The Seventh International Conference on Woodfiber-Plastic Composites
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Hybrid Composites: Combining Cellulose Fibers and Wollastonite Mineral Fibers into a Nylon 6 Matrix

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Abstract

The objective of this research was to develop a high purity cellulose/wollastonite pellet that could then be accurately metered and feed into a laboratory scale twin-screw extruder and compounded with a nylon 6 resin. The major focus was targeted on a 20 percent cellulose/20 percent wollastonite/60 percent nylon 6 composite. Limited research with nylon 6,6 resins was also attempted and will be discussed briefly. A process for developing a cellulose/wollastonite pellet was successful and 100 Kg were produced for twin screw extrusion processing with nylons. The 100 Kg of pellets were then compounded via a "low temperature compounding" technique as discussed in detail elsewhere (1). Further information can be obtained in U.S. Patent #6,270,833 B1 (2). The compounding process research was to determine if composites could be produced in small batches (50 Kg trial runs) on laboratory scale twin-screw extrusion compounding equipment. The result was 125 Kg of composite material for injection molding and ASTM mechanical property evaluation. Attempts to maximize the composite properties were not the focus of this research. Stable, controllable processing characteristics and repeatability of the twin-screw extrusion trials was the goal. It is the authors' opinion that this goal was accomplished. Future research will focus on maximizing composite properties and determining if cellulose fibers alone or in combination with mineral fibers can be compounded on larger commercial scale equipment. Extreme care and precise processing knowledge is needed to develop a commercial scale process that works. If this cannot be accomplished, then cellulose fibers as reinforcement in any of the high melting point engineering thermoplastics may remain as a laboratory oddity.

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Introduction

Hybrid composites of glass fiber/wollastonite fiber reinforced engineering thermoplastic (ETPs) are available for sale for use in commercial production applications. Blending various levels of glass to wollastonite or visa versa allows for tailored composites with properties high in strength (i.e., high glass content) or good dimensional stability and warp resistance (i.e., high wollastonite content). Years of research and commercial development has provided an excellent understanding of glass and wollastonite fiber reinforced ETPs,

but never a reduction in densities from utilizing these two components. Chemical foaming agents can be utilized and micro-cellular injection molding can reduce weights. This density issue is one of the reasons for utilizing cellulose in combination with wollastonite fiber or glass fibers in reinforcing nylon 6 or other ETPs.

If half of the wollastonite or glass fibers can be replaced with high purity cellulose in commercial grades of ETP hybrid composites, then an approximate weight saving of 5 to 8 percent can be realized in a final automotive part, for example. Properties of cellulose hybrid composites must meet current mechanical property needs for applications, raw material costs must be minimized, and stable raw material supplies are necessary to enter the automotive sector with cellulose hybrid ETP composites. Rayonier, Performance Fibers, Jesup, GA has a scale-up processing plant for developing TerraCel-10J, a 100 percent high purity pulp fiber pellet (3) for reinforcement fibers for the polymer industry. Small modifications to existing infrastructure could lead to a 50 percent cellulose/50 percent wollastonite fiber pellet for hybrid composite applications. The reader should take note that the suggested modifications at a Rayonier scale-up plant is my opinion and may not reflex the business/marketing plans of Rayonier Performance Fibers.

With the publication of the proceedings from the Seventh International Conference on Woodfiber Plastic Composites, the 20-year mark will have been crossed since Klason et al. (4) attempted to compound cellulose flour and cellulose fibers into nylon 6 resins in 1984. Technological advancements in polymer processing equipment and bridging the knowledge gap in processing techniques allows for the routine compounding of cellulose fibers alone or in combination with mineral fibers into nylon 6 on a small laboratory 32 mm twin-screw extruder. The next and most critical stage in the technical development is to scale up to a small commercial scale extruder and determine if the viscosity shear heating effects can be controlled to produce ETP composites containing cellulose.

Materials and Pellet Processing

The high purity cellulose fibers were provided by Rayonier, Performance Fiber Division. The fibers are a hardwood prehydrolyzed kraft (HPK) with 98 percent alpha cellulose content. Wollastonite mineral fibers were provided by three suppliers, VANCOTE W-50AS is a surface treated grade from R.T. Vanderbilt Company, Inc. Wollastonite-520S treated grade was provided by FIBERTEC, Company and an un-treated PG Grade from Intercorp, Company. Ashlene Polymers Nylon 6 - 829LSW and Ashlene Polymers Nylon 6,6 - 529L grades was used as the base matrix polymer.

Materials handling problems associated with low bulk density materials, such as cellulose fibers, are a critical hurdle to overcome when compounding cellulose into nylon or other ETPs. The same problem exists with the hybrid composites. Extensive details of pelletizing 100 percent HPK fibers is reported in reference 1 and with some slight modifications to the overall moisture content is all that was needed to progress further with the hybrid composite research. Consistent feed rates into the extruder via a V-type feed hopper, such as an accurate feed hopper and potentially a K-Tron twin screw feed hopper with mixing paddles, is an appropriate method of delivering cellulose/wollastonite pellets into a sidefeeder attached to a twin-screw extruder. Without accurate and consistent feed rates, there will be problems associated with die face surge, torque (i.e., percent load) variations, and a twin-screw extrusion process that is less stable during start-up, transition phase, and steady-state conditions. Compounding cellulose fibers or cellulose fibers in combination with mineral fibers is difficult with limited experience. Removing all potential problems to the process stability is critical to successfully producing these composites in any ETPs.

A brief review of the pelletizing process for cellulose fiber/wollastonite fiber pellets is reported. Never dried cellulose fibers were shipped to the Forest Product Laboratory and stored in a 36°K 50 percent relative humidity cold storage room prior to fiber pelletizing to prevent biological growth and subsequent fiber degradation. The never dried pulp fibers were shipped at 39 to 40 percent solids as per prior research criteria. Wollastonite fibers were obtained in a dry form from the suppliers. Research objectives were to develop a 50 percent cellulose fiber/50 percent wollastonite fiber pellet, which could then be compounded into a nylon 6 matrix at 40 percent loading level resulting in the 20 percent cellulose/20 percent wollastonite/60 percent nylon 6 composite. A Hobart batch

mixer with 60-liter capacity was used in the first step of the pelletizing process for creating the 50 percent cellulose/50 percent wollastonite fiber pellet. Prior research indicated that 40 percent solids content was optimum for 100 percent cellulose fibers. Water was added during the Hobart mixing to accommodate for the dry wollastonite fibers so the total percent solids of cellulose and wollastonite was 40 percent. The results in the kahl pelletizing process were a failure. Subsequent trial runs decreased the amount of water so the resultant batches were 45 percent solids, 50 percent solids, and finally 55 percent solids before optimum kahl pelleting was obtained. Surface interactions with the cellulose hydroxyl radical and silane treated wollastonite fiber maybe the reason for the shift in percent solids or particle size interactions, compactions factors, etc. A full factorial study was not conducted on the pellet process. In brief, based on experience of quality pellets that would feed effectively into the twin-screw extruder, the research moved forward at pelletizing the cellulose/wollastonite blend at 55 percent solids. The researchers believe that fiber length, fiber surface chemistry, percent solids, and initial fiber preparation play a critical role in fiber pelletizing related to quality and fiber damage during processing, (fiber length, fiber curl, and temperature degradation). When pelletizing hybrid pellets, the choice of wollastonite or even glass fiber will shift the percent solids needed to produce commercial quality pellets ready for the marketplace. A complete fiber pelletizing study is required to understand and optimize the fiber pellet for optimum mechanical properties in the final composites.

During the blending stage, a Hercules carboxymethylcellulose 7H4F (CMC) viscosity modifier was added into the Hobart mixer to change the rheology of the cellulose/wollastonite blend. CMC was added at a level of 0.005 by weight of the batch size and blended for 15 minutes in the Hobart to assure good dispersion and prevent any de-watering during the kahl pelletizing. After 15 minutes of mixing, the resultant blend of 50 percent cellulose/50 percent wollastonite was ready for kahl pelletizing. A Kahl Pellet-Press (laboratory scale model #175 mm) was used for pelletizing the cellulose/wollastonite blend with the CMC additive. The Kahl pelletizer has a horizontal pellet die plate with dual rotating roll mills that provides the downward force required to press the cellulose/wollastonite blend through the die plate. As a note: a fiber dispersion agent such as Berocell 509HA could also have been used in the Hobart mixer at low levels to aid during the compounding phase. Again, this would result in “fine tuning” the pellet process for optimum pellet quality. A 3-mm die plate with a 6 to **1** press way was used to produce the hybrid composite fiber pellets. The 3 mm diameter pellets have a good ratio in size to the neat polymer pellets if a pre-blending stage is used for twin-screw extrusion processing. In addition, the 3-mm pellets provided more accurate feed rates though a feed hopper verses larger pellet diameter as previously attempted in other research efforts.

After the kahl pelletizing process, the 50 percent cellulose fiber/50 percent wollastonite fiber pellets were oven dried at 105°C to reduce the moisture content near 0.25 percent pellet moisture content. Moisture plays an extremely critical role in the compounding sequence and great care must be taken to follow the nylon manufactures drying process and keep the total moisture content below 0.5 percent. If the pellets are exposed to moist ambient conditions prior to the twin-screw extrusion sequence, then care should be taken to re-dry the pellets before extrusion. The cellulose component is hygroscopic and can easily gain 8 to 10 percent moisture, which could result in 4 percent total moisture of the cellulose/wollastonite pellets. This level of moisture will certainly result in foaming of the compounded composites, off-gassing, and extrusion process control in-stabilities.

Twin Screw Processing and Discussion

A complete and detailed description of ‘Low Temperature Compounding’ (LTC) is referenced in the proceedings of the Sixth International Conference on Woodfiber-Plastic Composites (1). Only figures will be provided in this text to review the process. LTC is characterized by three stages: start-up, transition phase, and steady-state conditions as shown in **Figures 1, 2, and 3.** This technique was used for the compounding of the 125 Kg of 20 percent cellulose/20 percent wolastonite/60 percent nylon 6 composites as stated in the abstract. The authors believe this technique can be used for most engineering thermoplastic matrix’s. An overview of the temperature settings for compounding the hybrid composites on a Davis-Standard (32 mm) co-rotating, fully segmented screws

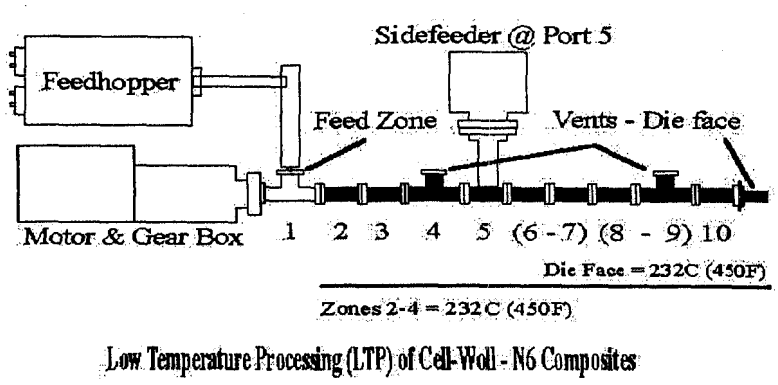

Figure 1. ~ *Schematic of start-up conditions, constant function heat profile.*

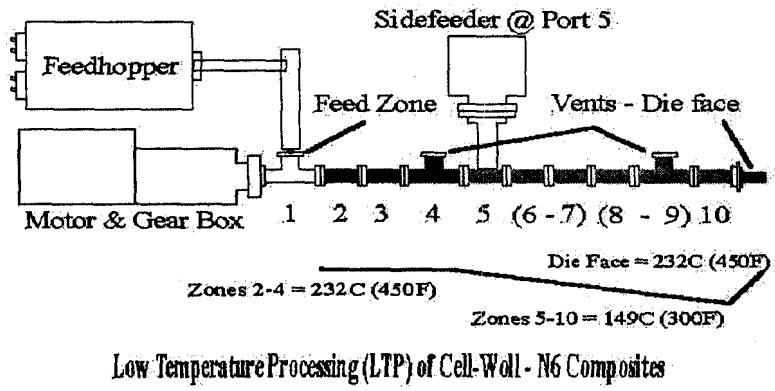

Figure 2. ~ *Schematic of transition pnase, constant function heat profile.*

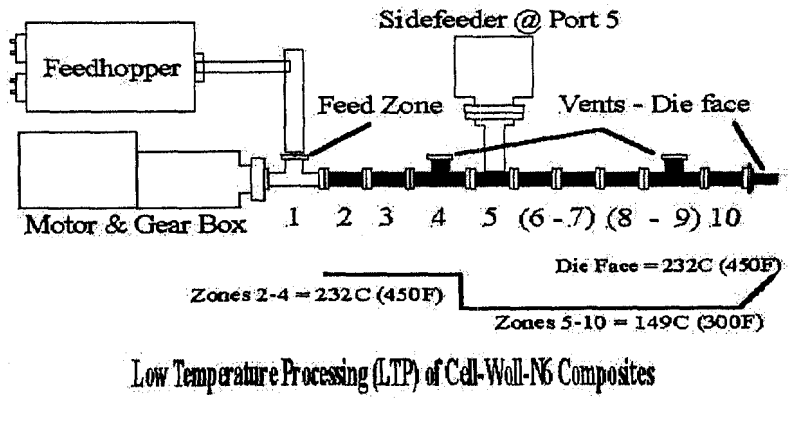

Figure 3. ~ Schematic of steady-state conditions, constant function heat profile.

with a Davis-Standard (28 mm) sidefeeder, co-rotating, fully segmented screw is reported. The critical heat variables associated with the steady-state compounding of 20 percent cellulose/20 percent wollastonite/60 percent nylon 6 were the following:

Zone 1 is an un-heated feed throat segment,

Zones 2 to 4 temperatures = 232°C (450°F), and

Zones 5 to 10 temperatures = 149°C (300°F).

Die face temperature = 204° to 232°C (400° to 450°F).

At start-up conditions, all the temperature zones are set at 232°C (450°F), and the settings are gradually reduced through the transition phase to the steady-state conditions. Temperature ranges will vary depending on screw configuration, screw rpm, and fiber loading levels. Loading levels of 20 percent reinforcing fibers are suggested to start an exploratory research trial and working toward the 40 percent loading levels; to become familiar with the LTC process.

The critical heat variables associated with the steady-state compounding of 12.5 percent cellulose/12.5 percent wollastonite/2 percent lubricant/ 73 percent nylon 6,6 were the following:

Zone 1 is an un-heated feed throat segment,

Zones 2 to 4 temperatures = 268°C (515°F), and

Zones 5 to 10 temperatures = 149°C (300°F),

Die face temperature = 260° to 274°C (500° to 515°F).

At start-up conditions, all the temperature zones are set at 268°C (515°F) and the settings are gradually reduced through the transition phase to the steady-state conditions. Temperature ranges will vary depending on screw configuration, screw rpm, and fiber loading levels. Compounding any amount of cellulose in combination with wollastonite is extremely difficult at these temperatures in a high melting point polymer. The lubricant (Dow Master Batch - Poly-siloxane) acts as a processing aid to help facilitate the production of the 12.5 percent cellulose/12.5 percent wollastonite N6,6 composites. Limited research trials were attempted with the N6,6 polymer matrix due to the difficultly of compounding at these extreme temperatures.

If reference 1 is available, then the discussion should move toward small-scale commercial twin-screw extrusion equipment. Moisture and viscosity shear heating are two of the most critical components in moving toward commercial development. As a note to the reader: the authors have not attempted compounding on larger commercial equipment, but with years of process control development of cellulose polyamide composites (CPCs) we would welcome the opportunity. The viscosity shear heating effects must be controlled during compounding. Numerous discussions have been sparked by the volume issues associated with twin-screw extrusion. The cross section of a twin-screw extruder is proportional to the square of radius of the size of the extruder screws. Therefore, it may be possible to extract the viscosity shear heating component of LTC on small laboratory equipment Davis Standard (32 mm diameter), but not on a Davis Standard 69 mm twin-screw extruder. American Liestritz Extruder Corporation has the ZSK-50 mm with 24 high intensity cooling bore around the circumference of the screws. Can this equipment extract the viscosity shear heating effects associated with cellulose or hybrid composites fast enough during commercial production? The steady-state conditions of LTC require a step function approach as shown in Figure 3. The short times required for commercial production and the low thermal conductivity of polymers suggests there will be challenges.

Targeted additives and polymer modifiers have yet to be developed for cellulose polyamide composites or hybrid of cellulose/wollastonite or cellulose/glass fiber composites. If commercial manufactures cannot produce these composites, then there is no market for the targeted additives. With luck, Dow Master Batch Poly-siloxanes have a tremendous effect on the stick-slip effects within the twin-screw extruder. Polymer-sidewall, polymer-screw, and polymer-die face interactions are reduced. This in turn reduces; the torque levels and allows for reduced extruder temperatures. Hence, more opportunities for reducing temperatures and extracting or controlling the viscosity shear heating effects on larger commercial equipment. With proper attention paid to the processing conditions, it maybe possible to produce these hybrid composites on full-scale commercial compounding equipment in the future.

Mechanical Property Evaluation

Table 1 shows the mechanical property date for various polymer composites. Tensile strength, flexural strength, tensile modulus, and flexural modulus are reported. The polymers and polymer composites range from polypropylene, woodflour reinforced PP, nylon 6, hybrid composites with nylon 6 and nylon 6,6 composites, and glass-reinforced polymers. The baseline of mechanical properties is a foundation from which to compare and improve on the mechanical properties of the hybrid composites in the future. As stated in the abstract, the focus of this research project was to establish stable processing conditions from which to expand the research of other research projects focused on the mechanical property improvements of hybrid composites. Without the ability to maintain stable and consistent compounding, there is no reason to attempt improving the composites properties. The glass-reinforced polymers out perform all other composites in their class. In general, the wollastonite fiber composites also out performed the hybrid composites in both nylon 6 and nylon 6,6 matrix's.

Three types of wollastonite were used in this study. The two treated wollastonite fibers were evaluated and have similar characteristics to Values stated in Table 1. The un-treated wollastonite fibers have mechanical properties slightly lower then the treated fibers in combination with the cellulose fibers. Research to investigate the compati-

Table 1. ~ *Mechanical properties of various polymers and composites.*

	Flexural modulus	Tensile strength	Flexural strength	Tensile modulus
	(10^3 psi)	(psi)		(10^3 psi)
Polypropylene	4,007	4,166	201	202
33-Pine/PP	4,798	7,153	490	462
Nylon 6	8,729	9,309	399	345
30-Woll/N6	9,092	15,327	944	909
20-Ce1/20-Woll/N6	10,743	14,480	870	754
33-Cellulose/N6	11,876	17,632	828	853
33-Glass/N6	16,139	21,272	1,163	1,095
Nylon 6,6	10,983	10,789	541	467
33-Woll/N6,6	9,770	14,190	800	761
17.5-Cel/17.5-Wol/N6,6	9,696	12,238	784	523
33-Glass/N 6,6	18,750	2,4287	1,233	1,218

bility of cellulose/wollastonite fiber pellets as well as the compatibility in the nylon 6 matrix need further investigation. This study was done to prove that these composites could be produced in the laboratory. Future investigations should incorporate the experts in the mineral fiber field to improve the composite properties of hybrid cellulose/wollastonite or cellulose/glass composites.

Conclusions

A 50 percent cellulose fiber/50 percent wollastonite fiber pellet has been developed and can be used to produce a 20 percent cellulose/20 percent wollastonite/60 percent nylon 6 hybrid composite. The goal of this research was to make small lab scale productions trial runs to determine if compounding process stability could be obtained and repeated. Three days of compounding trials resulted in 125 Kg of composite pellets from a small 32 mm twin-screw extruder. Following precise compounding guidelines, the viscosity shear heating effects could be controlled to produce high quality (i.e., surface quality, pellet density) composite pellets. Although the current mechanical properties do not compete with glass fiber-reinforced polyamide composites, hybrid composites of cellulose/mineral fiber (wollastonite or glass) make good sense in terms of density evaluations. Currently, there are too few researchers investigating the use of cellulose as an additive in ETPs. Progress will remain slow until the issue of scale up processing to commercial size equipment is finalized. At that moment, the economics of the product will determine if it can survive in the marketplace.

Acknowledgments

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