Injection Molded Hybrid Composites Based on Corn Fibers and Poly(Vinyl Alcohol)

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Summary: Ongoing research cooperation between USDA and the University of Pisa, Italy has yielded several composite blends of poly(vinyl alcohol) (PVA) and corn fibers (CF). The USA is the largest producer of ethanol from cereal grains. Composites based on natural fibers alone are extremely sensitive to water. Their mechanical properties deteriorated upon the absorption of water, thus suggesting a limited usefulness of such formulations in practical applications. In this study, corn-fibers produced during the wet milling process of corn for fuel ethanol were used to prepare composites. CF and PVA were processed in variable amounts in the presence of both dry/fluid plasticizers, such as glycerol and pentaerythritol. Composites prepared from CF in combination with PVA showed little change in their mechanical properties even after conditioning at variable relative humidities, as well as complete soaking in water. Composites tested after storage for one year under 50% relative humidity and 23°C exhibited mechanical properties similar to those of freshly prepared composites. Cornstarch was introduced in the formulation for the purpose of reducing the cost of the final product and to further increase the composition of natural components in the composites. Addition of starch moderately reduced the mechanical properties of the composites.

Keywords: composites; fiber; fillers; mechanical properties; poly(vinyl alcohol); renewable resources; starch; tensile

Introduction

The waste management problems associated with petroleum based synthetic plastics have provided the opportunity to focus on environmentally compatible materials derived from renewable sources that can serve in some applications as substitutes of petroleum-based polymers. Of particular interest is the use of natural fibers as fillers and reinforcement materials in plastic composites [1-5]. Thus, natural fibers seem to have little resistance towards environmental

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influences. This can be recognized in the composite and can be advantageously utilized for the development of biologically degradable composites with good physical properties. Thus, natural fibers can be added to composites to confer stiffness, increase degradability and lower cost of the final item. Particularly, the market related to single use products such as cups, containers, transplanting pots, cutlery, etc., appears suitable for the applications of these types of composites. Degradable-plastic composites are emerging materials that offer benefits to the environment. This results in minimizing waste that would be otherwise deposited in landfills.

The USA is the largest producer of ethanol from cereal grains. Annual ethanol production from corn and wheat is estimated to be in the order of 1.7 billion gallons/year, and this volume is expected to increase further in the future. After the fermentation and ethanol extraction process a, large amount of corn fiber is left as a co-product. Corn fiber is an industrial name given to he pericarp fraction of the corn kernel. Because of the inefficiency in the milling during removal of the paricarp fraction, some of the kernel endosperm is also removed. This means that not only does corn fiber contain pericarp, it also contains starch and protein from the endosperm. Corn fiber is a fiberous material with a 60% residual moisture content. Its main use is in animal feeds. The wet CF cost about $15 a ton, while dried ground CF (about 10 Mesh) cost about $50 a ton. The animal feed market cannot use all of the CF currently on the market.

In this study, corn-fibers (CF) produced during the processing of corn for fuel ethanol were used to prepare composites with poly(vinyl alcohol) (PVA) as a continuous matrix. PVA, a hydrolysis product of polyvinyl acetate, is well suited for blending with natural polymers since it is a highly polar synthetic polymer and is also considered biodegradable [6,7]. For these reasons, PVA has been extensively used to improve mechanical properties in blends with natural polymers [8-11]. This paper reports the investigation of suitable composition for the production of composites by injection molding. In particular, the maximum amount of corn fiber and starch in the composite that can be injection molded has been evaluated. The effects on mechanical properties of fluid plasticizers such as glycerol, and dry plasticizers such as penthritol have been compared. Composites based on natural fibers are usually extremely water sensitive. The change in mechanical properties of composites stored at different relative humidities was also studied.

Materials

PVA was obtained from Air Products, Inc., Allentown, PA. The percentage of hydrolysis and average molecular weight of the A523S PVA were 88% and 85,000-124,000 Mw respectively. Corn starch was purchased from A. E. Staley Co., Decator, IL, USA. Glycerol was purchased from Fisher Scientific, Polyethylene glycol 2000 and pentaerythritol were purchased from Aldrich. Corn fibers were kindly supplied by Williams, Pekin IL, USA, which are a coproduct of ethanol production. The wet corn fiber was stored in a freezer and kept frozen until needed. Before use, the frozen corn fibers were layered onto metal trays and dried overnight in a forced air oven set at 50 °C. After drying, the fibers were ground in a pin mill (Alpine Augsburg 160Z model, Germany, U/m 18,000). The ground fibers were sieved and the fraction passing through a 12xx Swiss Silk (0.110 mm) sieve were collected. Analysis on this fraction of corn fiber had a composition of 1% fat, 14% protein, 25.5% starch, 59% lignocellulosic component, and 0.5% ash.

Sample Preparation

All ingredients for the composites were first blended together in a mixer prior to their compounding. The sample mixtures were compounded using a Leistritz 18 mm co-rotating double screw extruder running at 100 rpm. Extruder temperature control zones were set to 123/145/165/165/160/155°C (feed to die). The extrudate strands were pellitized and the pellets stored in sealed ziplock bags before injection molding. Tensile bars (ASTM type IV, 16.51x1.191x0.318 cm) were injection molded using a Cincinnati Milacron Act-75-B molder with a four cavity mold. Processing temperature during molding was between 82°C (first zone) and 170°C (nozzle). The mold temperature was maintained at 45°C.

SEM (Scanning Electron Microscopy)

Samples were mounted on aluminum stubs with graphite-filled tape and vacuum coated with gold-palladium. Specimens were examined with a JEOL JSM 6400V scanning electron microscope.

Mechanical Testing

Tensile bars were conditioned for 1 week at 23 °C and 50% Relative Humidity (RH) before testing. Tensile bars of selected composition were stored at 25 °C and 50% RH for 365 days. Tensile tests were performed on the tensile bars using an Instron 4201 (Canton MA, USA) according to ASTM D638. Crosshead speed was 50mm/min. Tensile data presented are the average of 5 replicate bars. Selected samples were stored at 25% and 80% RH (23°C), respectively, for two weeks before testing.

Water and Sensitivity

Five tensile bars of selected compositions were soaked in water at 25 °C for 30 min. After soaking, samples were removed from water and weighted. Water uptake was recorded.

Results and Discussion

Corn fibers are composed of lignocellulose long fibers and starch granules, as shown in Figure 1.

Figure 1. SEM Micrograph of CF, 400X.

Formulations of the sample composits are reported in Table 1.

Table 1. Composition of the prepared items.

Sample	PVA (%)	Corn Fiber (%)	Starch (%)	Glycerol (%)	PentaErythritol (%)	PEG (%)
PCF1	42	26	-	21	11	-
PCF2	40	25	-	20	10	5
PCF3	40	25	-	10	20	5
PCFS1	36	23	9	18	9	5
PCFS2	33	21	17	17	8	4
PCFS3	33	21	17	8	17	4
PCFS4	31	27	15	15	8	4
PCFS5	29	32	14	14	7	4
PCFS6	27	37	13	13	7	3

P= PVA, CF= Corn Fibers S=Starch, PEG=Poly(ethylene glycole).

A preliminary study was performed to to identify potential plasticizers to be used in the composites. Plasticizers chosen for further investigation were glycerol, pentaerythritol and polyethyleneglycol (PEG). Composites were prepared using variable amounts of glycerol, pentaerythritol and (PEG), but the same ratio of PVA and CF. By using plasticizers, compounding could be done at lower temperatures (< 160-170°C), thus avoiding fiber decompostion during processing. In the first composite (PCF1), glycerol was the plasticizer present in the greatest amount (21%) with a smaller amount of pentaerythritol (11%). This mixture produced a composite that is cohesive and flexible. Its mechanical properties are reported in Table 2.

Table 2. Mechanical properties of tensile bars stored at (23 °C, 50% RH) for 7 days.

Sample	El (%)	StDv (MPa)	UTS (MPa)	StDv	YM	StDv
PCF1	599	26	11.7	0.2	52.0	4.1
PCF2	645	34	7.1	0.3	27.5	0.8
PCF3	152	19	13.5	0.1	224.8	10.4
PCFS1	396	16	8.3	0.1	94.2	2.0
PCFS2	297	20	8.0	0.1	112.0	3.7
PCFS3	361	7	8.8	0.1	81.5	3.6
PCFS4	302	20	8.1	0.2	92.7	9.2
PCFS5	101	15	7.8	0.2	122.2	10.4
PCFS6	35	2	8.8	0.2	171.6	14.4

StDv=Standard Deviation, UTS= Ultimate Tensile Strengh, YM= Young's Modulus

In the second mixture (PCF2), a limited amount of PEG (5%) was introduced to further lower viscosity of the melt. The introduction of PEG (PCF2) seemed to lower melt viscosity as indicated by the reduction of the extruder motor load and reduced die pressure. Due to the greater amount of plasticizer in this composite, percent elongation at break (%E) increased in PCF2 compared to PCF1, with a corresponding decrease in ultimate tensile strength (UTS) and Young's Modulus (YM). In the third mixture, pentaerythritol was present in higher proportion (20%) than glycerol (10%). The different plasticizers' ratio affected both the processing parameters and mechanical properties of the produced items. Glycerol is more effective in reducing melting temperature and melt viscosity than pentaerythritol, as indicated by the increased motor load and die pressure compared to PCF2. Composite PCF3 was stronger and less flexiable compared to composites PCF1 and PCF2. In particular, a sharp increase in Young's modulus is observed when using pentaerythritol in larger ratio than glycerol.

For the rest of the composites, the plasticizer ratio of PCF2 was used and the amount of CF was progressively increased up to a value of 37% in the mixture. Increasing the fiber content made it more difficult to injection molder these composites. Increasing CF content of the composites above 27% made the injection molding more difficult and injection pressures had to be increased from 20,000 psi to 27,000 psi. Composites made with fiber content greater than 37% could not be injection molded. The effect of the CF increase on the properties of the final material partially followed the same general trends as with other fillers. As CF volume fraction increased, elongation to break decreased while the modulus generally increased. Interestingly, ultimate tensile strength was not significantly changed by increasing corn fiber. Also, composite made with 37% fibers and only 27% PVA resulted in a cohesive extrudate.

Since moisture sensitivity represents a limit for the practical applications of natural fiber based composites, representative composites were conditioned for 30 days at 25%, 50%, and 80% relative hymidity (RH) and their tensile properties measured. The selected composites were PCF2 and PCF3, which contained no starch. Composite PCFS1 was aged at the same RHs. It contained 17% starch, but had the same ratio of plasticizers and fibers as PCF2.

Figures 2 and 3 show the variation in mechanical properties with changes in RH. The trend in the tensile properties of the composites is consistent with water acting as a plasticizer for these composites. UTS and YM decreased for the composites as RH increased. Elongation at break increased with increasing RH for composite PCF3. Composites PCF2 and PCFS2 showed a slight decrease in %E when stored at 80% RH. This could be due to a weakening of the matrix upon the obsorption of water.

The composite containing starch showed a greater sensitivity to RH than did composite PCF2, which contained no starch. High RH had the greatest effect on composite PCF3. Since this composite was lower in glycerol and richer in pentaerythritol and we have already shown that pentaerythriol is not as effective a plasticier as glycerol for these composites, the absorbed water may have more of an affect on this composite.

All composites after 30 days of storage at 80% RH were still intact and cohesive. It was also interesting to note that all composites conditioned at 50% RH for 30 days did not show any significant change in tensile properties compared with the same composites tested after 7 days.

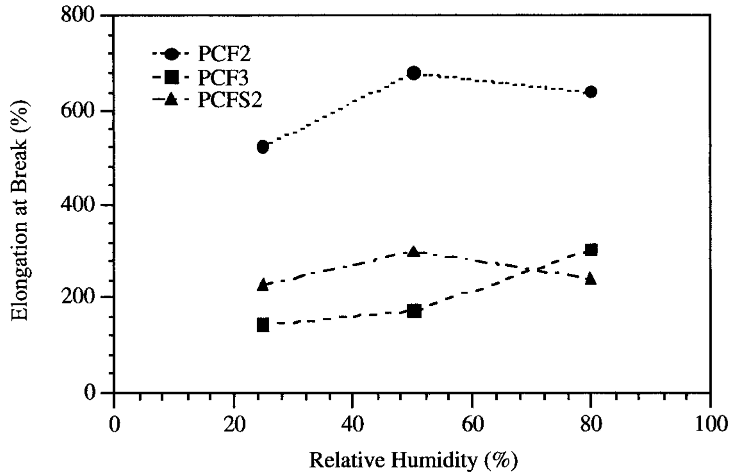

Figure 2. Elongation at Break for PCF2, PCF3, and PCFS2 at Different Relative Humidity.

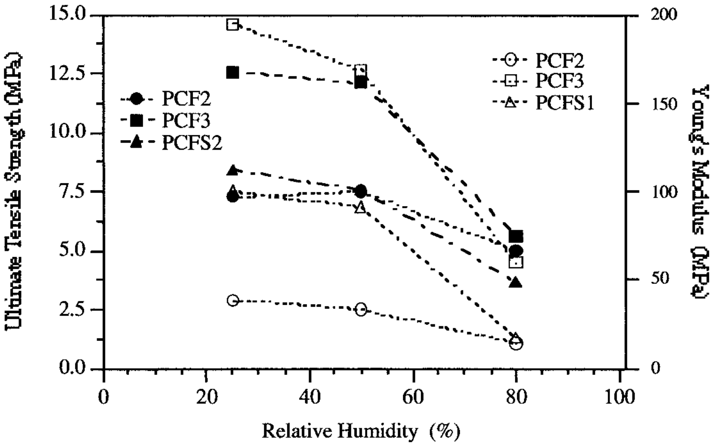

Figure 3. UTS and YM for PCF2, PCF3, and PCFS2 at Different Relative Humidity.

The effect of water action on composites was investigated by conditioning samples PCF2 and PCFS1 for 30 days at 50% RH, and soaking them in water for 30 min. After removing from water, both the composites had a water uptake of 19%. The composites appeared slightly swollen, but still intact. Surprisingly, the soaked composites remained intact despite the fact that the PVA used in these composites is cold water soluble. After reconditioning the composites at 50% RH for seven days they showed no loss in UTS for the composite with no starch and only a slight decrease in UTS for the composite containg starch (Table 3). Both composites increased their elongation and decreased their modules after soaking, most likely due to increased plasticization by the uptake of water.

Table 3. Comparison of mechanical properties of mixture PCF2 and mixture PCFS1, after soaking in water for 30 min and reconditioning at 50% RH for 7 days.

Mixture N°	Elongation (%)	StDv	UTS Mpa	StDv	YM Mpa	StDv
PCF2	645	29	7.5	0.1	33.8	1.1
PCF2[w]	764	33	7.7	0.4	18.8	1.5
PCFS1	445	25	7.8	0.1	80.2	2.0
PCFS1[w]	524	24	6.7	0.2	29.8	3.8

[w] after soaking in water and reconditioning at 50% RH for 7 days

Composites PCF1, PCF2, PCFS1, PCFS2, and PCFS5 were tested after storing at 23°C and 50%RH for 1 year (Table 4). Only small changes in tensile properties were seen for composites after one year compared to the composites stored for 7 days (Table 2). In composites containing no starch (PCF1 and PCF2), changes in %E were not significant. UTS and YM decreased moderately for PCF1, and were almost the same UTS or moderately increased YM for PCF2. For samples prepared with 9% and 17% starch and approximately the same fiber to PVA ratio as in composite PCF2, %E was slightly increased with storage, and UTS and YM were decreased. These changes are probably an indication that water was absorbed during storage. Composite PCFS5 containing a higher ratio fiber to PVA had an increase in UTS and YM and a decrease in %E. This indicates that this composite was getting stiffer and less flexible with age.

Table 4. Mechanical properties of tensile bars stored in a conditioned room (23 °C and 50% RH) for 365 days.

Mixture N°	Elongation (%)	StDv	UTS Mpa	StDv	YM Mpa	StDv	Age days
PCF1	613	15	9.5	0.2	34.2	2.5	365
PCF2	619	16	7.2	0.1	38.6	1.9	365
PCFS1	415	48	6.2	0.2	65.0	1.2	365
PCFS2	356	24	6.4	0.3	84.7	9.4	365
PCFS5	95	7	8.6	0.2	183.3	8.7	365

StDv=Standard Deviation, UTS= Ultimate Tensile Strengh, YM= Young's Modulus

Conclusion

In composites containing PVA and CF, glycerol was a more effective plasticizer than pentaerythritol. Pentaerythritol produced less flexible composites. In particular, a sharp increase in Young's modulus is observed when using pentaerythritol in a larger amount than glycerol. Addition of starch to the composites moderately reduced their tensile properties. Increasing the fiber content of the composites caused difficulties in their injection molding. Composites with greater than 27% CF need 27,000 psi of injection pressure and composites with greater than 37% CF could not be injection molded. Composite tensile bars could be produced with as little as 27%

synthetic polymer (PVA). Only small changes in tensile properties were observed in the composites after conditioning at different RHs or soaking in water. Composites tested after one year of storage had tensile properties similar to composites tested after seven days of storage.

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