

### Density

The density of composite films depends on starch content. Therefore, the higher the starch content, the higher is the density. By increasing the starch content, the hydrophilicity of the composites will increase. The densities of LDPE, LDPE/TPS composites, and pure starch films were from 0.9202 up to 1.4301 g/cc, respectively (Table I). The obtained data showed comparable results found by Raj. Baldev et al.<sup>29</sup>

### Water Absorption

The water absorption of composite films is directly proportional to starch amount incorporated into polymer matrix. In other word, the water absorption would increase by increasing the starch content in LDPE. The starch is responsible for water absorption due to hydrophilic nature of starch and ionic character of hydroxyl groups of starch.<sup>29</sup> Composites with more water absorption have lower mechanical properties. Regarding the starch content, the water absorption of pure PE, composites and pure starch is varied from 0.005 up to 96.61% (Table I),



**Figure 8.** SEM micrographs of (a) 100% PE, (b) 60/40%, (c) 50/50%, and (d) 40/60% of LDPE/TPS

which showed reasonable water absorption in comparison with Raj.Baldev et al work.<sup>29</sup> The water absorption of LDPE reported between 0.005 and 0.015 (%).<sup>41</sup>

### MECHANICAL PROPERTIES

#### Tensile Strength

The tensile strength is inversely proportional to starch content. It is seen that there is a gradual decrease in tensile strength with increasing starch content in LDPE/TPS films. The pure LDPE

has the highest tensile strength. This is because LDPE is a tough material and pure starch is a brittle material.<sup>11,22,26,42</sup> Incorporation of starch in LDPE/TPS composite, as expected, causes matrix embrittlement, because of replacement of a tough matrix with a brittle material. The obtained results showed that the tensile strength of composites containing different amount of starch in comparison with the reported results by Bikiaris et al.<sup>27</sup> has improved even at lower content of compatibilizer, 1.5 g of PE-g-MA (Table I).

### Elongation at Break

The elongation at break of LDPE/TPS composite films is inversely proportional with starch content due to its embrittlement properties. The elongation at break decreases from 690.971% down to 4.301% with increase in starch content from 0 to 100%. This is due to (i) physical incorporation of starch in the matrix of LDPE that weakens the London forces between LDPE layers and (ii) the fact that starch, a low molecular weight polymer, has lower elongation compared to LDPE.<sup>12,43</sup> Incorporation of starch causes discontinuity in the film matrix, leading to lower elongation due to lack of chemical interaction between starch and LDPE. An indication of the elongation at break results achieved is depicted in (Table I).

### Young's Modulus

The young's modulus is directly proportional to starch content. Therefore, the young's modulus increased by increasing the starch content (Figure 7). The molecular weight of starch is higher than that of polyethylene, so the starch young's modulus is higher than polyethylene young's modulus. The young's modulus achieved showed better results in comparison with other researcher's works.<sup>11,23,26</sup>

### Morphological Studies

The effect of starch contents of 0% (A), 40% (B), 50% (C), and 60% (D) on biodegradability of the composites films in 120 days was studied (Figure 8). The results showed that the biodegradability of composites increased by increasing the starch content. It was because hydrophilicity of composite due to higher water absorption and micro-organisms attack. This is evidence that the consumption of starch and the holes that are created increase the surface of the LDPE, and as a result, the micro-organisms can attack the LDPE matrix more easily, creating favorable conditions for the consumption of polyethylene oligomers.<sup>29,40</sup>

The biodegradability of the films was confirmed in comparison with morphological analysis by burying the films in wet soil and measuring the weight loss during the monthly intervals.<sup>22</sup> The weight loss of the films after 30, 45, 75, 105, and 120 days confirmed the obtained results from morphological studies.

### CONCLUSIONS

To prepare LDPE biodegradable films, a series of composite containing different amounts of starch and LDPE was planned. Various combinations including starch concentrations ranging from 40 to 60 wt %, and LDPE were mixed and converted into films. In this regard, the mechanical properties of composites in comparison with synthetic polymers decreased but biodegradability improved. The FTIR studies verified the chemical structure of composites and incorporation of starch, LDPE, and coupling agent. Disappearance of absorption peaks of anhydride group at 1719 and 1714  $\text{cm}^{-1}$  and the presence of absorption peak at 1642  $\text{cm}^{-1}$  is indicative of interaction between the composite components. On the basis of SEM micrographs, the biodegradability of the composite films increased by increasing the amount of starch. It could be concluded that the starch has direct effect on biodegradation because micro-organisms would attack to starch leading to biodegradability of the composite films. The water absorp-

tion and density of composite films increased from 2.81 to 96.61% and 1.0854 to 1.4301, respectively, by increasing the starch content. Tensile strength and elongation at break decreased gradually from 9.6 to 2.3 MPa and 13.302 to 4.301%, respectively, and young's modulus increased from 316.626 to 579.272 MPa as the starch concentration increased from 40 to 100%. The DMTA results clearly showed two relaxation temperature peaks for LDPE/TPS composites. It could be concluded that starch is distributed uniformly at LDPE matrix and compatible composite was formed. The optimum value of starch in composite to improve the polymer biodegradability, with less sacrificing the mechanical and physical properties were obtained to be 60 wt % of starch content.

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