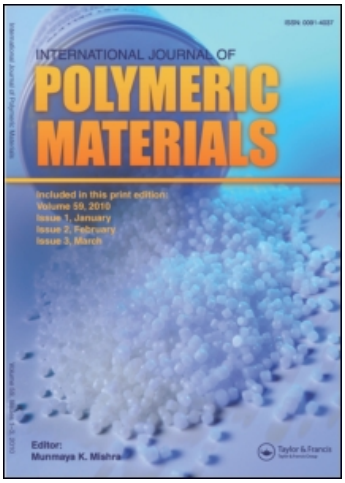

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Rietveld, Jeroen X. and Simon, Mark J.(1992) 'Processability and Properties of a Wood Flour Filled Polypropylene', International Journal of Polymeric Materials, 18: 3, 213 — 235
To link to this Article: DOI: 10.1080/00914039208029322
URL: http://dx.doi.org/10.1080/00914039208029322

Intern. J. Polymeric Mater., 1992, Vol. 18, pp. 213–235
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Printed in Malaysia

Processability and Properties of a Wood Flour Filled Polypropylene

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(Received May 15, 1992)

The successful manufacture of natural fiber reinforced thermoplastic composites is complicated by the hygroscopic and hydrophylic nature of cellulosic fillers, as well as by their limited thermal stability at typical melt processing temperatures. This study examines the processability and properties for several wood flour (WF)-polypropylene (PP) composites. Other studies on natural fiber reinforced thermoplastics have concentrated on the properties of these composites rather than on their processability, as such, relatively more is known about the hydrophylic consequences of cellulosic fillers relative to the hygroscopic consequences. A focus of this study was to carefully evaluate the positive and negative implications of absorbed moisture (within the WF) on the mechanical and rheological behavior of such composites. Filler-matrix dry blends of 45wt% WF-PP and 55wt% WF-PP were compounded/pelletized on a 38 mm single screw extruder. The pelletized feedstock was subsequently melt-processed on a 667 kN/108 cm^3 injection molding machine (into a standard tensile bar mold) and on a 19 mm single screw extruder (through a capillary die). The results from an analysis of process monitoring and material property data were then used to identify the impact of absorbed moisture on the processability and performance of cellulosic/thermoplastic composites.

KEY WORDS Injection molding, natural fibers, polypropylene, mechanical properties, hygroscopic.

INTRODUCTION

Cellulosic fillers are renewable resource materials which are available in a variety of forms, from physically processed wood flours to chemically-thermally-physically processed cellulose fibers. The use of cellulosic materials as a filler in polymeric materials is commercially significant within the thermoset industry, but not nearly as much within the thermoplastic industry. Over the last decade, research results have demonstrated that cellulosic fillers are, at a minimum, a low-cost additive for commodity thermoplastics and, at a maximum, capable of acting as a reinforcing agent.[1–21] For a well-mixed and well-wetted filler, the possibility of obtaining reinforcement is most promising when the additives are cellulose fibers rather than lignocellulose particulates (wood flour). The reinforcement prospects are due to the fact that pure cellulose fibrils are actually quite strong and rigid, having a

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theoretical tensile modulus on the order of 50 GPa (7,000,000 psi) and a theoretical tensile strength on the order of 300 MPa (40,000 psi). Compared to other low-cost (inorganic) fillers, cellulosic fillers are lower in density and less abrasive to processing equipment. In terms of mechanical properties, the modulus and creep resistance of commodity thermoplastics can be improved via the addition of cellulosic fillers. The research data base on cellulosic-thermoplastic composites is most developed for the following fiber-matrix components: wood flour and cellulose fiber, and polyethylene, polypropylene and polystyrene.

For cellulosic materials, some of the primary obstacles to their successful utilization in thermoplastics include: (1) the fillers are hydrophylic and hygroscopic, and (2) the fillers exhibit limited thermal stability at the temperatures typically encountered during polymer processing. All of the above add to the difficulty of manufacturing natural fiber reinforced thermoplastic composites. The hygroscopic and hydrophylic nature of cellulosic fillers will influence both the processability and properties of the composite. Because filler-matrix compatibility is required to optimize the mechanical properties of a composite, many studies have concentrated on improving filler-matrix affinity.[2,6,9,11,15,16,19–21] Besides affecting the level of filler-matrix adhesion, the hydrophylic nature of cellulosic fillers influences the extent of filler-matrix dispersion that occurs during the fabrication step.

The tendency of cellulosic fillers to absorb moisture will cause outgassing (void formation) during the processing operation and will lead to moisture-related environmental aging of the fabricated product. In a high humidity environment the cellulosic component of the feedstock could reach an absorbed moisture content on the order of 10wt%. For injection molded articles (a closed-mold process) outgassing can be particularly troublesome because the volatiles become trapped within the molded part during the injection molding cycle. The presence of absorbed moisture may also tend to aggravate thermal degradation of the cellulosic material. Degradation becomes quite noticeable as the melt processing temperature approaches 200°C and is accompanied by the release of volatiles as well. Thus, when using undried feedstock, the result would be a molded article having a variable porosity microstructure which may resemble that of a high density foam. The exact porosity distribution within an injection molded cellulosic/thermoplastic composite will be further influenced by the processing conditions (pressure, temperature, time), and the subsequent porous microstructure will be detrimental to the properties (mechanical behavior) of the molded article. However, as this paper will reveal, the presence of absorbed moisture may not be completely negative in terms of the processability of natural fiber reinforced thermoplastics.

Research to-date has favored property- over processing- related studies and for either issue has largely ignored the effects of absorbed moisture. In particular, information about the rheological behavior of natural fiber-filled thermoplastics is scarce.[22,23] Rheological data such as melt viscosity can be used to quantify the processability of the fiber-filled system. This paper presents the results of several studies on the processability and properties of an injection molded wood flour (WF) filled polypropylene (PP) composite, with particular emphasis on the formation and effects of density variations within the molded article; as well as an examination of the role of the moisture levels within the cellulosic component.

EXPERIMENTAL PROCEDURE

The processes involved in this study are outlined in Figure 1. The wood four (WF) was dried overnight at 110°C and then dry-blended with polypropylene (PP) powder plus several processing stabilizers. Two batches of WF-PP, one at 45wt% WF and the other at 55wt% WF, were separately compounded on a 38 mm extruder. The air-cooled extrudate strands were subsequently pelletized. After pelletization the feed-stock was stored in air-tight cans. The moisture content of the pelletized feed-stock within these cans was then adjusted to either 2.5wt% or 5.0wt% (based on the mass of dried wood flour present in the WF-PP pellets). Melt processability studies were run using a 19 mm extruder and a 667 kN/108 cm^3 injection molding machine. Relevant processing conditions were monitored throughout all of the processing trials. Finally, the rheological, mechanical and physical properties of the WF-PP mixtures were evaluated and analyzed. The injection molding trials were executed according to a statistical experimental design.

Materials

Powdered polypropylene (PP) from Soltex (Fortilene 9101, MFI = 2.5) and nominal 40 mesh wood flour (WF) from American Wood Fibers (402 western yellow

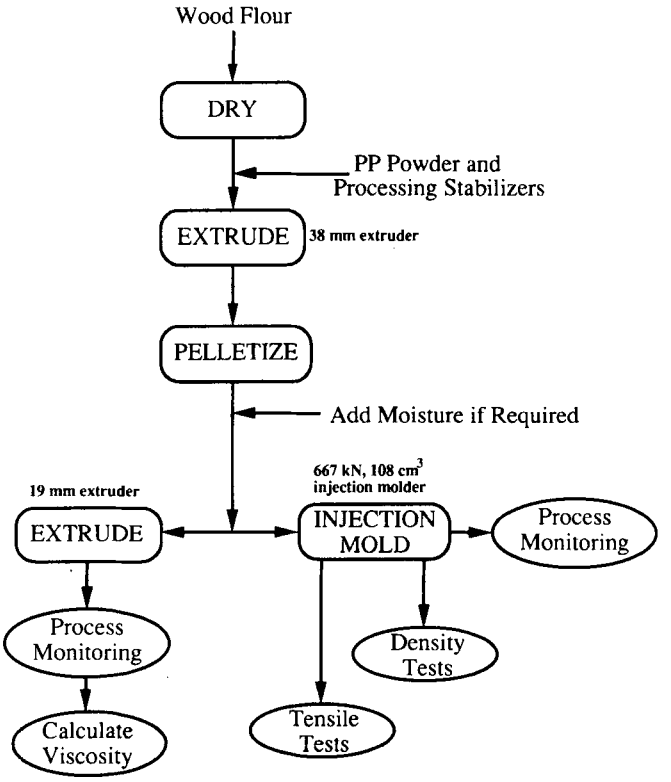

FIGURE 1 Schematic of the Experimental Procedure.

pine) were used as the respective matrix and filler material for the WF-PP composite study. The undried WF typically had an initial moisture content of about 8–9wt% by weight of dry wood. The average projected area of the as-received WF particulates was 0.08 mm^2 with an average particulate L/D aspect ratio (pre-processing) of about 5. The processing stabilizers used for the polypropylene were Ionol (butylated hydroxy toluene) from McKesson Chemical, and Irgonox-1010 [tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))] from Ciba-Geigy. These were added in the amount of 0.20 wt% and 0.10 wt%, respectively, by weight of polypropylene.

Statistical Methods

Statistical experimental design is a group of statistical techniques which can be used to relate a response output to the levels of a number of input variables that effect it.[24] Due to the large number of factors that could individually and interactively affect the processability and properties of the WF-PP mixture, a series of preliminary experiments were carried out to identify four important variables that would be congruous for the controlled series of experiments. The preliminary experiments were also used to determine the range of values over which the four independent variables could be adjusted while still resulting in the injection molding of "good" specimens. All other machine settings and material conditions, besides those noted as independent variables, remained constant throughout the final series of experiments.

The processability and properties of the injection molded WF-PP mixtures were evaluated in terms of the following independent variables: (1) percent wood flour in the polypropylene (WF/PP), (2) absorbed moisture content of the WF (H_2O), (3) hydraulic pressure during the packing/holding segment of the injection molding cycle (PRESS), and (4) nozzle/barrel temperature settings on the injection molding machine (TEMP). To reveal the significant main effects and significant interaction effects of these four variables, the injection molding trials were examined using a 2^4 full factorial statistical experimental design. This means that each of the independent variables were studied at two different levels (high and low), and the four parameters create a possible sixteen combinations ($2^4 = 16$). The low and high levels of each of these variables, shown in Table I, were chosen through previous experimentation to produce reproducible tensile specimens at all 16 possible experimentation levels.

TABLE I

Independent variables and their levels

VARIABLE NAME	LOW (-)	HIGH (+)	UNITS
1. Wood Flour/Polymer Ratio *	45/55	55/45	wt%/wt%
2. Wood Flour Moisture Content *	2.5	5.0	wt%
3. Hydraulic Pack/Hold Pressure	2.07	6.21	MPa
4. Barrel Temperature Settings **	166/177/191	182/193/199	°C

*Based on dry wood flour.
**Barrel Rear/Barrel Front/Nozzle.

The ratio of WF/PP is based on the total weight of the polymer (polypropylene plus processing stabilizers) and the weight of dry wood flour. The pack/hold hydraulic pressure levels were chosen so that there would be both a slight as well as a dramatic drop from the peak injection pressure at the instant-of-fill switch over point (change from constant velocity mode to constant pressure mode). Temperature profiles were set within the narrow limits available after consideration of all the other parameters. The relatively high wood filler loading caused the melt viscosity to increase dramatically, which limited how low the barrel temperatures could be set. Too high of a viscosity, whether caused by low temperatures or high filler content, resulted in an incomplete filling of the long, narrow tensile bar cavity. On the other hand, rapid degradation of the wood filler occurred near 200°C, which then placed a limit on the high end of the melt temperature.

This paper only addresses the effects of the above four variables on certain aspects of the following measured responses: (1) pressures within the tensile bar cavity during mold filling, (2) tensile testing behavior of the WF-PP composites, and (3) lengthwise density distribution within the injection molded tensile bar. A comprehensive discussion and analysis of the injection molding trials can be found elsewhere.[18]

Table II shows the full factorial design matrix in standard order, along with the tensile strength response (to be discussed later in greater detail). The plus and minus signs represent the high and low levels of each of the independent variables

TABLE II

The 2^4 full factorial design matrix with tensile strength response

Standard	INDEPENDENT VARIABLES				Tensile Strength Response (MPa)	
Run #	WF/PP	H_2O	PRESS	TEMP	I	II
1	-	-	-	-	26.74	26.12
2	+	-	-	-	21.03	21.74
3	-	+	-	-	24.88	25.39
4	+	+	-	-	20.66	20.54
5	-	-	+	-	27.88	27.52
6	+	-	+	-	22.61	22.48
7	-	+	+	-	27.16	27.41
8	+	+	+	-	22.48	21.45
9	-	-	-	+	24.98	25.23
10	+	-	-	+	20.86	21.24
11	-	+	-	+	24.12	23.78
12	+	+	-	+	19.99	20.35
13	-	-	+	+	26.85	27.85
14	+	-	+	+	22.56	22.59
15	-	+	+	+	26.78	26.85
16	+	+	+	+	22.05	21.90
-	45/55	2.5wt%	2.068 MPa	166/177/191 °C		
+	55/45	5.0wt%	6.205 MPa	182/193/199 °C		

(listed in Table I). In the first response column are the results of tensile bars molded during the sixteen trials of Series I, the first day of molding. The second column consists of the responses from the sixteen trials of Series II, also called the replicate series, which were molded on the second day using identical levels of the independent variables. Replication allows an independent estimate of the experimental error to be obtained.

Series I and Series II were carried out in a random order. In addition, the two series had to be run in two different random orders for true replication. Randomization of both the experimental procedures and testing procedures ensures that any systematic variations that may affect the responses are distributed randomly throughout the experiment. For example, if the hydraulic fluid temperature of the injection molding machine varies as the day progresses, there may be an observable influence on the injection molded parts. Running the experiments in random order gives any standard combination of independent variables an equal chance of being any run number (within a given series).

Despite the argument above, there are situations in which true replication and complete randomization may not be feasible. This study happened to be one of those cases. From a rigorous point of view, it is essential that all sixteen runs from each series be done as close together in time as possible (i.e. all in one day, without shutting the machine off). However, the time required for purging, molding, and barrel temperature changes for the sixteen random runs could have exceeded 20 hours. Hence, to complete the molding trials in a reasonable amount of time, the four possible combinations of pressure and temperature ($- -/- +/+ -/+ +$) were

TABLE III

Random orders for original and replicate series

Standard Run #	Order of Random Run #	
	ORIGINAL (I)	REPLICATE (II)
1	14	2
2	16	3
3	13	4
4	15	1
5	12	9
6	11	10
7	10	12
8	9	11
9	8	7
10	5	5
11	6	8
12	7	6
13	4	15
14	3	13
15	1	14
16	2	16

drawn at random for each series. Then, for each of these levels, the four possible combinations of WF/PP and % H_2O were drawn randomly. This was done for both Series I and Series II, thereby creating a semi-random order in which to run the experiments as illustrated in Table III.

As indicated above, the statistically designed experiment will yield the main and interaction effects of the variables on the responses.[24] A main effect is the average change in a response when the variable is increased from the low level to the high level (ignoring the influence of all other variables) while an interaction effect, e.g. Interaction ($\alpha\beta$), reveals the difference between the average effect of α at the high level of variable β, and the average effect of α at the low level of variable β (no distinction being made on the levels of any other variables). For a 2^4 experiment, there are sixteen possible effects for each response: four main effects (1, 2, 3, 4), six two-factor interactions (12, 13, 14, 23, 24, 34), four three-factor interactions (123, 234, 124, 134), one four-factor interaction (1234), and the average (which is the average of all the responses).

It is highly unlikely that all of the effects will turn out to be statistically significant. Significance is determined by using an estimate of the true experimental error, which is calculated from the differences in responses of the original and replicate series (Series I and Series II), and by assigning a confidence level, which in this study was set at a conservative 95%. One reason why replication is so important is that a numerical procedure can be used for error calculation. Table IV lists those effects that were determined to be statistically significant at the 95% confidence level, i.e. the individually and interactively "important" variables. Note that many of the sixteen possible effects for each response did not show up as being significant. Some of the results shown in Table IV will be discussed later.

All of the experimental results summarized and discussed in this paper are sta-

TABLE IV

Significant main and interaction effects at the 95% confidence level

Effect	Tensile Strength @ Break (MPa)	Tensile Modulus (GPa)	% Elongation @ Break	Cavity Pressure Decay Time (sec)	Cavity Pressure Losses (MPa)	Gage Region Density at Position 6 (g/cm^3)
average	23.877	4.070	2.535	11.790	10.608	1.0773
1	-4.688	-	-0.721	-4.693	4.231	0.0397
2	-0.781	-	-	1.290	-2.398	-0.0097
3	1.798	-	0.196	6.643	-	0.0159
4	-0.507	0.222	-	3.746	-3.474	-
12	-	-	0.186	0.630	-2.026	-
13	-0.334	-	-	0.465	-	-
14	0.326	-	-	-1.281	-1.975	-
23	-	-	0.187	-0.425	-	0.0141
24	-	-	-	-	1.304	-
34	0.312	-	-0.151	-	-	0.0041
123	-	-	-	-	-	-
124	-	-	-	-	1.288	-
134	-	-	0.177	1.034	-	-
234	-	-	-	-	-	-

1. Wood Flour/Polypropylene Ratio (45/55 or 55/45)
2. Wood Moisture Content (2.5wt% or 5.0wt%)
3. Pack/Hold Pressure (2.068 MPa or 6.205 MPa)
4. Barrel Temperature (166/177/191 °C or 182/193/100 °C)

tistically significant at the 95% confidence level. However, because of the total number of results that were determined to be significant, several of the main effects and 2-factor interactions have been excluded from the discussion. In addition, all of the significant three factor interactions have been omitted. This is an important point to make because the relative influence of any effect can be altered due to interactions with other effects, i.e. the influence of an effect may depend upon the level of the other effects. As such, the significant main effects by themselves represent only an averaged influence over the entire range of all other variables. Another important point concerning the statistical results must be stressed: the magnitude of any of the effects is dependent on the range over which the variable is changed. That is, if there is a larger spread in the high and low levels of an independent variable, it is likely that more of the variables will show up as being significant (as a main or interaction effect) in the analysis. Therefore, in this paper, the effects that were determined to be significant are pertinent only with reference to the specific high and low levels of the independent variables.

The extrusion trials were not implemented according to a statistical experimental design and they were simply run to provide additional information about the rheological behavior of the WF-PP melt. Specifically, the extrusion trials provided information about the effects of percent WF in the PP, absorbed moisture content in the WF, extruder die/barrel temperature settings,and screw rotation speed on the viscosity of the WF-PP melt and on the torque required to rotate the extruder screw.

Injection Molding Methods

Injection molding trials were run on a 667 kN/108 cm^3 Cincinnati Milacron toggle-clamp injection molding machine (Model T-75). The machine contained a 33 mm single screw and was controlled via a Cincinnati Milacron MPC 81/86 programmable controller. Throughout the molding trials the processing conditions were held such that mold filling occurred in roughly one second and the average cycle time was about 45 seconds. During plastication the screw speed was set at 75 rpm and the screw back pressure was held at 0.69 MPa. The settings for the hydraulic pack/hold pressure variable were either 2.07 MPa for the low level or 6.21 MPa for the high level. The pack/hold pressure was held for 16 sec during all of the trials, followed by 16 sec of additional cooling time. The rear-to-front (hopper to nozzle) temperature profiles were regulated at either 166/177/191°C or 182/193/199°C as the respective low and high levels of the temperature variable. A dual-zone Sterlco (Model F-6026) circulating water temperature controller was used to regulate the temperature of the mold cavity which was maintained at 71°C during all of the molding trials.

The mold used in the machine produced two ASTM D-638 Type I tensile bars per cycle, which required about 25% of the molding machine's plasticating capacity. A schematic of the bar is shown in Figure 2, which reveals the relative locations of three flush mounted Dynisco pressure transducers (Model PT-435A) installed within the tensile bar cavity. The dogbone-shaped bars were 3.2 mm thick along the entire length, with a rectangular gate located 4.5 cm from one end. Positions 1–10 shown on the bar in Figure 2 were the sections used for determining the

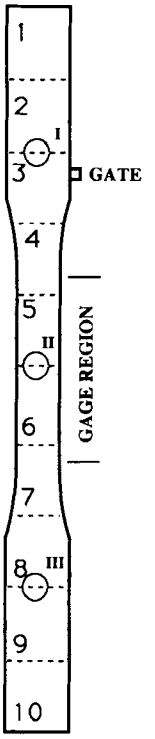

FIGURE 2 Schematic of tensile bar specimen with relative positions of pressure transducers I, II, and III, and density measurement samples 1–10.

density distribution along the length of the bar. The molding cycles were monitored via a PC-based data acquisition system consisting of a Zenith Z-386 equipped with Burr-Brown A/D boards. Two separate software packages were utilized as part of the process monitoring procedure, Snapshot Storage Scope for data acquisition and DADiSP Worksheet for data analysis.

Extrusion Methods

Two extruders were used, a 38 mm Modern Plastics Machinery (MPM) single screw extruder and a 19 mm Brabender (Model 2503 Plasti-Corder) single screw extruder. The former was used to compound all of the WF-PP dry blends mixtures and the latter was used to evaluate the rheological behavior of the WF-PP melt. Both extruders utilized three separate zones of temperature control on the barrel and a single zone of temperature control for the die. The screw of the MPM extruder was of a standard square-pitched design with an 8 turn feed section of channel depth 8.5 mm, an 8 turn linearly tapered transition section, and a 9.5 turn metering section of channel depth 2.7 mm. A dual-strand 3 mm circular-orifice die was used with the MPM extruder to produce the strands for subsequent pelletization. During compounding, the screw speed of the MPM extruder was maintained at 20 rpm, and the temperature controllers for the barrel and the die were all set at 180°C.

At these conditions the material residence time in the MPM extruder was on the order of 5 minutes, and the flow rate through the extruder was about 75 g/min.

The 25 turn screw of the Brabender extruder was of a continuous linear taper square-pitched design with a first turn channel depth of 3.6 mm and a last turn channel depth of 1.3 mm. The Brabender had the capability to monitor and display the torque required to rotate the screw during the extrusion process. An 89 L/R ratio capillary die (D = 1.78 mm, L = 80 mm) was attached to the Brabender extruder during the rheological studies. The pressure loss for the WF-PP melt flowing through the capillary die was monitored with a Dynisco pressure transducer (Model TPT-432) which was installed 20 mm upstream from the capillary die entrance. A schematic of the capillary die assembly is shown in Figure 3. During the processability extrusion trials the screw speed was varied between 5 and 25 rpm, and the rear-to-front (hopper to die) temperature profiles were held at either 166/177/191/191°C (low temp profile) or 182/193/199/199°C (high temp profile). The Brabender experiments provided the following rheological information: torque required to rotate screw and apparent viscosity of WF-PP melt.

Mechanical, Physical and Rheological Measurements

Tensile Property Measurements. Tensile tests were performed on an Instron Model 4206 Universal Testing Instrument. A 150 kN load cell was used, with a load weighing system accuracy of 1.0% of reading. Strain measurements were taken with a Model 2630-031 self-identifying strain extensometer, which had a 25.4 mm gage length and maximum extension of 12.7 mm (50% strain). The strain measuring system accuracy was 0.6% of reading. Load/strain curves were made using an Instron X-Y recorder.

Density Measurements. Density measurements were performed using a sink-float methodology. Various 500 ml controlled-density solutions of sodium chloride in distilled water were prepared in 0.005 g/cm^3 increments and stored in sealed glass jars. These solutions were calibrated using an ERTCO Plain Form hydrometer. Tensile specimens from each experimental run were cut into ten pieces (see Figure 2) and each piece was immersed in several solutions to see if it would sink

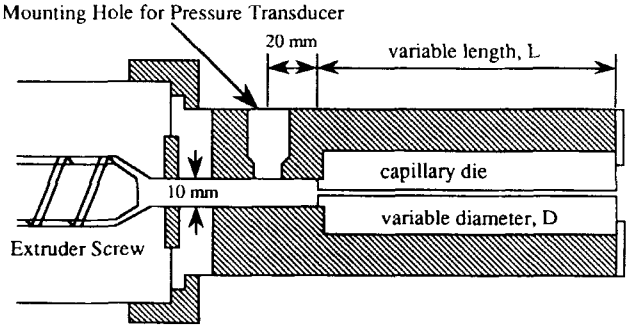

FIGURE 3 Schematic of capillary die (D = 1.78 mm, L = 80 mm) attached to the 19 mm extruder.

or float. Via this technique the densities along the length of the tensile bar could be determined to the nearest 0.01 g/cm^3.

Viscosity Measurements. Apparent viscosity (η_{app}) data for the WF-PP melt were obtained via the pressure drop and flow rate data from the capillary die extrusion trials. For the flow of a non-Newtonian fluid through a capillary die, the apparent viscosity can be calculated from a knowledge of the apparent shear stress and apparent shear rate data for the streaming fluid.[25] The magnitude of the apparent shear stress and apparent shear rate of the fluid at the capillary die wall can be calculated from the following two equations respectively:

$$\tau_w = \frac{\Delta P_{die} R}{2L} \tag{1}$$

$$\dot{\gamma}_w = \frac{4Q_{vol}}{\pi R^3} \tag{2}$$

where ΔP_{die} = pressure drop of the fluid through the capillary die, R = radius of the capillary die (0.9 mm), L = length of the capillary die (80 mm), Q_{vol} = volumetric flow rate of the fluid through the capillary die, and η_{app} is then obtained by dividing Equation (1) by Equation (2). Bagley and Rabinowitsch corrections were not applied to the capillary die data. The measured mass flow rate of the extrudate had to be converted to a volumetric flow rate before Equation (2) could be used, and an estimate of the extrudate density within the die was required for this conversion. The extrudate density within the die was estimated via the following expression:

$$\frac{1}{\rho_{EXT}} = \frac{1}{\rho_{PP}}\left(\frac{\text{wt\%PP}}{100}\right) + \frac{1}{\rho_{WF}}\left(\frac{\text{wt\%WF}}{100}\right) \tag{3}$$

where ρ_{EXT} = approximate density of the extrudate within the capillary die, ρ_{PP} = melt density of the polypropylene ($\approx$0.8 g/cm^3), ρ_{WF} = cell wall density of the wood flour ($\approx$1.4 g/cm^3).

RESULTS AND DISCUSSION

Processability

A primary objective of this study was to determine the influence of absorbed moisture on the processability and properties of the WF-PP composites. An indication of the processability of a polymer melt can be obtained by measuring the cavity pressure losses at the instant of mold filling (ΔP_{I-III} for the tensile bar molding trials) during the injection molding process. Representative cavity pressure data

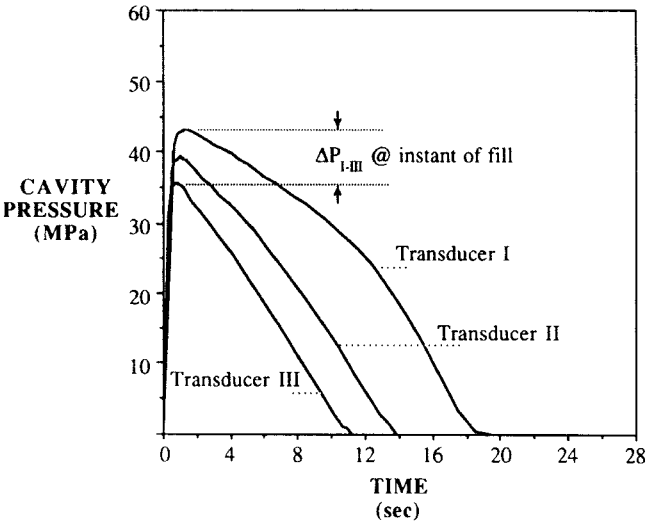

FIGURE 4 Representative transient cavity pressure traces for a 45wt% wood flour filled polypropylene.

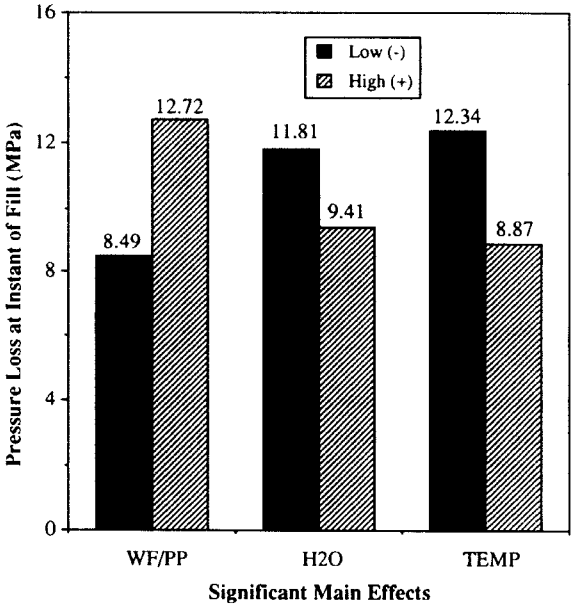

FIGURE 5 Influence of the significant main effects on the pressure required to fill the tensile bar cavity.

as recorded with the three flush-mounted pressure transducers during the injection molding of a 45wt% WF filled PP are shown in Figure 4. Relative to the cavity pressure losses for PP without WF, the presence of the WF (at the molding conditions used here) resulted in a three- to four-fold increase of the pressure losses during filling. As ΔP_{I-III} increases it indicates that mold filling becomes more

difficult, and in the extreme case incomplete mold filling would be the end result. Figure 5 shows the three independent variables that had a statistically significant effect on the cavity pressure loss ΔP_{I-III}. Figure 5 illustrates that, on the average, the higher WF concentration and the lower melt temperature significantly increased the flow resistance of the WF-PP melt, and, surprisingly, the flow resistance of the WF-PP melt decreased at the higher absorbed moisture level. These same results are presented somewhat differently in Table IV.

A specific example will provide additional information on how to interpret the cavity pressure loss data (as well as the other results) shown in Table IV or Figure 5. Table IV indicates that main effect 1 (the WF-PP ratio) is a positive main effect that causes the cavity pressure loss on the average to increase by (+)4.23 MPa as the WF-PP ratio is increased from its low level to its high level, which is similarly shown in Figure 5 by the change of the WF-PP bar-graphs from 8.49 to 12.72. Furthermore, Table IV indicates that main effect 2 (the H_2O content) is a negative main effect that causes the cavity pressure loss on the average to decrease by (−)2.40 MPa as the H_2O content is increased from its low level to its high level, which is similarly shown in Figure 5 by the change of the H_2O bar-graphs from 11.81 to 9.41.

There were several significant 2-factor interactions of interest for the pressure loss data, which can be identified in Table IV as Interaction (12) = −2.03, Interaction (14) = −1.98, and Interaction (24) = 1.30. Unlike the meaning of the sign (positive or negative) of a main effect, the meaning of the sign of an interaction effect is not as straight-forward to interpret. However, regardless of the sign, the presence of a 2-factor interaction indicates that the exact influence of a variable on a response will depend upon the level of another variable. Furthermore, the interaction can be such that the influence of the variable on a response could

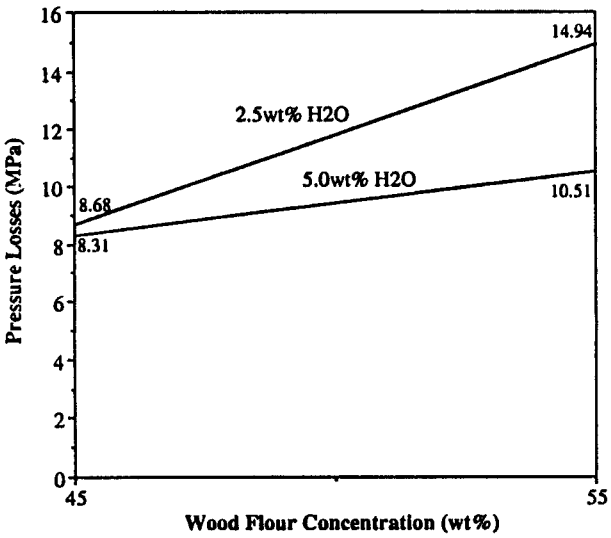

FIGURE 6 Significant (12) interaction effect of wood flour concentration and moisture content on cavity pressure losses.

become much less, could become much greater, or could become reversed as the level of another variable is changed. The first and largest (statistically) 2-factor interaction listed in Table IV is that of Interaction (12), involving the WF-PP ratio and the H_2O content. As seen in Figure 6, at the high level of absorbed H_2O (when compared to the low level of absorbed H_2O) the cavity pressure losses were lower for both the 45wt% and 55wt% WF filled PP. However, the moisture effect on the pressure losses was almost negligible for the 45wt% WF filled PP (8.31 MPa vs. 8.68 MPa) but quite large for the 55wt% WF filled PP (10.51 MPa vs. 14.94 MPa). Therefore the effect of absorbed moisture seems to become more prominent at the higher level of filler concentration. Another way to interpret this result is that if all of the molding trials (where the moisture content was varied) had been run at a 45wt% WF concentration then the effect of moisture on the cavity pressure losses may have gone unnoticed.

Figure 7 shows Interaction (24) between absorbed moisture and processing temperature. As indicated by the main effect results, the low temperature trials were more difficult to inject into the cavity than the high temperature trials and the high moisture level provided for somewhat lower pressure losses during cavity filling. However, it appears that in terms of reducing the pressure losses during cavity filling, the reducing influence of a higher moisture content was more noticeable for the low temperature materials (ΔP_{I-III} went from 14.20 MPa to 10.49 MPa as the moisture level was increased) than for the high temperature materials (ΔP_{I-III} went from 9.42 MPa to 8.32 MPa as the moisture level was increased).

The decreased resistance to flow of the WF-PP melt at a higher level of absorbed moisture is further supported by the data shown in Figures 8 and 9. Lower viscosities would result in decreased pressure losses during mold filling, and Figure 8 clearly shows that the melt viscosity of the WF-PP blend was lowered at higher levels of

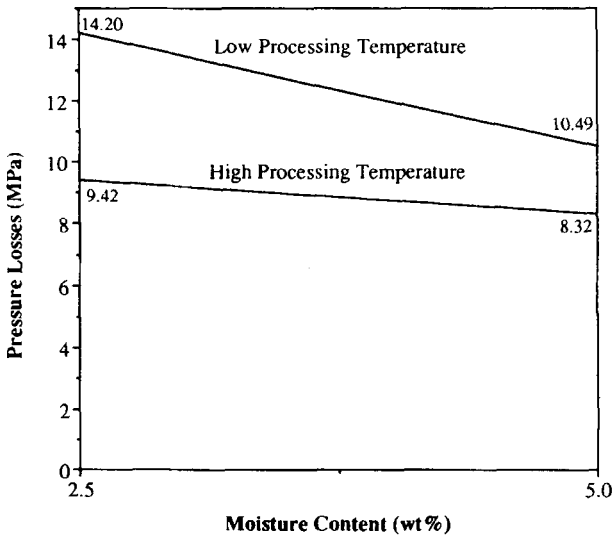

FIGURE 7 Significant (24) interaction effect of moisture content and processing temperature on cavity pressure losses.

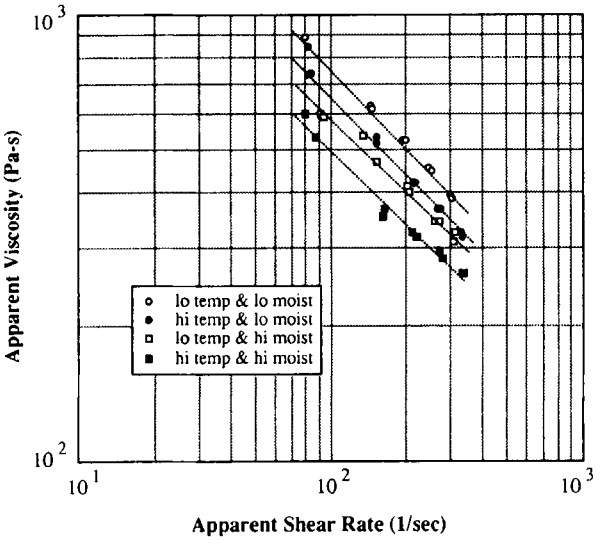

FIGURE 8 Apparent viscosity vs. apparent shear rate for a 45wt% wood flour filled polypropylene melt measured at different temperatures and absorbed moisture levels.

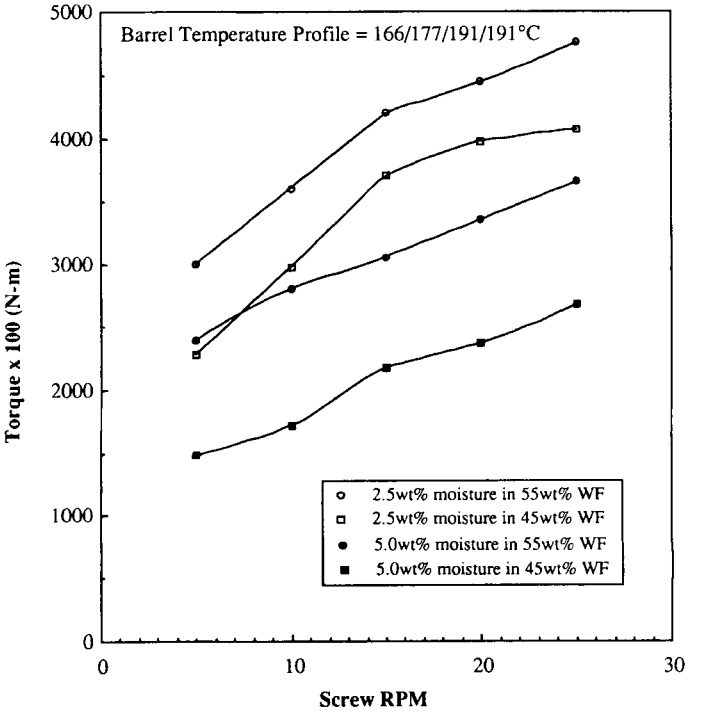

FIGURE 9 Torque requirements of the Brabender extruder as a function of screw RPM, wood flour concentration and absorbed moisture level.

absorbed moisture. It is interesting to note that the influence of moisture on the viscosity change (due to an increase from 2.5wt% to 5.0wt% in the absorbed moisture content) was of the same magnitude as the influence of temperature on the viscosity change (due to an increase from 166/177/191/191°C to 182/193/199/199°C in the barrel temperature profile). The "equivalent" relative influence of moisture and temperature on the magnitude of ΔP_{I-III} has already been seen in Figure 5. Figure 9 reveals that the decreased resistance to deformation of the WF-PP melt at higher moisture levels also manifested itself in terms of the energy required to rotate the screw at a constant screw speed, i.e. for a given set of conditions the torque requirement went down as the absorbed moisture level was set at its higher value. A possible explanation for the above observations is that if the moisture within the filler acts as an internal lubricant or plasticizer of the cellulosic material, then the WF-PP mixture would be less resistant to deformation at higher absorbed moisture levels. A separate detailed study on the effects of absorbed moisture during the extrusion of a cellulose fiber filled polypropylene has also confirmed the processability improvements in the presence of moisture.[26]

Another processing variable that was measured as a response was the decay time for cavity pressure transducer #1 (recall that transducer #1 is the one nearest to the gate.) The cavity pressure decay time was defined to be the time needed for the cavity pressure to decrease from the peak injection pressure (that at fill) to atmospheric pressure. In Figure 4, that value would be about 17 seconds. At any given constant set point of the pack/hold pressure, the transient pressure reading will give an indication of how long it takes for the material to "set up" (i.e. cool and solidify) within the cavity near the transducer. Table IV reveals that increasing the wood flour content from 45% to 55% decreased the decay time (the "set up" time) on the average by 4.7 seconds, while increasing the barrel temperature increased this time by 3.7 seconds. It is interesting to note that increasing the material moisture content lengthened the decay time by an average of 1.3 seconds. Furthermore, as shown in Table IV, the Interaction (12) between wood filler loading and moisture content had a value of (+)0.630 which indicated that on the average the material moisture content had a larger effect on increasing the decay time [which was (+)1.92 s] at the higher filler loading relative to the decay time [which was (+)0.66 s] at the lower filler loading. These "moisture influenced" results could be consistent with a microvoid argument, wherein a material with a high absorbed moisture content would give off more volatiles, thereby creating an insulating effect (a more porous structure) that would slow down the solidification process.

Properties

Figure 10 contains representative force-elongation curves for both filled and unfilled polypropylene. Several trends can immediately be seen from Figure 10 that are characteristic of the change in properties typically encountered when a rigid filler is added to a ductile polymer, namely that: (1) the elongation to break decreased significantly when WF was added to the PP matrix (the unfilled PP had a percent elongation to break of 590% and a percent elongation to yield of 10%), (2) the addition of WF dramatically increased the tensile modulus of the PP matrix (the

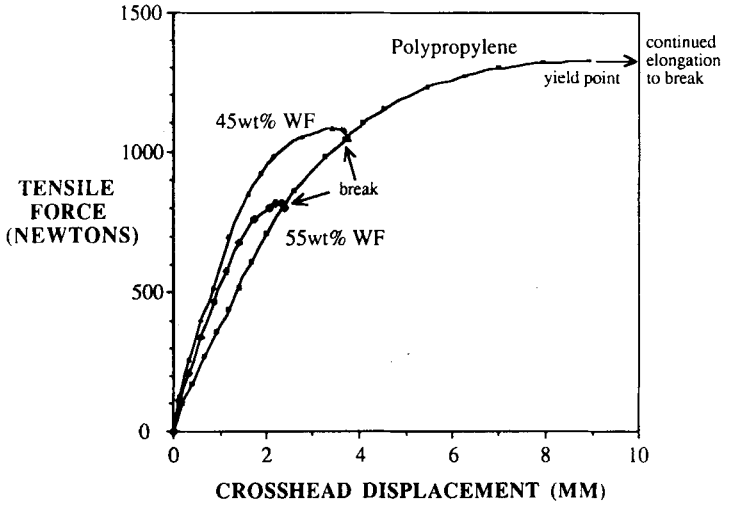

FIGURE 10 Representative tensile behavior for wood flour filled and unfilled polypropylene tensile bar specimens.

unfilled PP had a tensile modulus of 1.38 GPa), and (3) the WF by itself did not act to reinforce the strength of the PP matrix (the unfilled PP had a tensile strength at yield of 33.5 MPa). At the conditions studied in this series of statistically designed experiments, only two main effects were found to be significant in terms of influencing the percent elongation to break and surprisingly only one main effect (and no interaction effects) were found to be significant in terms of influencing the modulus. These results are shown in Table IV. It is interesting to note that the only effect that showed up as influencing the modulus response (at the 95% confidence level) was the processing temperature, which at it high level resulted in a relative increase of the modulus.

In terms of reproducibility and consistency, the best mechanical property data were in the form of the tensile strength response data which are listed in Table II for the original and replicate experimental runs. The results from the statistical analysis of the tensile strength response are contained in Table IV and Figure 11 where it can be seen that each of the four variables affected the tensile strength of the WF-PP composite. As already mentioned the presence of the WF additive (without an appropriate coupling agent) does not act to reinforce the PP matrix, but it does appear that the extent of the loss in strength can be moderated via the processing conditions. From Figure 11 it is interesting to note that, on the average, the resulting tensile strength of the WF-PP composite increased at: (1) the lower absorbed moisture level within the WF, (2) the higher post-fill pack/hold pressure within the cavity, and (3) the lower processing temperature within the barrel. Furthermore, the influence of absorbed moisture may become even more critical at the kind of moisture levels found within as-received WF (typically about 8–9wt%), especially since that during the experiments the absorbed moisture level was only varied between 2.5wt% and 5.0wt%.

Based upon the relative influence on the tensile strength of the variables listed

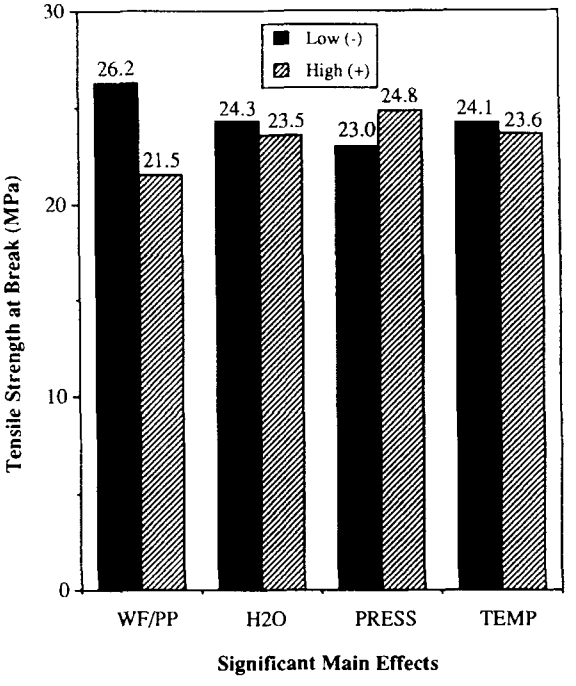

FIGURE 11 Influence of the significant main effects on the tensile strength at break for wood flour filled polypropylene composite.

in Figure 11 it was speculated that porosity within the WF-PP composite (as affected by the formation of microvoids within the composite) was to some extent dictating the final mechanical behavior of the composite. The absorbed moisture within the WF will outgas at the high temperatures encountered during the melt processing operation, additionally, there may be a synergistic effect between absorbed moisture within the WF and thermal degradation of the WF which would lead to an even higher degree of volatile formation. For a closed-mold process such as injection molding, the volatiles remain trapped inside of the composite as it cools and solidifies within the mold cavity. This could create a variable porosity microstructure (perhaps similar to that of a high density foam.) The final porosity (density) distribution within the molded tensile bar would be influenced by the extent to which microvoid growth could be suppressed by the prevailing pack/hold pressures which occur within the cavity during the molding cycle.

Figure 12 illustrates the degree to which the density was observed to vary along the length of the tensile bar. A reference point for Figure 12 is that the predicted density (from rule of mixtures with ρ_{WF} = 1.4 g/cm^3 and ρ_{PP} = 0.9 g/cm^3) of a 45wt% and a 55wt% WF filled PP would be 1.07 g/cm^3 and 1.12 g/cm^3 respectively. Assuming that these ρ_{WF} and ρ_{PP} values are reasonable, then deviations from the predicted values of 1.07 g/cm^3 and 1.12 g/cm^3 would be caused by either the presence of voids or the occurrence of filler-matrix segregation. The effects of these two phenomena can be seen in Figure 12, with the later point explaining the relative maximum in the measured density seen at position 9. The density maximum within the gate region is likely due

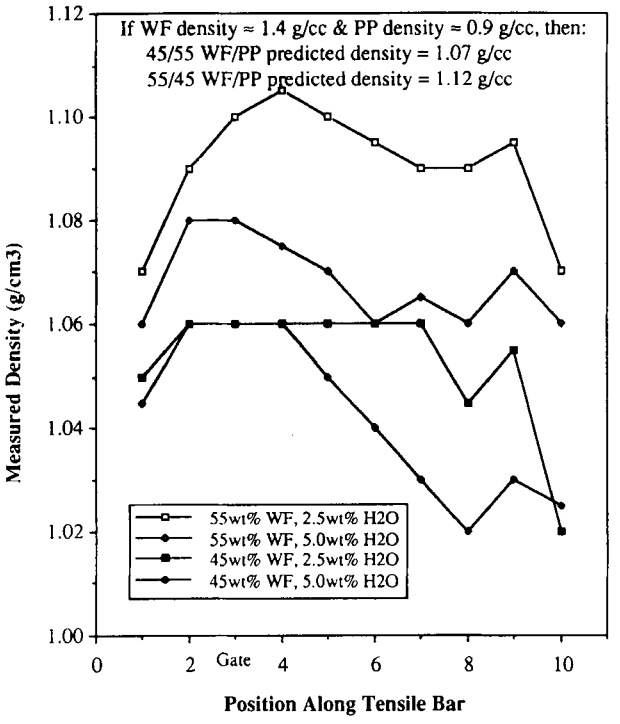

FIGURE 12 Lengthwise density distribution for various wood flour filled polypropylene tensile bars molded at the low pack/hold pressure and high barrel/nozzle temperature settings.

to the high prevailing pack/hold pressures (which occur within the gate region) during the injection molding cycle. A more detailed analysis of the density variations within the injection molded WF-PP specimens is forthcoming.[27]

Table IV and Figure 13 report the significant main effects on the density at position #6, the cumulative average of which was 1.08 g/cm^3. Recall that position #6 is within the gage region of the tensile bar. The position #6 density value was most significantly affected by the wood flour concentration. The high wood flour level resulted in a density increase of 0.04 g/cm^3 relative to the low wood flour level. On the average such an increase is to be expected, since the filler density (1.4 g/cm^3) is higher than the matrix density (0.9 g/cm^3). Another main effect revealed that increasing the moisture from the low level to the high level decreased the density by 0.01 g/cm^3 which was likely due to an increase in the trapped void volume within the specimens. The final significant main effect was that of the post-fill pack/hold pressure. On the average, the high level of pressure increased the density by 0.016 g/cm^3 compared to the low level of pressure. Under a higher pack/hold pressure, the released gasses within the moldings are kept from expanding, thus resulting in an increased density. Figure 14 contains the most significant 2-factor interaction effect on the density measurement at position #6, which was Interaction (23), that of moisture content and pack/hold pressure. At the low moisture level, the measured densities were almost identical (1.081 g/cm^3 versus 1.083 g/cm^3) irrespective of the pressure level. However, at the high moisture level,

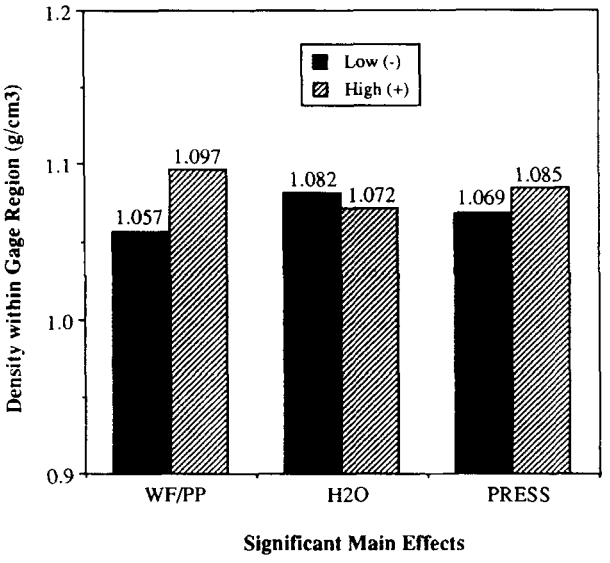

FIGURE 13 Influence of the significant main effects on the gage length density (position #6) within wood flour filled polypropylene tensile bar.

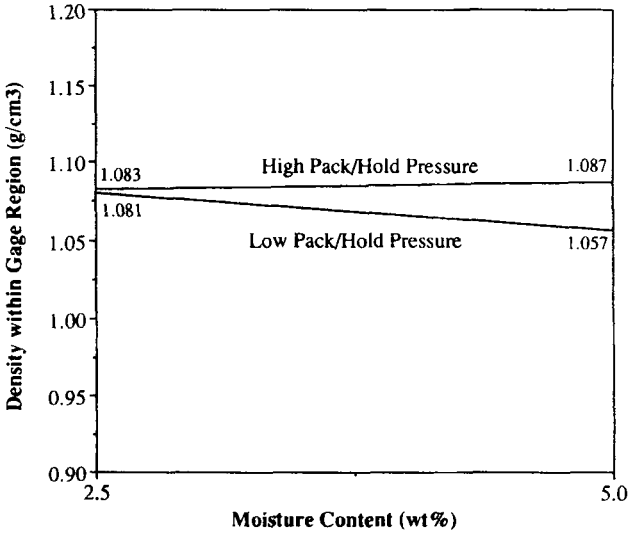

FIGURE 14 Significant (23) interaction effect of moisture content and pack/hold pressure on the gage length density (position #6).

the high pack/hold cavity pressure resulted in a slight density increase (up to 1.087 g/cm^3) while the low pack/hold cavity pressure resulted in a sharp density decrease (down to 1.057 g/cm^3). This shows that (at least at position #6) the lower pressure level will readily allow a porous microstructure to form in the presence of a high absorbed moisture level.

The density reductions (relative to the theoretical values of 1.07 g/cm^3 and 1.12

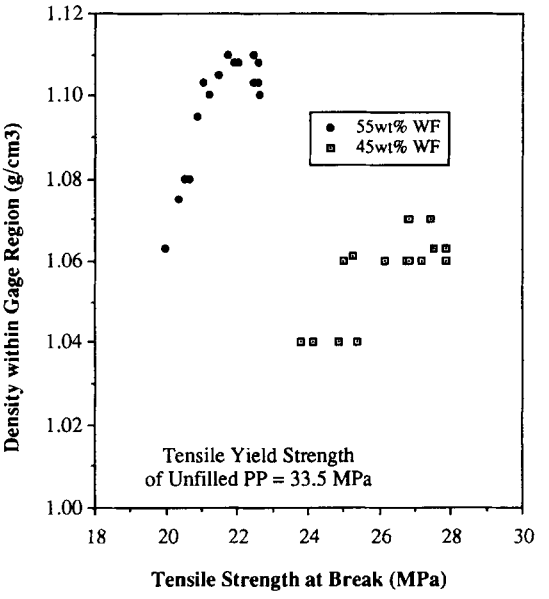

FIGURE 15 Correlation between gage length density (position #6) and tensile strength at break for 45wt% and 55wt% wood flour filled polypropylene composites.

g/cm^3) within the central region of the tensile bar appear to be caused by the presence of a void volume, and the processing and material conditions that would lead to an increased void volume are lower pack/hold pressures and higher moisture levels. Such a conclusion is consistent with the observation (see Figures 13 and 14) that a lower pack/hold pressure and a higher moisture content caused the density reduction to increase. Furthermore, the final density of the composite will affect its mechanical behavior, hence it is important to understand how the processing and material conditions affect the density of the composite. Figure 15 reveals that the tensile strength of the WF-PP composite did indeed correlate with the density (measured in the gage region of the tensile bar) of the WF-PP composite, and that the sensitivity of the correlation was greatest for the 45wt% WF filled PP composite. Figure 15 also shows that under certain conditions the composite density of the 55wt% WF filled PP can be reduced (due to porosity) to that of the 45wt% WF filled PP.

CONCLUSIONS

The results demonstrate that the processing conditions and the initial material conditions have a strong influence on the mechanical and rheological properties of cellulosic-thermoplastic composites, and that the measured density variation in the along-the-flow direction can be quite significant for these types of composites.

The hygroscopic nature of cellulosic fillers may be as important as their hydrophobic nature. And although the two are not independent of each other, they each lead to different kinds of processing/property concerns.

Absorbed moisture within the cellulosic filler directly influences the porosity within natural fiber reinforced injection molded thermoplastic composites, which consequently influences the mechanical properties of such composites.

Absorbed moisture within the cellulosic filler appears to improve some aspects of the processability of natural fiber reinforced thermoplastics. If the absorbed moisture tends to "soften" the cellulosic component then perhaps it behaves as a plasticizer during processing.

The positive/negative effects of absorbed moisture in cellulose filled thermoplastics could be even more pronounced if an undried wood flour feedstock is used which would contain an equilibrium moisture content of about 8–9wt% (based upon the mass of cellulosic material).

Future efforts will examine the processability and properties of cellulose (rather than wood flour) reinforced thermoplastics. Here the influence of absorbed moisture may be even more pronounced, because for a given set of environmental conditions cellulose has a greater equilibrium moisture content than wood flour.

Acknowledgment

Financial support for these studies was received through the USDA's (Forest Service) Forest Products Laboratory and from American Wood-Stock, Inc. The 19 mm extrusion trials were carried out by Mr. Salam D. Al-Ramahi. The assistance of Dr. George E. Myers and Prof. Donald S. Ermer is also appreciated.

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