August 10, 2005

Dr. Chris Ibeh
Professor, Director of CNCMM
Plastics Engineering Technology
Department of Engineering Technology
KTC, Room W 122b
Pittsburg State University
Pittsburg Kansas 66762

RE:

Dear Dr. Chris Ibeh

I am pleased to inform you that I have completed the above stated project that you assigned on June 28

The main objective of this report is to inform you on what was accomplished in the physical experiment part of the project; HDPE/TPS blended polyethylene have the same properties as pure polyethylene with reduced cost more environmental safe. This report evaluates the procedures, and the results of the experiment used to do this paper.

I hope that this report with meet and succeed your expectations.

Sincerely

Nathan A. Baker

High performance HDPE/Thermoplastic Starch Blends: Alternative to pure Polyethylene

By

Nathan Baker, Student
Pittsburg State University / Pitt Plastic Inc
Pittsburg Ks, 66762

For

Dr Chris Ibeh, Professor
Pittsburg State University
Pittsburg Ks, 66762

Due Date
Wednesday August 10, 2005

Table of Content

Summary

With the use of starch, glycerol and water the price of virgin polyethylene can be decreased by roughly 20%. As show by the results in the tables below. The TPS 27 has the almost the same properties as pure polyethylene with a little increase in tensile and impact. The more Glycerol added to the composition the better the impact resistance, but lower the tensile and modulus. The 27% being compatible to virgin polyethylene as based on the result of the impact and mechanical testing. Although virgin PE is slightly better in some aspects such as max load and tensile strength. The TPS 27 has also has it advance such as modulus. After reviewing the information the use of starch would be expectable under most condition that virgin PE is used for today, allowing for a more environmental friendly product.

Introduction

With the rising cost of oil, and biodegradable concerns, the price of gasoline, is not the only price that has gone up. For example 2 years ago today, the price of polyethylene was roughly $0.30 per railcar lbs. Today the average price is $0.62 per lb railcar. With the raising costs, is only just, that starch is used as a substitute for pure resin. TPS is composed of virgin polyethylene, water, starch and glycerol. The mixture is compounded in a twin screw extruder until a slurry is formed. After the slurry is formed it is injected directly into the side of other extruder, where the slurry mixes with virgin PE. This is the first time that a starch has been added to polyethylene in any other way, then as filler. The new PE/TPS blends are composed of 60 virgin and 40 TPS. The are a few different types of TPS as will be shown below in the paper. The two samples that are demonstrated below are 27% glycerol, and 30% glycerol TPS blends. Not only with the TPS lower the cost of the resin, but is a step forward in the right direction to cutting down on the waste of pure petroleum resin products in landfills.

Literature Review

High Performance LDPE/thermoplastic starch blends: a sustainable alternative to pure polyethylene

By F.J Rodriquez-Gonzalez, B.A. Ramsay, B.D. Favis

Thermoplastic starch as opposed to dry starch is capable of flow and hence when mixed with other synthetic polymers can behave in a manner similar to conventional polymer blends. This article presents an approach to preparing polyethylene/thermoplastic starch blends with unique properties. A one step combined twin-screw/single screw extrusion setup is used to carry out the melt-melt mixing of the components. Glycerol is used as the starch plasticizer and its content in the TPS is varied for 29 to 40%. Starch is a natural carbohydrate storage material accumulated by green plants in the form of granules. Starch is an inexpensive renewable and natural polymer. It can be added to synthetic polymers to lower the cost of the final product. Under the one step processing condition used it is possible to develop continuous TPS and cocontinous polymer/TPS extruded ribbon which posses a high elongation at break, modulus and strength in the machine direction. Effective control of the glycerol content, TPS concentration and processing conditions can result in a wide variety of morphological structures including spherical, fiber like, highly continuous morphologies.

Polyethylene/TPS Blend Alternative to Pure Polyethylene

By Dr Stephan P. Weeks First Principals Inc

A novel material based on a blend of polyethylene and thermoplastic starch prepared via a unique one step process

Material Properties

- Polyethylene like properties with high ductily and high modulus even at high loadings of TPS
- Reduced cost as compared to pure PE
- High flexibility in tailoring the properties to particular needs
- Low sensitivity to moisture (less than 10% after 10 days)
- Large supply of Renewable resources
- Starch can be made to be fully accessible for biodegradation

Process Characteristics

- Preparation via novel one-step compounding/processing operation using off the shelf polymer processing equipment
- Availability in pellets
- Process that is readily adapted to other polymers such as PP, PS, and biodegradable polyester

The technology is the worlds first to succeed in blending polar starch with commodity resin. Prices of starch are consistently cheaper (80%) than synethic plastics.

Biodegradable Plastics from Wheat Starch and Polyactic acid (PLA)

By Susan Sun , Paul Seib (KSU Department of Grain Science and Industry

Advanced technology in petrochemical polymers has brought many benefits to the human race. However, it becomes more evident that the ecosystems considerably disturbed and damaged as a result of the non-degradable materials for disposable items. The environmental impact of persistent plastic wastes is growing more global concerns. Incineration may cause toxic air pollution, and the petroleum resources are finite and are becoming limited. It becomes important to find durable plastic substitutes, especially in short term packaging and disposable items.

Starch may offer a substitute for petroleum based plastics. Starch is a renewable degradable carbohydrate biopolymer that can be purified from various sources by environmentally sound processes. Starch, by itself, has severe limitation due to its water solubility. Articles made from starch will swell and deform upon exposure to moisture. To improve some of the properties, starch is often blended with hydrophobic polymers.

Fully biodegradable synthetic polymers have been commercially available since 1990 such as poly(lactic acid) (PLA). By the addition of starch to virgin PLA the increase of tensile was 30MPa from original tensile of PLA.

Tensile strength and elongation are two major mechanical properties for a plastic to have market potential. The elongation for pure PLA is about 6%, and the elongation of the starch/PLA blends was about 4.5%, which is brittle for many packaging or fast food utensil materials. Further research needs to increase the flexibility of the new material.

Biodegradability /Cost further research on petroleum substitute

Advanced technology in petrochemical polymers has brought many benefits to the human race. However, it becomes more evident that the ecosystems considerably disturbed and damaged as a result of the non-degradable materials for disposable items. The environmental impact of persistent plastic wastes is growing more global concerns. Incineration may cause toxic air pollution, and the petroleum resources are finite and are becoming limited. Based on these concerns many scientific advances have been made in the way of making plastic more biodegradable. As stated by the article by Susan Sun "synthetic polymers have been around since the 1990's" but do the overwhelming cost they are not used everyday.

One step in the right direction is by adding in a small amount of wheat starch as many companies are doing. At Pitt Plastics, Inc. has devised a plan to produce starch slurry into pure polyethylene creating a semi biodegradable product that is roughly 20% starch.

Research being done at KSU has accomplished from previous research is that one chemical has been identified for co-polymer or diblock formation in reactive blending of wheat starch and PLA, that would link starch and PLA resulting in high strength. For example, with about 0.5% of this chemical, the tensile strength of a blends (starch:PLA = 50:50 wet base) was about 6lMPa, which was very close to 64MPa for pure PLA, and was significantly increased as compared to the blends *(50:50)* without the chemical (about 30 Mpa). Water absorption of the blend was less than 10% after ten days of water soaking test. In addition, the modulus of the blends above its glass transition temperature (about 60^0C) was significantly improved, which is the drawback of pure PLA.

Although both research faculties are striving to use an alterative to pure petroleum based product, to both lower cost and produce a more efficient way to dissolve waste. There are still major steps that need to be taken until these problems can be solved.

Methodology

Materials

Equistar 1122 ALATHON 6908 Pure Virgin Polyethylene (HDPE)
Cerestech Inc TPS30 (30%Glyercol
Cerestech Inc TPS27 (27%Glyercol)

Equipment

Boy – ton injection molding machine
Instron 4400 Tensile Tester
TMI – Impact Test Machine

Procedure

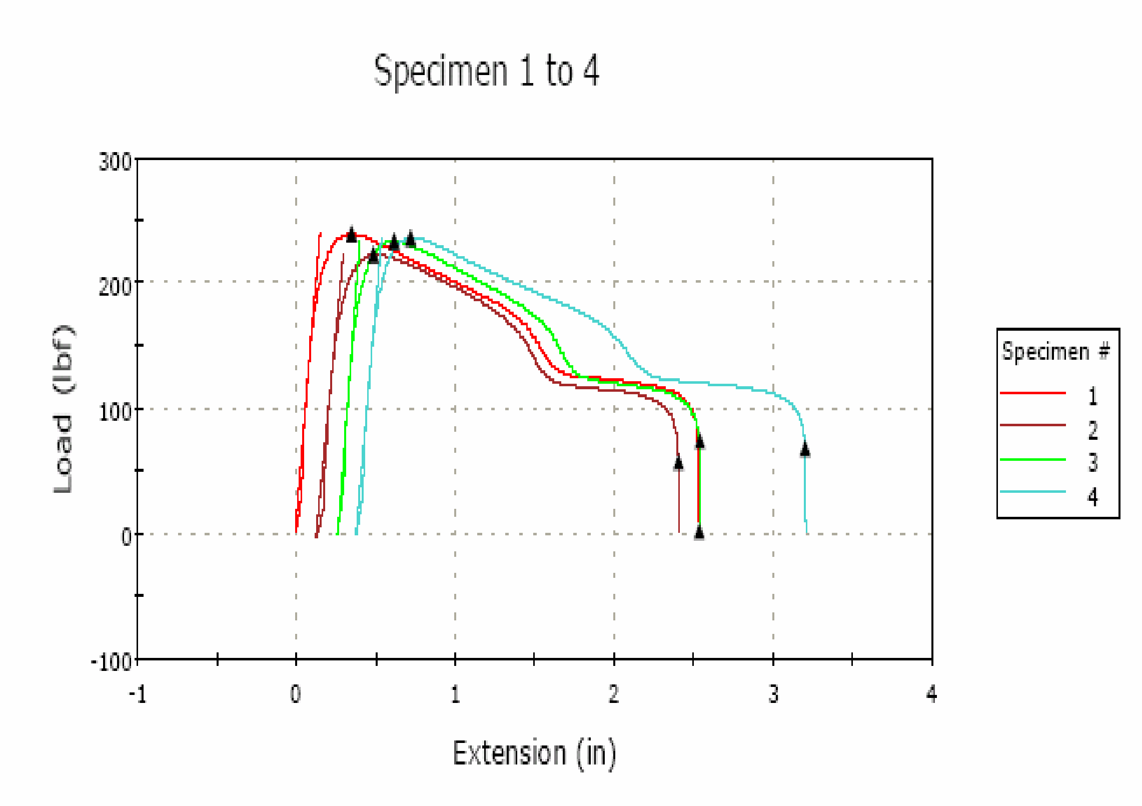
1. Obtain a standard of 6908 pure polyethylene(to base results against)
2. Mix 40% virgin polyethylene and 60% TPS30
3. Mix 40% virgin polyethylene and 60% TPS27
4. Run 20 samples of PE, PE/TPS30, PE/TPS27 in BOY injection machine
5. Test 5 sample of each resin tensile and impact

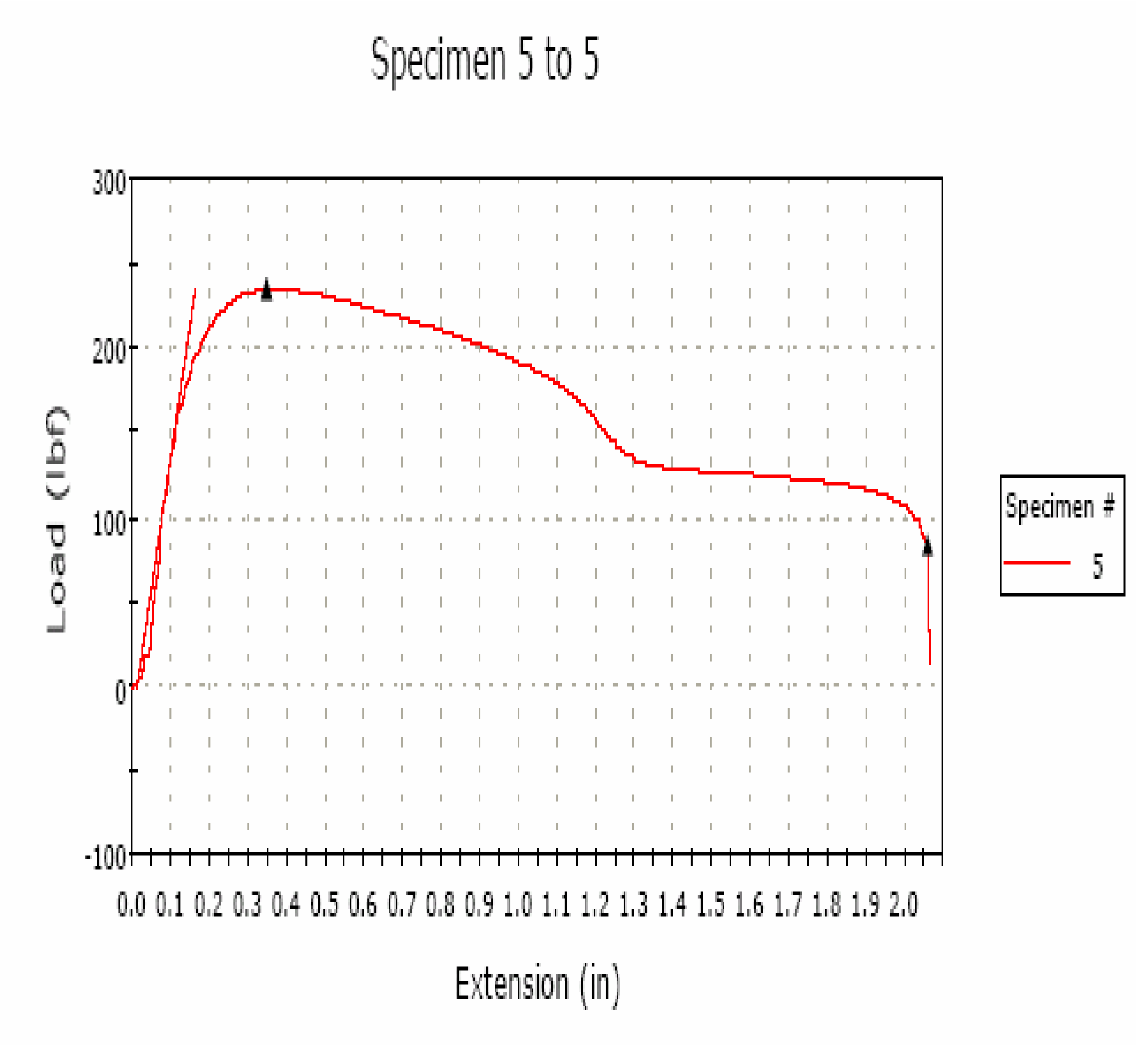
Composition

Both samples are 50% HDPE /50% TPS
Difference being final Glycerol Content 27% 30%
For each material dry mix 60% masterbach TPS with 40% HDPE to get final composition of 70% HDPE and 30% TPS

Results /Evidence

Standard/HDPE





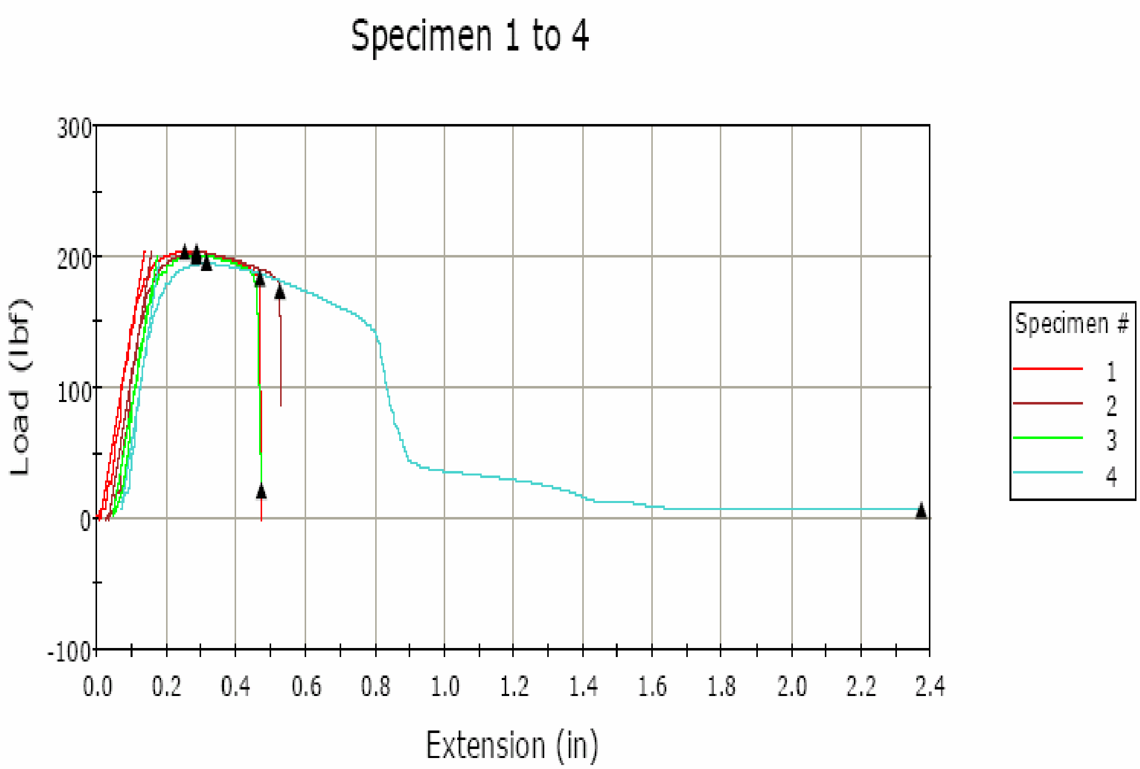
Specimen 5 to 5
300
200
100
0
-100
Load (lbf)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
Extension (in)
Specimen #
5

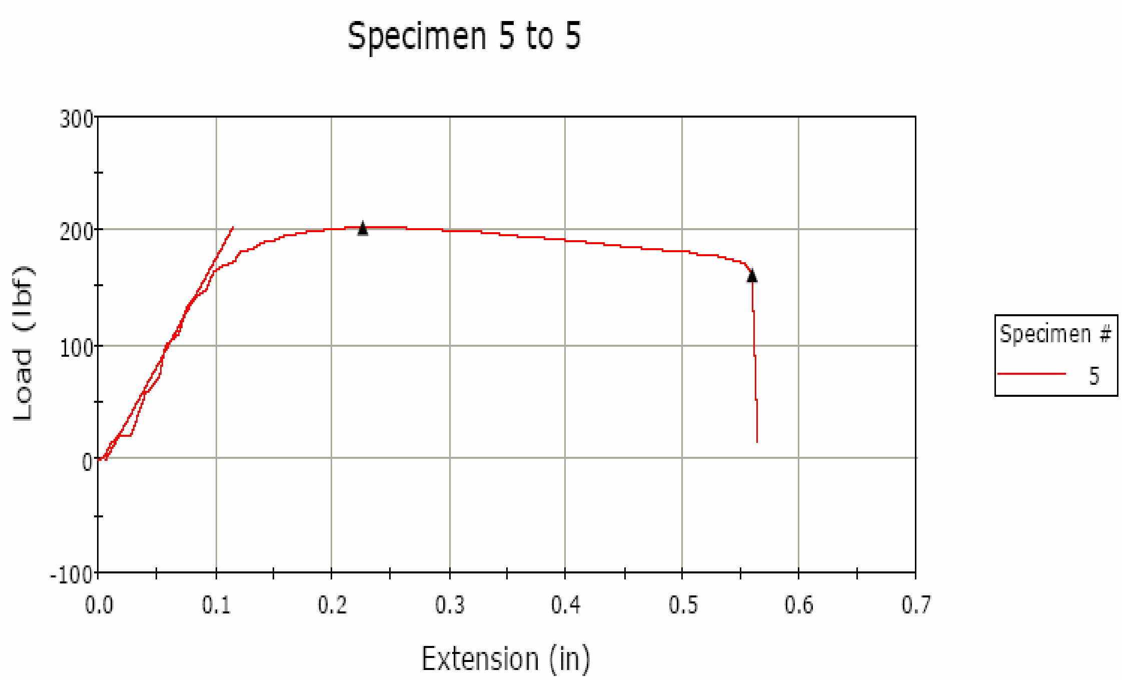
	Specimen label	Maximum Load (lbf)	Tensile stress at Maximum Load (ksi)	Tensile strain at Maximum Load (%)	Load at Break (Standard) (lbf)	Tensile stress at Break (Standard) (ksi)	Tensile strain at Break (Standard) (%)	Tensile stress at Yield (Zero Slope) (ksi)
1	SPECIMEN 1	239.03	3.82	9.01	2.25	0.04	66.12	3.82
2	SPECIMEN 2	222.60	3.56	9.26	58.30	0.93	59.37	3.56
3	SPECIMEN 3	233.55	3.74	9.43	74.25	1.19	59.54	3.74
4	SPECIMEN 4	235.81	3.77	8.79	68.45	1.10	73.52	3.77
5	SPECIMEN 5	235.00	3.76	9.10	83.91	1.34	53.73	3.76
Coefficient of Variation		2.68247	2.68247	2.66782	56.09180	56.09180	12.14437	2.68247
Maximum		239.03	3.82	9.43	83.91	1.34	73.52	3.82
Mean		233.20	3.73	9.12	57.43	0.92	62.45	3.73
Median		235.00	3.76	9.10	68.45	1.10	59.54	3.76
Minimum		222.60	3.56	8.79	2.25	0.04	53.73	3.56
Range		16.43	0.26	0.64	81.66	1.31	19.79	0.26
Standard Deviation		6.25547	0.10009	0.24326	32.21464	0.51543	7.58458	0.10009
Mean + 1 SD		239.45	3.83	9.36	89.65	1.43	70.04	3.83
Mean - 1 SD		226.94	3.63	8.88	25.22	0.40	54.87	3.63

	Modulus (E-modulus) (ksi)	Comment
1	93.06	
2	80.72	
3	104.26	
4	89.42	
5	95.61	
Coefficient of Variation	9.29492	
Maximum	104.26	

	Modulus (E-modulus) (ksi)	Comment
Mean	92.61	
Median	93.06	
Minimum	80.72	
Range	23.54	
Standard Deviation	8.60837	
Mean + 1 SD	101.22	
Mean - 1 SD	84.01	

27% Glycerol TPS/HDPE



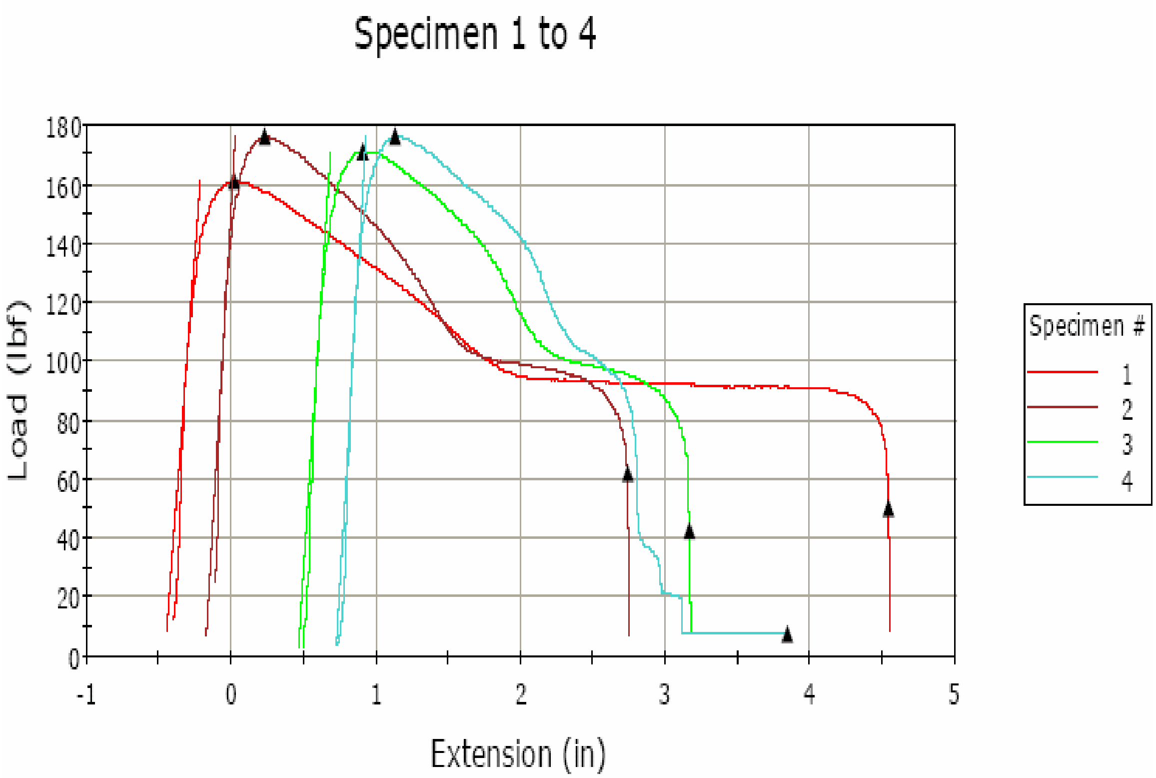


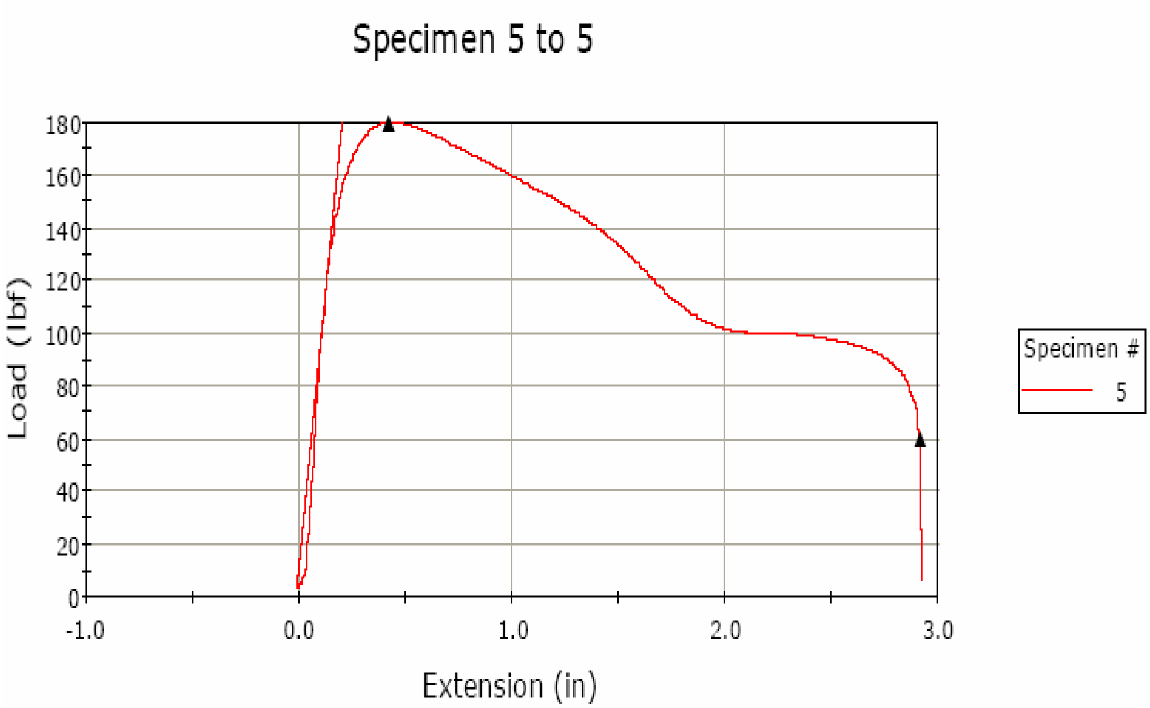
	Specimen label	Maximum Load (lbf)	Tensile stress at Maximum Load (ksi)	Tensile strain at Maximum Load (%)	Load at Break (Standard) (lbf)	Tensile stress at Break (Standard) (ksi)	Tensile strain at Break (Standard) (%)	Tensile stress at Yield (Zero Slope) (ksi)
1	SPECIMEN 1	204.24	3.27	6.60	183.46	2.94	12.24	-----
2	SPECIMEN 2	203.11	3.25	6.90	173.47	2.78	13.15	-----
3	SPECIMEN 3	201.02	3.22	6.21	21.74	0.35	11.08	-----
4	SPECIMEN 4	195.06	3.12	6.33	6.28	0.10	60.20	3.12
5	SPECIMEN 5	201.82	3.23	5.92	160.59	2.57	14.60	-----
Coefficient of Variation		1.77418	1.77418	5.90548	80.06847	80.06847	95.50763	-----
Maximum		204.24	3.27	6.90	183.46	2.94	60.20	3.12
Mean		201.05	3.22	6.39	109.11	1.75	22.25	3.12
Median		201.82	3.23	6.33	160.59	2.57	13.15	3.12
Minimum		195.06	3.12	5.92	6.28	0.10	11.08	3.12
Range		9.18	0.15	0.99	177.18	2.83	49.12	0.00
Standard Deviation		3.56699	0.05707	0.37749	87.36110	1.39778	21.25337	-----
Mean + 1 SD		204.62	3.27	6.77	196.47	3.14	43.51	-----
Mean - 1 SD		197.48	3.16	6.01	21.75	0.35	1.00	-----

	Modulus (E-modulus) (ksi)	Comment
1	101.04	
2	101.54	
3	94.99	
4	107.99	
5	113.42	
Coefficient of Variation	6.81880	
Maximum	113.42	

	Modulus (E-modulus) (ksi)	Comment
Mean	103.80	
Median	101.54	
Minimum	94.99	
Range	18.43	
Standard Deviation	7.07767	
Mean + 1 SD	110.87	
Mean - 1 SD	96.72	

30% Glycerol TPS/ HDPE



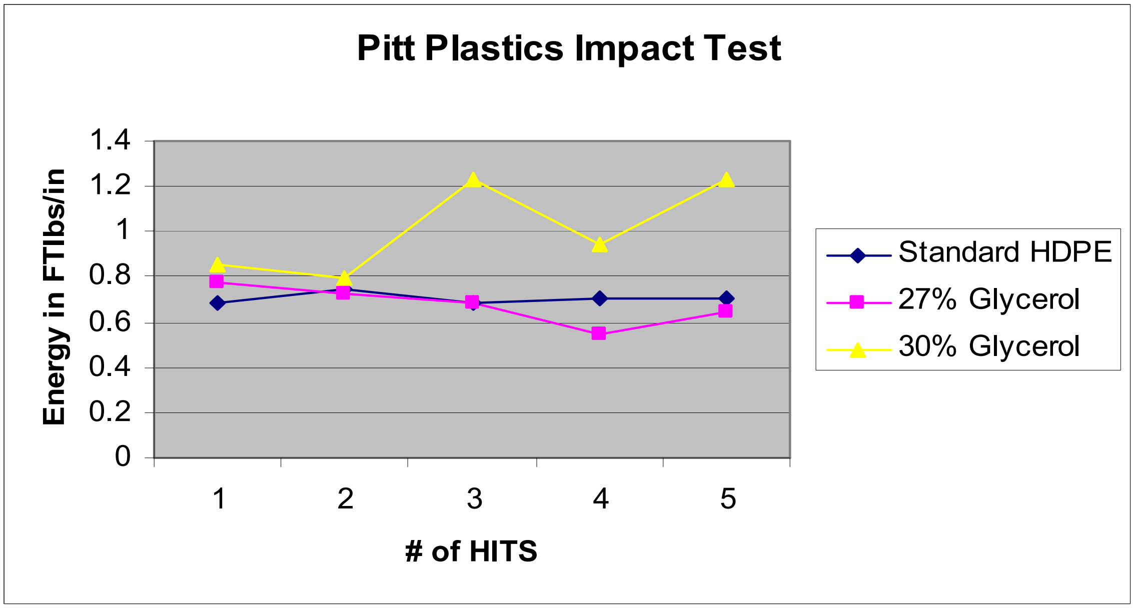


	Specimen label	Maximum Load (lbf)	Tensile stress at Maximum Load (ksi)	Tensile strain at Maximum Load (%)	Load at Break (Standard) (lbf)	Tensile stress at Break (Standard) (ksi)	Tensile strain at Break (Standard) (%)	Tensile stress at Yield (Zero Slope) (ksi)
1	SPECIMEN 1	161.07	2.58	0.55	49.93	0.80	118.73	2.58
2	SPECIMEN 2	176.05	2.82	-0.34	61.69	0.99	65.30	2.82
3	SPECIMEN 3	171.22	2.74	10.95	42.36	0.68	69.89	2.74
4	SPECIMEN 4	176.21	2.82	10.35	7.73	0.12	81.02	2.82
5	SPECIMEN 5	179.59	2.87	11.03	59.75	0.96	76.22	2.87
Coefficient of Variation		4.17622	4.17622	90.00694	49.38657	49.38657	25.86021	4.17622
Maximum		179.59	2.87	11.03	61.69	0.99	118.73	2.87
Mean		172.83	2.77	6.51	44.29	0.71	82.23	2.77
Median		176.05	2.82	10.35	49.93	0.80	76.22	2.82
Minimum		161.07	2.58	-0.34	7.73	0.12	65.30	2.58
Range		18.52	0.30	11.37	53.96	0.86	53.43	0.30
Standard Deviation		7.21769	0.11548	5.85943	21.87430	0.34999	21.26572	0.11548
Mean + 1 SD		180.05	2.88	12.37	66.17	1.06	103.50	2.88
Mean - 1 SD		165.61	2.65	0.65	22.42	0.36	60.97	2.65

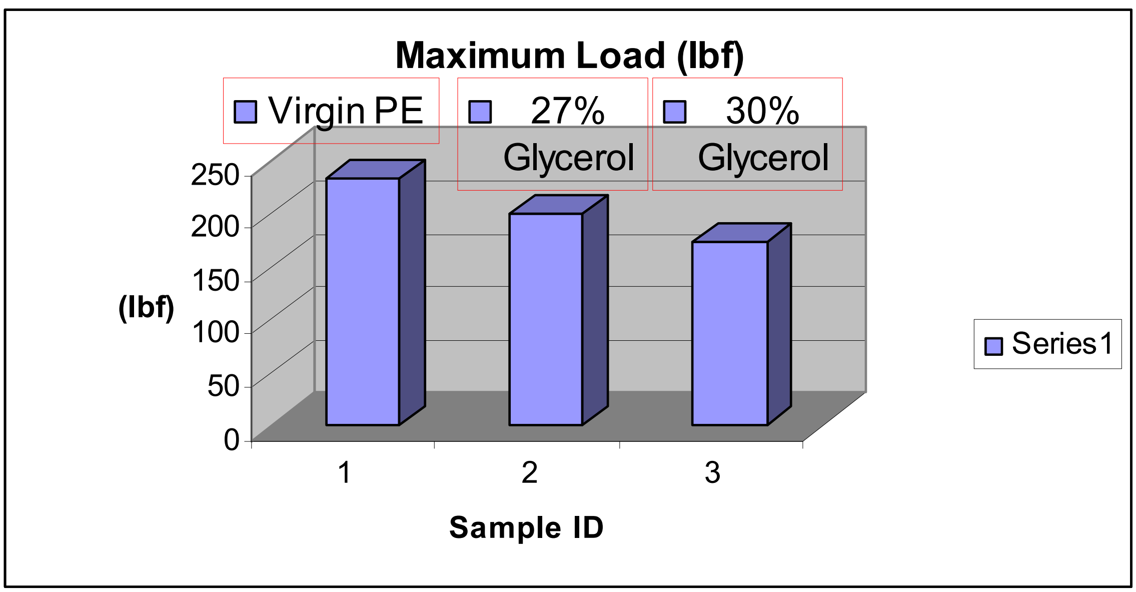
	Modulus (E-modulus) (ksi)
1	39.43
2	52.26
3	46.03
4	52.79
5	51.36
Coefficient of Variation	11.74268
Maximum	52.79

	Modulus (E-modulus) (ksi)
Mean	48.37
Median	51.36
Minimum	39.43
Range	13.36
Standard Deviation	5.68013
Mean + 1 SD	54.05
Mean - 1 SD	42.69

Impact Test



Maximum Load



Discussion of Results

The main objective of this experiment is to lower the cost of virgin resin by the mixing of starch slurry. Results based on above testing goes as followed; as seen above the 30% Glycerol Contents in the Impact test is by far a better material for impact resistance with an avg value of .9975 ft-lb/in, with the 27% glycerol and virgin polyethylene with a close second with a value of close to .74 ft-lb/in. Using the Universal Testing machine the Max Load was tested showing that virgin polyethylene had a value of 233.20 lbf while 27% had a 201.05 and 30% at 172.83. Next dimension that was tested was Tensile stress at max load, showing that 30% test result of 2.77 ksi wasn't good enough to stand up to Virgin PE 3.73 ksi. Although may of the test are about the same results 30% had a much better Tensile stain at break with a 82.23% while PE only had 62.45. The modulus was overwhelming with Virgin at 92.61 and 27% at 103.01 and 49.37 with 30%.

Conclusion

In conclusion it is safe to say that with the starch technology the price can be reduced when place in the right application. The more Glycerol added to the composition the better the impact resistance, but lower the tensile and modulus. The 27% being compatible to virgin polyethylene as based on the result of the impact and mechanical testing. Although virgin PE is slightly better in some aspects such as max load and tensile strength. The TPS 27 has also has it advance such as modulus. After reviewing the information above the use of starch would be expectable under most condition that virgin pe is used for today to prevent landfill build up of non-degradable plastic

Recommendations

1. Better machines to mix PE/TPS
2. Using more accurate weighing systems to get precise weights.
3. More test to be performed
   - Thermal Analysis
   - Water spec
   - Biodegradability (over time)

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13. *Dr Stephan P. Weeks Polyethylene/TPS Blend Alternative to Pure Polyethylene First Principals Inc. 2001*

Appendixes

Chemical Formulas

Polyethylene [-CH2CH2-]n

Thermoplastic Starch Slurry [Wheat starch with water and Glycerol] in different amounts to produce a set mix

Starch: type of polysaccharide found in plants which is not crystalline in structure; a complex carbohydrate. In general, a pure starch has the chemical formula of [$C_6H_{10}O_5$]n

Water [H20]

Glycerol: A thick, sweet syrupy polysaccharide that is soluble in both water and alcohol and is a byproduct of lipid hydrolysis. It melts at 18°C and boils at 290°C, and has the chemical formula [CH2OHCHOHCH2OH]

Machines used

Boy Injection Machine

1. Turn on breaker (Floor next to the machine)
2. Turn on the pump
3. Set the temps (Nozzle, Front Zone, Rear Zone)

Processing Temperatures				
	Nozzle Zone	*Front Zone*	*Middle Zone*	*Rear Zone*
Set Temp	356	347	320	302

4. Allow 20 min to heat up
5. During the wait check the mold so be sure it properly closes
6. If needed add Mold release to help release part
7. When up to temp purge machine by using PP
8. Fill the hopper with selected material
9. Clean the nozzle
10. Check sprue bush (not clogged)
11. Push carriage forward so nozzle and sprue bush are connected
12. Build up shot size (3.6)
13. Close mold
14. Inject shot
15. Allow time for cooling
16. Open mold
17. Eject part
18. Repeat steps 12 – 17 until desired amount of parts have been produced
    Shut down procedure reverse of Start up

Processing conditions

- Plasticizing Screw speed 100 rpm
- Injection speed 60 mm/s
- Holding time 7 sec

- Cooling time 8 sec
- Mold Temp (room temp)

Instron 4400

1. Turn on power to the computer and Instron machine
2. Log on computer ALL CAP: INSTRON
3. Double click the instron icon
4. Calibrate machine using a test strip, set clamp were test strip starts to curve (to move arm turn IEEE off).
5. Test Tension Test
6. Set extension file name
7. Type in operator name
8. Set size of test strip .5, .125, 4 in
9. Set Unit Us customary

TMI Impact Testing Machine

1. Turn on Machine (Black button of back of the machine)
2. Press PENDL key choose ASTM
3. Calibrate Pendulum by releasing
4. Choose Test (Izod, Charpy, Tension)
5. Enter Units (Ft/lbs/in) by pressing UNIT key
6. Set Limits by Using LIMITS key .1 as min and 10 as max (depends on material)
7. Secure Sample in holder
8. Press TEST key
9. Release Pendulum
10. After Pendulum Swings record the break type. (Partial, Complete break, Hinge).
11. Write down results.
12. Repeat steps 8 – 11 with all samples of same material.
13. All Test complete press the STATS key and except all the result you need.
14. Hit the next key until the Standard Deviation, Avg, and Coefficient of Variation is given.