IPPI

Polyolefins Journal, Vol. 6, No. 2 (2019)
DOI: 10.22063/poj.2019.2390.1130

ORIGINAl PAPER

Impact, thermal and biodegradation properties of high impact polystyrene/corn starch blends processed via melt extrusion

Ali Mahmoudi Yayshahri[1], Seyed Jamaleddin Peighambardoust[1*], Abolfazl Shenavar[2]

[1]Faculty of Chemical and Petroleum Engineering, University of Tabriz, Tabriz, 51666-16471, Iran
[2]R&D Centre of Tabriz Petrochemical Complex (TPC), Tabriz, 51335-1996, Iran

Received: 31 January 2019, Accepted: 19 March 2019

ABSTRACT

High impact polystyrene (HIPS)/corn starch blends were prepared in presence of glycerol as a plasticizer via melt extrusion process by a twin-screw extruder. The novelty of this work is the use of pre-gelatinized corn starch which is a new modified corn starch. In addition, the procedure of making blends by extruder is easy and practical from the industrial point of view. The blends were then characterized by scanning electron microscopy (SEM) to visualize their morphology and dispersion of starch in HIPS matrix, soil burial test (SBT) to investigate blend biodegradability by measuring weight loss of samples, Izod impact strength test to evaluate impact properties, and melt flow index (MFI), thermo-gravimetric analysis (TGA) and Vicat softening point (VSP) tests to evaluate their thermal properties. The results indicated that these properties were affected by the amount of starch and glycerol used for preparation of blends in a way that the addition of starch and glycerol led to a faster degradation rate especially in the first two weeks, more decomposition stages, and a decrease in the values of Izod impact strength and VSP. Measurements also showed that higher amount of starch led to a decrease in the value of melt flow rate (MFR), although it was increased by addition of glycerol. **Polyolefins J (2019) 6: 151-158**

Keywords: High impact polystyrene; corn starch; glycerol; melt extrusion; biodegradation.

INTRODUCTION

Use of conventional plastics made of fossil fuels has been increased recently in different industries because of their low price and proper mechanical characteristics. On the other hand, their resistance against attack of microorganisms has caused many environmental problems. So, the discussion about their degradation methods has been a topic of many recent studies in order to find out how to control the problems [1-3].

The purpose of making biodegradable plastics is to produce polymer blends with the same properties or at least near to them, but convertible to non-toxic materials. For this purpose, biomaterials should be used like biopolymers as prominent examples [4]. High impact polystyrene (HIPS) is a modified polystyrene which is made of a kind of rubber as a dispersed phase in PS matrix in order to improve its impact strength. High-

---

* Corresponding Author - E-mail: j.peighambardoust@tabrizu.ac.ir

impact polystyrene (HIPS) is a multiphase copolymer system in which polybutadiene (PB) rubber particles are dispersed in the polystyrene (PS) rigid matrix. HIPS is employed in a wide range of applications, such as packaging, automotive components, building materials, electronic instruments and electrical appliances due to its low cost, good impact resistance and easy processing [5-6]. HIPS is widely used in packaging industries [7] and because of high molecular weight, high crystalline level and mechanical properties, it is degraded very slowly in the environment [8]. Microbial degradation is the primary process in the natural decaying, and this involves adherence and subsequent colonization of microorganisms on the surfaces. Plastics contain complex polymeric bonds that resist normal deterioration. The microbial extracellular enzymes can bind to plastic substrates and catalyze hydrolytic cleavage. Polymers are converted into low molecular weight oligomers, dimers, and monomers and finally mineralized to CO_2 and H_2O [9-10]. Starch is an abundant low-priced natural biopolymer that its structure should be modified for conventional industrial processes like casting, extrusion, etc. because it is degraded before molding [11]. One of the modified starches is pre-gelatinized one which is known as quick starch. It is produced by gelatinizing in presence of heat then dried by extruder, spray or roller dryers [12].

Studies approve that addition of starch to synthetic polymers like HIPS, aids the production of biodegradable polymer blends since the microorganisms consume the starch so the blend loses its integrity [8]. For increasing the flexibility of the blends containing starch, glycerol is utilized as a plasticizer [13]. It has three hydroxyl groups that make its structure to be hydrophilic and flexible. Some studies have been done in order to prepare biodegradable PS/starch so far [14-16]. In these studies, thermoplastic starch has been used as the modified starch which is not produced widely. The aim of this study is to prepare HIPS/corn starch blends by pre-gelatinized corn starch as modified one which is produced industrially in large scale. On the other hand, an extrusion process with use of a twin-screw extruder has been applied. These kinds of processes are used widely for compounding, mixing and reacting polymeric materials in polymer industries [15-17].

EXPERIMENTAL

Materials

High impact polystyrene (HIPS) grade 7240 (ρ=1.04 gr/cm^3) was purchased from Tabriz Petrochemical Co. This grade is mostly used in industries related to food production. Analytical grade glycerol was purchased from Dr. Mojallali Co. (ρ=1.26 gr/cm^3). Glycerol is an alcohol with three hydroxyl groups, which is used as a plasticizer. Pre-gelatinized corn starch composed of 26-30 wt% amylose, 74-70 wt% amylopectin and 7 wt% moisture was supplied from Glucozan Co.

Samples preparation

HIPS, starch and glycerol were mixed in nine different ratios listed in Table 1. After making them as a uniform mixture, they were fed into a co-rotating twin-screw extruder (SM-PLATEK, South Korea) with a screw diameter of 20 mm and L/D ratio of 32. Also, it is formed of eight parts that their temperatures were set to 136, 166, 172, 175, 185, 193, 194 and 210°C, respectively for this study. Rotation speed of the feeder and extruder was 35 rpm and 142 rpm, respectively. Also, extruder pressure was 8 bar. Melted blends were cooled with water and then made as granules by a specific cutter. The granules should be processed as films in order to have a right comparison with non-biodegradable HIPS films found in food markets. A twin-screw film extruder (Castiny, Italy) was used for processing of granules as films.

Characterization methods

Scanning electron microscopy (SEM)

SEM was used to study the morphology of prepared films cross-section. Blend specimens were prepared by quick freezing of the dry samples in liquid nitrogen

Table 1. Code name and composition of blend samples (%wt.).

Glycerol (%)	Starch (%)	HIPS (%)	Sample Code
0	0	100	Pure HIPS
3	15	82	HIPS -ST15-GL3*
5	15	80	HIPS -ST15-GL5
7	15	78	HIPS -ST15-GL7
3	10	87	HIPS -ST10-GL3
5	10	85	HIPS -ST10-GL5
7	10	83	HIPS -ST10-GL7
3	5	92	HIPS -ST5-GL3
5	5	90	HIPS -ST5-GL5
7	5	88	HIPS -ST5-GL7

*ST : Starch and GL : Glycerol

followed by breaking it to produce fresh cross-sections. Fresh cross-sectional cryogenic fractures of the samples were vacuum sputtered with a thin layer of gold (Au) using an ion sputtering before observing on the scanning electron microscope (VEGA\\TESCAN, Czech Republic) with a potential of 300 V to 20 kV.

Thermal studies of blend samples

Thermal degradation analysis was carried out using a Pyris Diamond thermo-gravimetric analyzer. Temperature was raised from 25 to 500°C at a heating rate of 10°C min^{-1} and under helium atmosphere in order to determine mass loss of blends.

Izod impact strength test

This test was determined in accordance with ASTM D256 using a Resil impactor (coded 6967.00, Ceast, Italy). Five specimens were tested for every sample and then were averaged. In addition to notched Izod impact strength test, un-notched test was applied too. The ASTM test method for un-notched Izod is D4812. It is similar to ASTM D256 except that the specimens are not notched. It is used to measure the ability of a polymeric sample in absorption of energy. As the amount of impact strength is lower, sample is more brittle.

Melt flow index (MFI)

Flow rate of polymer melt was determined in accordance with ASTM D1238 using a melt flow index tester (Ceast, Italy) for specimen of 5 gr weight in 10 min. In fact this test is used to evaluate facilitation of polymer flow.

Vicat softening point (VSP)

Vicat softening point (VSP) was measured according to ASTM D1525 using an HD-PC (Yasuda, Japan) machine for at least two specimens with size of 10×10 mm prepared by injection molding then was averaged. It is mostly used for measurement of softening point of materials with unknown melting point like plastics.

Soil burial test (SBT)

Biodegradation of HIPS/starch blends was investigated by soil burial test in accordance with ASTM G160 under conditions explained in the standard method. Total moisture of soil was 20-30% wt. and pH was 6.9-7.1. Samples were cut into pieces of 5×5 cm with thickness of 100±5 μm. Three specimens of each sample were buried in plastic containers (28 L). Every 14 days for a period of 12 weeks, one group of samples were taken out, washed, dried and weighed carefully. Weight loss of specimens with time was used as an index of biodegradation.

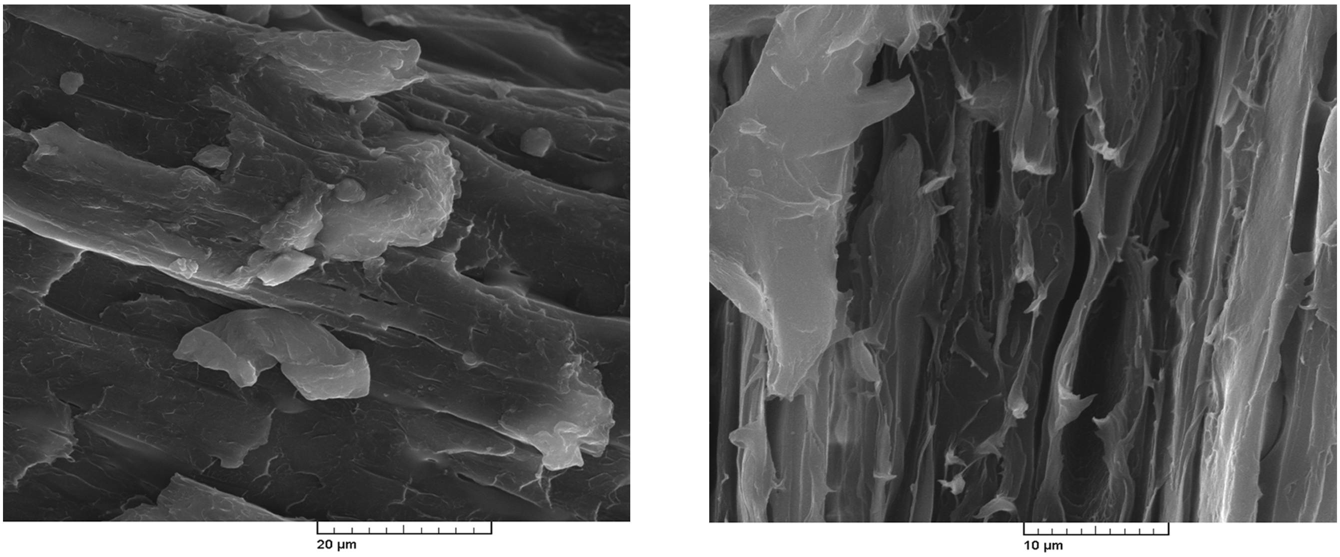
RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The changes in properties of blends depend on their morphologies [18] which are affected by the amount of both starch and glycerol. Obviously when the amount of starch is low, the effect of glycerol prevails and vice versa. The morphology of HIPS/starch blend was evaluated by SEM. Figure 1 shows microstructures of the blend with 10% wt. of starch and 5% wt. of glycerol. Figure 1-a shows the fractured surface of the sample before soil burial test and Figure 1-b, after 4 weeks buried in soil. Vacant regions in Figure 1-b are related to elimination of starch because of microorganisms actions. These parts are dispersed all over the image indicating of a good dispersion of starch in HIPS matrix. The same result is observed in Figure 2 which shows microstructure of the blend with 15% wt. of starch and 5% wt. of glycerol. As seen in these two figures, morphology of blends is affected by glycerol/starch ratio. Figure 3-a shows morphology of the blend with 15% wt. of starch and 5% wt. of glycerol and Figure 3-b shows the morphology of blends with 10% wt. of starch and 5% wt. of glycerol. As the glycerol/starch ratio is increased, blends with more entire morphology are produced. As time passes, the amount of degradation increases too, as shown in Figure 4. Figure 4-a shows the morphology of blend with 15% wt. of starch and 5% wt. of glycerol after 4 weeks buried in soil and Figure 4-b shows the morphology of same blend after 8 weeks buried in soil. As it is observed, the amounts of vacant regions in Figure 4b are more than those in Figure 4-a.

Thermal studies of blend samples

Depending on starch and glycerol content in a blend, TGA curves show decomposition stages. Figure 5 shows thermo-gravimetric analysis of samples with different amount of starch and glycerol. For the sample with 15% wt. of starch and 5% wt. of glycerol as it is observed from the Figure 5, first weight loss which has been started from 210°C, is related to degrada-



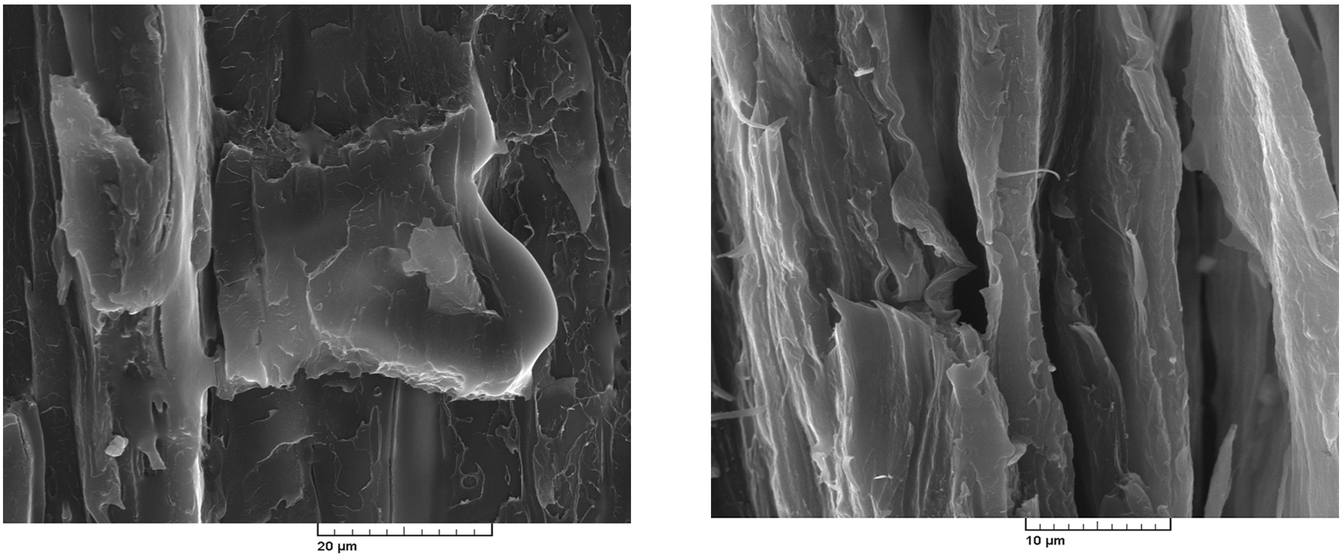
(a) (b)

Figure 1. SEM micrographs of HIPS-ST10-GL5 (a) before soil burial test, (b) after 4 weeks buried in soil.

tion of glycerol and the next one which is started from 300°C happens because of degradation of starch. The last weight loss is started from 350°C due to depolymerization of high impact polystyrene. For the same sample but after 8 weeks buried in soil, no weight loss is observed in the degradation of glycerol and starch, meaning these materials have been removed by micro-organisms actions in burying period in the soil. Also sample with 10% wt. of starch and 5% wt. of glycerol is shown. Weight loss due to the degradation of glycerol is similar to the behavior observed in Figure 5, but it shows a lower weight loss for starch because the amount of starch is smaller (10% wt.). On the other hand, for the sample with 10% wt. of starch and 7% wt. of glycerol, weight loss due to degradation of glycerol is more than what is shown earlier and the same sample after 8 weeks buried in soil shows neither weight loss of glycerol nor starch, which means elimination of these materials by micro-organisms, as it was mentioned earlier and very similar to the TGA curve of pure HIPS shown there.

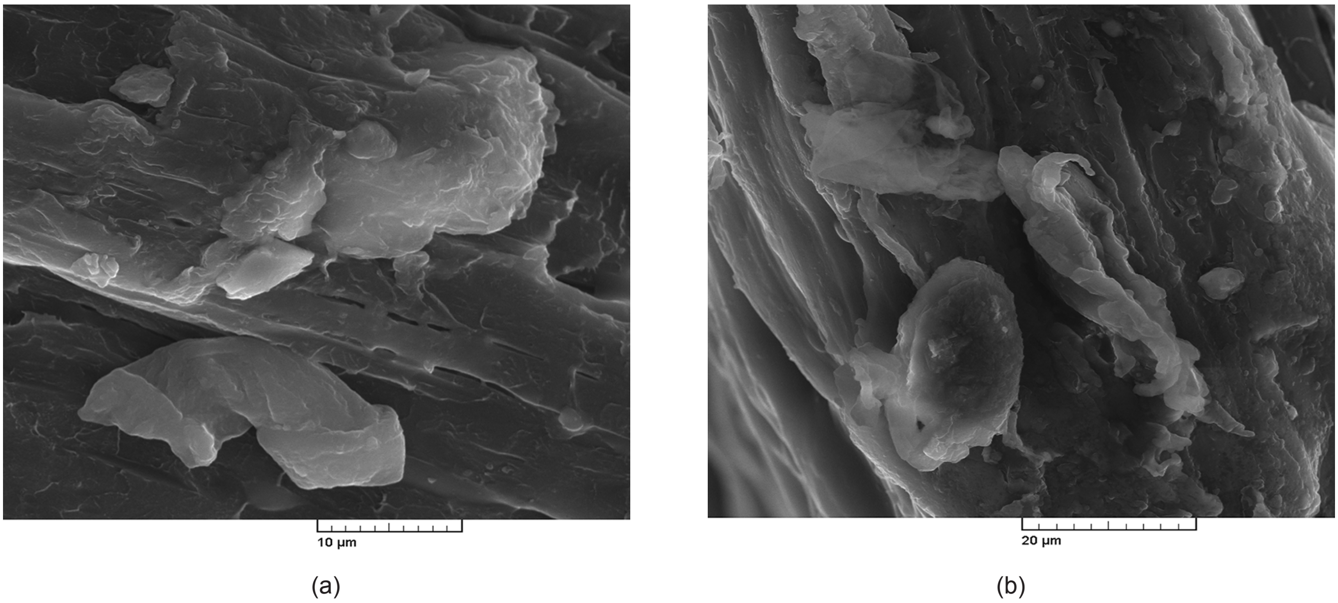
Izod impact strength test

The changes in notched Izod impact strength are shown in Figure 6. Since starch has a rigid and brittle characteristic, as the amount of starch increases, the



(a) (b)

Figure 2. SEM micrographs of HIPS-ST15-GL5 (a) before soil burial test, (b) after 4 weeks buried in soil.



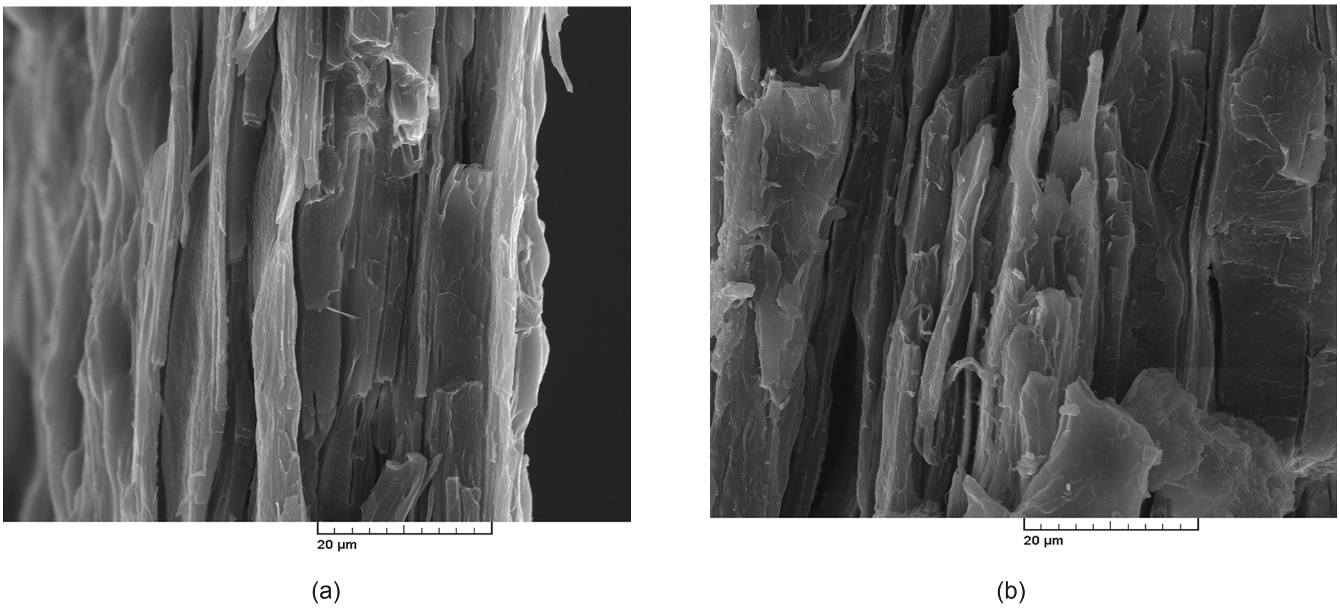
(a) (b)

Figure 3. SEM micrographs of (a) HIPS-ST10-GL5 and (b) HIPS-ST15-GL5.

rigidity of blends increases too, so impact strength decreases. On the other hand, increasing glycerol content in a constant amount of starch decreases the value of impact strength due to decreasing viscosity. In addition, it should be noted that because high impact polystyrene is resistant to impact, so the addition of materials like starch or glycerol decreases the amount of HIPS content of blend so total impact strength decreases. The explained trend of changes has been repeated for un-notched Izod impact strength but the values are greater than the values of the notched samples as shown in Figure 7. It should be noted that failure of a material under impact conditions requires forming a crack, and then propagates through the specimen. In the notched Izod test, the notch acts like a crack and the test is primarily measuring crack propagation resistance. When the test is run without a notch, a crack must first be formed then propagated. Some feel that this test is better than notched Izod for predicting practical impact resistance.

Melt flow index (MFI)

It should be noted that starch is a high molecular weight biopolymer which has high melt viscosity so as its amount is increased in blends, the melt flow index of blend decreases, but because of reduction of



(a) (b)

Figure 4. SEM micrographs of HIPS-ST15-GL5 (a) after 4 weeks buried in soil, (b) after 8 weeks buried in soil.

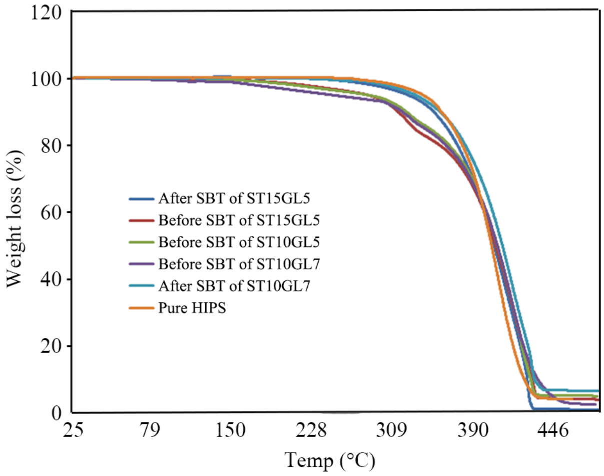


Figure 5. TGA curve of samples before and after soil burial test (SBT).

blend viscosity by addition of glycerol, the values of MFI are increased in constant amount of starch, as shown in Figure 8.

Vicat softening point (VSP)

Vicat softening point (VSP) is affected by the dispersion of a dispersed phase in the matrix of a basic polymer [19] (here HIPS). As mentioned earlier, because of high molecular weight and rigidity of starch, increasing its amount increases VSP values too. This explanation is right when the glycerol amount is not so much, as it can be seen in Figure 9 for 3% wt. of glycerol. But as its amount is increased since it results in blends with lower viscosities, changes of values in Figure 9 suggest prevalence in glycerol effect.

Soil burial test (SBT)

Soil burial test measures biodegradation of blends and is monitored by weighing the samples as a function of incubation time. As it was mentioned earlier, every 2 weeks one series of specimens which was buried in soil was taken out and after washing and drying was weighed. The changes in the appearance of film sample buried in the soil by passing of time are shown in Figure 10. In this figure, appearance change of HIPS -ST10-GL7 has been shown before soil burial test, after 4 weeks buried in the soil and after 8 weeks buried in the soil. The degradation of film structure has obviously well-defined in whole surface of samples in 4 and 8 weeks. The weight loss of samples for 12 weeks was measured, and this variation is shown in Figure 11. The degradation in first 2 weeks was fast because the amount of starch consumed by microorganisms

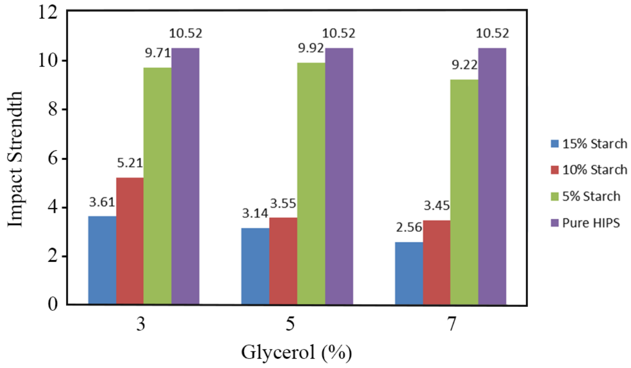


Figure 6. Comparison of changes in notched Izod impact strength values for different blends of HIPS/starch.

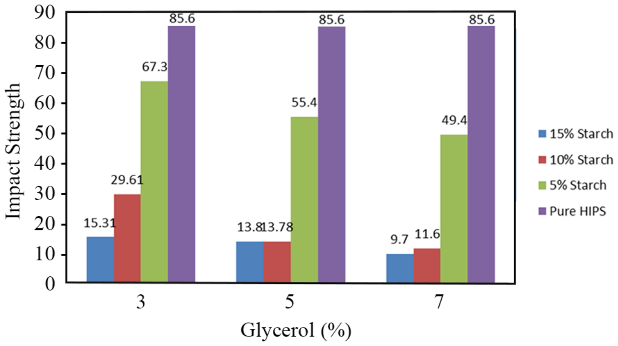


Figure 7. Comparison of changes in un-notched Izod impact strength values for different blends of HIPS/starch.

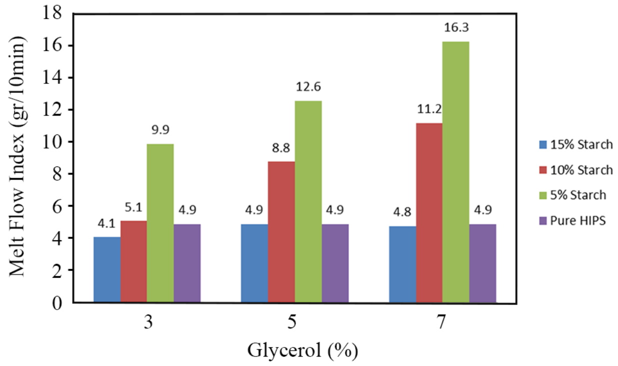


Figure 8. Comparison of changes in melt flow rate values for different blends of HIPS/starch.

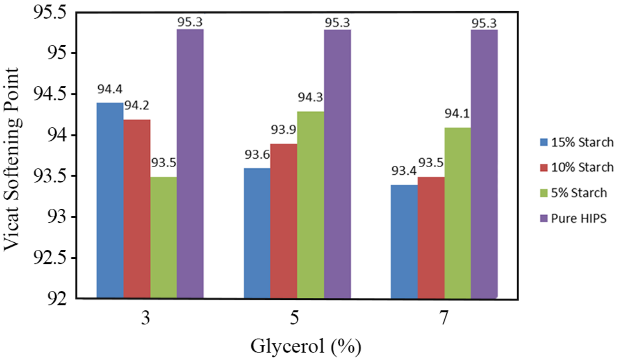


Figure 9. Comparison of changes in Vicat softening point (VSP) values for different blends of HIPS/starch.

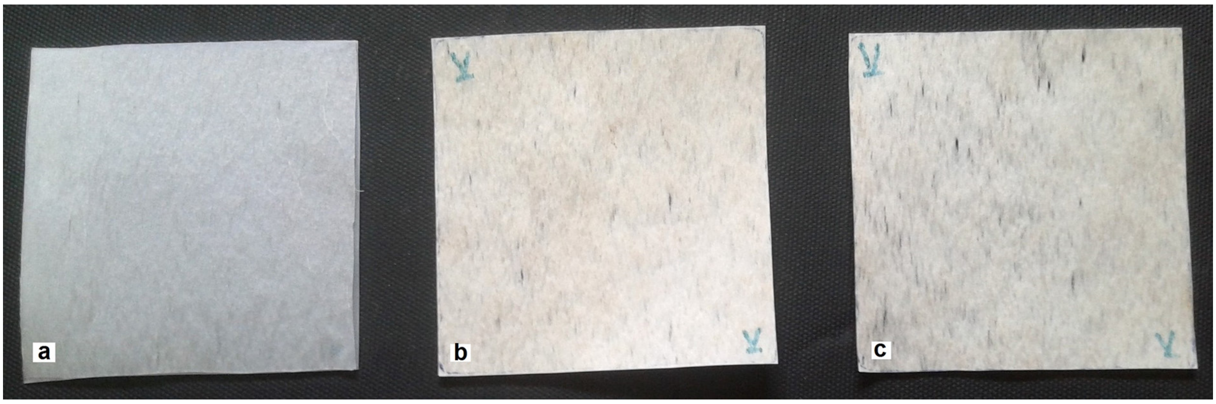


Figure 10. Changes in appearance of HIPS -ST10-GL7 in a: before soil burial test b: after 4 weeks buried in soil c: after 8 weeks buried in soil.

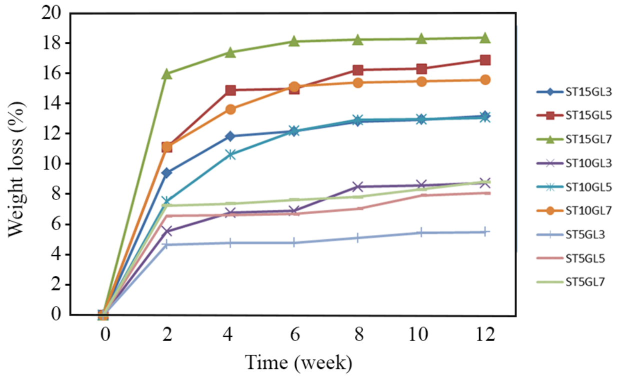


Figure 11. Comparison of weight loss of all samples with time.

was high. As the time passed, this rate was decreased. The highest weight loss was related to the blend with higher amount of biodegradable fraction which is 15% wt. of starch and 7% wt. of glycerol. It should be noted that in none of the blends, complete degradation was not available because of penetration of starch into matrix of HIPS so microorganisms were unable to consume all the starch in blends and less time available for degradation.

CONCLUSION

High impact polystyrene/starch blends were prepared by a melt extrusion process using a twin-screw extruder. The SEM results proved that dispersion of starch in HIPS matrix was good and as the glycerol/starch ratio was increased, blends with more entire morphology were produced. The TGA curves showed that starch and glycerol in the samples buried in the soil for 8 weeks were eliminated by actions of micro-organisms. It was verified that thermal and impact properties of blends are dependent on their morphology in a way that Izod impact strength was reduced by increasing the amount of starch and glycerol. The same result was repeated for un-notched Izod but in larger values of impacts. MFI was reduced as the content of starch was increased and glycerol was reduced. By the increase in glycerol amount, its effect prevailed as compared with starch effect, so VSP values were reduced. Soil burial test showed that as the amount of glycerol and starch was increased, degradation rate and weight loss were increased too. Weight loss was rapidly raised in the first two weeks of the test but then it was reduced by time.

ACKNOWLEDGMENTS

We gratefully acknowledge and thank R&D Centre of Tabriz Petrochemical Complex (Tabriz, Iran) for providing their pilot plant facilities.

REFERENCES

1. Ammala A, Bateman S, Dean K, Petinakis E, Sangwan P, Wong S, Yuan Q, Yu L, Patrick C, Leong K (2011) An overview of degradable and biodegradable poly-olefins. Prog Polym Sci 36: 1015-1042
2. Tokiwa Y, Calabia BP, Ugwu CU, Aiba S (2009) Biodegradability of plastics. Int J Mol Sci 10: 3722-3742
3. Berruezo M, Luduena LN, Rodriguez E, Alvarez VA (2014) Preparation and characterization of polystyrene/starch blends for packaging applications. J Plast Film Sheet 30: 141-161
4. Schlemmer D, Oliveira ERD, Sales MJA (2007)

Polystyrene/thermoplastic starch blends with different plasticizer: Preparation and thermal characterization. J Therm Anal Calorim 87: 635-628

5. Wang B, Zhang Y, Tao Y, Zhou X, Song L, Jie G, Hu Y (2018) Monitoring the degradation of physical properties and fire hazards of highimpact polystyrene composite with different ageing time in natural environments. J Hazard Mater 352: 92-100
6. Zhang JZ, Wang X, Lu LD, Li D, Yang XJ (2013) Preparation and performance of high impact polystyrene (HIPS)/nano-TiO_2 nanocomposites. J Appl Polym Sci 87: 381–385
7. Oliveira CIR, Cunha FR, Andrade CT (2010) Evaluation of biodegradability of different blends of polystyrene and starch buried in soil. Macromol Symp 290: 115-120
8. Schlemmer D, Sales MJ, Resck IS (2009) Degradation of different polystyrene / thermoplastic starch blends buried in soil. Carbohydrate Polym 75: 58-62
9. Sekhar VC, Nampoothiri KM, Mohan AJ, Nair NR, Bhaskar T, Pandeya A (2016) Microbial degradation of high impact polystyrene (HIPS), an e-plasticwith decabromodiphenyl oxide and antimony trioxide. J Hazard Mater 318: 347-354
10. Tokiwa Y, Calabia BP, Ugwu CU, Aiba S (2009) Biodegradability of plastics. Int J Mol Sci 10: 3722–3742
11. Janssen LP, Moscicki L (2009) Thermoplastic starch a green material for various industries. Weinheim, Wiley-VCH
12. Peerapattana J, Phuvarit P, Srijesdaruk V, Preechagoon D, Tattawasart A (2010) Pregelatinized glutinous rice starch as a sustained release agent for tablet preparations. Carbohydrate Polym 80: 453-459
13. Pimentel TAPF, Duraes JA, Drummond AL, Schlemmer D, Falcao R, Araujo Sales MJ (2007) Preparation and characterization of blends of recycled polystyrene with cassava starch. J Mater Sci 42: 7530-7536
14. Subburaj J, Soundrarajan S (2012) Effect of starch on mechanical, electrical, physical, thermal properties and photo/bio-degradation of HIPS - Starch blend IOSR. J Appl Chem 1: 1-9
15. Ashamol A, Sailaja RRN (2012) Mechanical, thermal, and biodegradation studies of polystyrene–phthalated starch blends using epoxy functionalized compatibilizer. J Appl Polym Sci 125: 313-326
16. Mihai M, Huneault MA, Favis BD (2007) Foaming of polystyrene / thermoplastic starch blends. J Cellular Plast 43: 215-236
17. Funabashi M, Ninomiya F, Kunioka M (2009) Biodegradability evaluation of polymers by ISO 14855-2. Int J Mol Sci 10: 3635-3654
18. Oommen Z, Thomas S (1997) Mechanical properties and failure mode of thermoplastic elastomers from natural rubber/ Poly (methyl methacrylate) / Natural Rubber-g-Poly(methyl methacrylate) Blends. J Appl Sci 65: 1245-1255
19. Ghada B, Rachida Z, Rachida A, Ahmed M, Fayacal D (2010) Effect of marble powder and dolomite on the mechanical properties and the thermal stability of poly(vinyl chloride). Asian J Chem 22: 6687-6692