Fiber reinforced engineering plastics

Daniel F. Caulfield (1), Rodney E. Jacobson (2), Karl D. Sears, (3) and John H. Underwood (3)
(1) USDA, Forest Products Laboratory, One Gifford-Pinchot Drive, Madison, WI, 53 705-2398
(2) A-J Engineering, 222 Randolph Drive –203A, Madison, WI, 53717
(3) Rayonier Inc., Performance Fibers Division, 4474 Savannah Highway, Jesup, GA 31598

Introduction

Although natural fiber reinforced commodity thermoplastics have a wide range of non-structural applications in the automotive and decking industries, there have been few reports of cellulosic fiber-reinforced engineering thermoplastics. The commonly held belief has been that the only thermoplastics amenable to natural-fibre reinforcement are limited to low-melting (below 180°C) commodity thermoplastics like polyethylene and polypropylene. However, in three recent papers we have shown that the high-melting engineering plastics, nylon-6 and nylon 66 can indeed be reinforced with cellulosic fibers using lowtemperature processing with a twin-screw extruder to produce composites of promising structural applications. In this paper we report two additional examples of high-melting engineering thermoplastics, ECM (an aliphatic polyketone) and PBT (polybutyllenephthalate) that can be reinforced with cellulosic fibers using our methods.

Objectives

The objectives of this research were

1) to develop methods and proceduresfor the melt-blending of cellulose fibers with 1) an aliphatic polyketone (ECM) and 2) a high-melting thermoplastic poly(ester), polybutyleneterephthalate (PBT) by twin-screw extrusion technology,
2) to injection mold ASTM test samples from these composites, and
3) to evaluate the mechanical properties of these composites as potential replacements for mineral and glas-fibre reinforced composites presently used in these thermoplastics.

Background

The earliest reported attempt to use cellulose flour and cellulosic fibers to reinforce polyamides was that of Klason, Kubàt and Strömvall in 1984 (1). In that paper, which followed an earlier report (2), that demonstrated the potential of wood flour and cellulosic fibers as reinforcement for commodity thermoplastics like polyethylene and polypropylene. However, the results with polyamides were generally discouraging. Although there was some success in reinforcing PA-12 (melting range 176-180°C) with cellulose, however when PA-6 was used (melting point 215°C), cellulosic fiers showed poorer reinforcing potential than wood flour and cellulosic flour. In all cases the PA-6 materials exhibited severe discoloration and pronounced pyrolytic degradation. These authors (1) concluded that for the higher melting thermoplastics like PA-6, "cellulosic fibers do not produce any significant degree of reinforcement despite their obvious stiffness and strength potential." Since those initial experiments, it has been commonly believed that the use of cellulosic fibers as reinforcement in thermoplastics is limited to the low-melting commodity thermoplastics (melting points below 180°C) (3). Furthermore, it has been commonly believed that the higher melting engineering thermoplastics (m.p. >220°C) cannot be effectively reinforced with cellulosic fibers because of the severe thermal degradation of the cellulose that occurs at temperatures needed to process these high-melting engineering thermoplastics (4). In a recent patent application we have demonstrated that this common belief is erroneous, and described materials and methods for achieving composites containing cellulosic fibers in high-melting engineering thermoplastics (5). This report has been followed by three recent papers in which we demonstrated that the high-melting engineering plastics, nylon–6and nylon-66 can indeed be reinforced with cellulose fibers using low-temperature or "chill processing" method developed by us using a twin-screw extruder to produce composites of promising structural potential (6,7,8).

Materials

Cellulose fibers:
Because of the greater thermal stability of cellulose over lignin and hemicellulose we chose as reinforcing fibers purified mixed southern hardwood prehydrolyzed kraft fibers. These pulp fibers are manufactured by Rayonier Performance Fibers to possess alpha cellulose content greater than 95%. In this report the cellulose fibers will be identified for convenience only as hardwood cellulose fibers. These pulp fibers were pelletized into either 6mm or 3mm pellets for ease of materials' handling and side-stuffed into pre-melted polymer at zone #4 of the twin-screw extruder. The details of these methods have been described in our earlier publications.

Polymers:
The aliphatic polyketone selected was Carilon^{TM} (Shell Chemicals). Carilon is an example of an aliphatic polyketone. Carilon is based on polymerization of ethylene and carbon monoxide (with a minor amount of propylene) into linear alternating structures. This polyketone is identified, in this report, as ECM (Ethylene-Carbon Monoxide), and has a reported melting point of 220°C. The Carilon grade used was polymer D26HM100 that has a reported MFI of 6.0g/10min @(240°C/2.16kg). (Note: On February 17, 2000 Shell Chemicals announced that its product, Carilon, has been withdrawn from the market and is no longer commercially available.)
The polyester selected for initial investigation was polybutyleneterephthalate (PBT) (Celenex^{TM}) manufactured by Ticona, LLC. Two grades were used; Celenex 2000 (MFI of 65cc/10min @ (250C/2.16kg)) and Celenex 2008 (MFI of 150cc/10min @250C/2.16kg)). Polybutylene-terephthalate (also known as polytetramethyleneterephthalate) has a reported melting point of 232°C. The melting points of both these polymers, ECM and PBT, are well above 200°C, the temperature usually cautioned "not-to-exceed" when melt processing with wood cellulose fibers.

Processing

The ECM and PBT polymers were compounded with hardwood cellulose fibers using the same low-temperature techniques developed for nylon-6 on FPL's 32 mm Davis-Standard co-rotating twin-screw extruder. In these initial investigations, no coupling agents or compatlbilizers were used. The main objective was to determine if these materials could be processed without undue thermal degradation or discoloration. The composite pellets produced were dried and injection molded into standard ASTM test coupons using a 33 Ton Cincinnati Milicron Inc. injection molder.

Testing

The test methods used for evaluating mechanical properties were:

1) D 638-90 "Standard test method for tensile properties of plastics".

2) D 790-90 "Standard test method for flexural properties of unreinforced and reinforced plastic and electrical insulating materials".

3) D 256-90b "Standard test method for impact resistance of plastic and electrical insulating materials".

Tables 1 and 2 contain the test results on the cellulose-fiber/ECM and the cellulose-fiber/PBT composites respectively.

Discussion

Processing of the high-melting thermoplastics, EMC and PBT, can be achieved using the twin-. screw extrusion processing methods previously described (8). In this method careful temperature control is necessary to avoid the viscous shear-heating that can potentially damage and char these cellulose fiber containing composites. A color analysis of injection-molded composites was evaluated using the Minolta Chroma-Meter CR2000 (Table 3). The Chroma-Meter was used to measure the lightness factor, L*, and the chromaticity factors, a* and b*, of the composite samples. The lightness factor, L*, indicates that although there is some color generated on processing, this effect is not serious. Fiber mechanical properties do not appear to be significantly degraded. Furthermore, composites of these engineering thermoplastics are usually colored black, so slight discoloration should not present a problem.

The measured tensile strengths of the fiber containing composites do not show any improvement over the tensile strength of the unreinforced polymer. This indicates that there is poor stress transfer between fiber and matrix polymers. These composites were prepared without compatibilizers or coupling agents to enhance this stress transfer. It is clear that development of appropriate coupling agents and compatibilizers for these polymers is necessary for achieving full reinforcing potential of cellulosic fibers.

The presence of cellulose fibers significantly improves the bending strength and stiffness (flexural modulus and tensile modulus) above those of the unreinforced polymers. The effect from cellulose fiber reinforcement lies between the reinforcing effects of wollastonite and glass-fiber. But the additional benefit that cellulose fibers provide the reinforcement with a smaller increase in density should not be discounted, especially for automotive applications.

In terms of fracture toughness, as measured by the notched and un-notched Izod tests, fiber reinforcement general decrease toughness. However, these composites were prepared without additives. Compatibilizers and coupling agents have been shown to improve impact performance. Impact modifiers added to the matrix polymer can also significantly improve impact performance.

Conclusions

The results of this investigation verify that low temperature processing techniques can be utilized to producing composites of cellulose fibers with two additional high-melting point thermoplastics, ECM(and aliphatic polyketone) and PBT (a polyester). Control of viscous shear heating during the extrusion processing of these composites is essential for avoiding the thermal degradation of the cellulosic component. These composites (without compatibilizers and other additives) possess stiffness and bending strength properties that are intermediate between similar composites prepared with wollastonite and glassfiber reinforcements. It is expected that with continuing research on coupling agents/compatibilizers that significant improvements in mechanical properties, especially tensile strength will be achieved.

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Table 1
Mechanical Properties of Cellulose-fiber/Aliphatic Polyketone (ECM) Composites

Sample Identification:	Fiber (%)	ECM (%)	Coupling Agent (%)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Failure Strain (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Notched Impact (J/m)	Unnotched Impact (J/m)
100% ECM	None	100% ECM	None	58.1	1.35	13.00	42.3	2.25	47.60	774.27nb
				0.8	0.02	0.10	0.4	0.09	4.81	12.26
33 HW-ECM	33% hardwood cellulose fiber	67% ECM	None	58.6	5.02	3.80	78.1	4.71	39.21	231.68
				0.8	0.12	0.20	0.7	0.10	2.68	25.9
30GLA-ECM *	30% glassfiber	67% ECM	None	129.1	7.57	3.00	161.5	8.50	88.81	538.17nb
				0.5	0.18	0.10	13.5	0.11	1.81	11.06
30% WOL-ECM	30% wollastonite	70% ECM	none	42.6	3.32	--	51.3	3.30	37.76	443.45
				0.1	0.04	--	0.5	0.05	0.57	8.05

*indicates commercial product for comparison, not compounded on FPL’s extruder.

Table 2

Mechanical Properties of Cellulose-fiber/Polyester (PBT) Composites

Sample Identification:	Fiber	PBT	Additive	Tensile Strength	Tensile Modulus	Failure Strain	Flexural Strength	Flexural Modulus	Notched Impact	Unnotched Impact
	(%)	(%)	(%)	(MPa)	(GPa)	(%)	(MPa)	(GPa)	(J/m)	(J/m)
PBT-Cx2000	None	100%PBT	None	58.0	3.14	7.00	67.9	2.81	21.20	678.10nb
				0.8	0.02	0.20	0.7	0.05	1.06	118.27
33HW-Cx2000	33% Hardwood cellulose fiber	67% PBT	None	59.1	6.53	3.00	87.6	5.76	23.55	97.76
				1.0	0.14	0.10	1.8	0.14	2.46	10.53
33HW1-Cx2000	33% Hardwood cellulose fiber	66% PBT	1% P900	59.2	6.13	3.20	90.1	5.69	22.87	143.12
				1.4	0.10	0.20	1.3	0.08	1.81	28.47
PBT-Cx2008	None	100% PBT	None	41.1	3.07	3.90	73.5	3.08	17.11	156.28
				4.3	0.10	0.60	0.6	0.04	3.16	28.86
33HW-Cx2008	33% Hardwood cellulase fiber	67% PBT	None	56.4	6.50	3.10	90.9	5.45	19.61	112.12
				2.1	0.54	0.20	2.2	0.05	1.29	25.65
30 GLA-PBT*	30% glass fiber	70% PBT	None	125.6	10.62	2.10	179.0	10.68	46.21	246.59nb
				1.6	0.72	0.20	1.4	0.18	2.70	45.24

*indicates commercial product for comparison, not compounded on FPL's extruder.

Table 3

Color analysis of fiber composite injection-molded specimens

	Fiber (%)	ECM or PBT (%)	L*	a*	b*
100% ECM	None	100% ECM	67.72	-2.28	8.74
33 HW-ECM	33% hardwood cellulose fiber	67% ECM	49.78	7.36	21.82
BOGLA-ECM *	30% glassfiber	67% ECM	41.39	6.90	23.38
30% WOL-ECM	30% wollastonite	70% ECM	-	-	-
PBT-Cx2000	None	100% PBT	88.80	-1.17	1.95
33HW-Cx2000	33% Hardwood cellulose fiber	67% PBT	49.34	6.69	14.04
33HW1-Cx2000	33% Hardwood cellulose fiber	66% PBT	50.23	6.65	13.88
PBT-Cx2008	None	100% PBT	90.10	0.36	-1.37
33HW-Cx2008	33% Hardwood cellulose fiber	67% PBT	50.22	6.90	14.14
30 GLA-PBT*	30% glass fiber	70% PBT	82.29	-1.17	1.95
WHITE STANDARD			92.76	0.31	0.33

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