DEVELOPMENT OF HIGH IMPACT STRENGTH FOR LONG-GLASS-FIBER REINFORCED POLYPROPYLENE

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Abstract

Recently long-glass-fiber-reinforced thermoplastics have become popular in the automotive industry. These materials have high rigidity and impact balance. However, there are still areas for improvement of mechanical properties, especially impact strength, which is desirable for new applications such as floors, roofs and trunk lids, as well as other structural parts. We have developed a way to improve the impact strength of this material. This paper offers the explanation for this method and suggests the best way how to use these materials.

Introduction

Recently the automotive industry has favored the use of component modules due to parts configuration circumstances, weight savings, cost savings, and parts consolidation. Long-glass-fiber-reinforced thermoplastics (LFTP) have received attention for their use as substrates in applications like front-end module carriers and doorplate carriers due to their properties and abilities. LFTP is basically an impregnate of several thousand filaments encapsulated within a thermoplastic resin matrix. Roving glass strands are uniformly dispersed within a resin binder and these strands are cut into lengths of 5-20 mm. Polypropylene-based LFTP (LGFPP) has received the most attention now from the viewpoint of low density, low cost, and unique processability, which allows for production of complex part designs. Figure 1 shows a comparison of properties between short-glass-fiber-reinforced polypropylene (SGFPP) and LGFPP. LGFPP is superior to SGFPP in tensile strength, flexural strength and Izod impact.

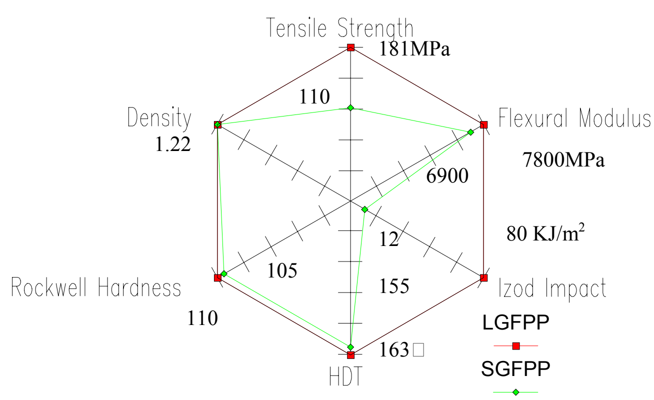

Figure 1. Property comparisons between SGFPP and LGFPP

This can be explained from the basis of the rule of mixtures. For example, tensile strength (*Tc*) is expressed in Eq. 1. One important parameter affecting *Tc* is the relationship between fiber length (*l*) and fiber diameter (*d*) according to this equation. We call L/D the aspect ratio, and for given value of *d*, *l* is most effective for increasing strength. Flexural modulus is another property expressed in Eq. 2. There is no factor L/D in the equation. Rather flexural modulus is influenced by the filler and, therefore, there is no difference between LGFPP and SGFPP. For impact strength, the expression shown in Eq. 3 was suggested, which includes the L/D parameter like the tensile strength expression. 3)

$$Tc = KVfTf\left(1 - \frac{dTf}{2\tau l}\right) + (1 - Vf)Tm \quad \Lambda\Lambda \quad \text{Equatoin } 1.$$

K : Fiber orientation Vf : Volum of fiber

Tf : Tensile strength of fiber Tm : Tensile strength of matrix

τ: Interfacial Tension between filler and matrix

d : Fiber diameter l : Fiber length

(1)

$$Ec = Em(1 - Vf) + EfVf \quad \Lambda\ \Lambda \quad \text{Equation } 2.$$

Em : Modulus of matrix Vf : volum of fiber

Ef : Modulus of fiber

(2)

$$Ic = KVfT\,\frac{l}{d}\,wt \quad \Lambda\ \Lambda \quad \text{Equation } 3.$$

K : Efficiency of reinforcement

T : Share stress between polymer and glass fiber

w : Width of test pieces t : Thickness of test pieces

(3)

One needs to consider the distribution of fiber length when more detailed assessment of LGFPP properties is needed. According to the above relations, fiber length, interfacial tension and fiber orientation are important parameters for improvement of properties. We studied ways to improve the impact from a material standpoint and the molding conditions needed to keep rigidity high on the material.

Objectives & Methodology

In this study our objective was to improve impact performance and maintain the stiffness by considering both the material composition and the molding conditions. The material composition, molding conditions, and test results are presented in their corresponding sections.

Material Composition

For material preparations, we used a modified type of polypropylene, which was manufactured by the Chisso Corporation, and a specially designed additive package for the product. We then introduced this mix along with roving glass fibers into our pultrusion process to produce a 48%-glass-fiber masterbatch. To adjust the final product, GF loading to 20%, 30%, and 40% for parts of this analysis, we blended another modified PP into the 48% LFGPP masterbatch and molded test pieces.

"*A Type*" consists of a modified matrix polymer made from a combination of a high-stereo-regularity polypropylene (HSPP) and reactor-made thermoplastic polyolefin (TPO) elastomer (R-TPO) with a GF content of 48%. "*B Type*" consists of a modified matrix polymer made from HSPP and two kinds of impact modifiers instead of R-TPO. These kinds of impact modifiers are designed to more finely disperse in the PP matrix and therefore have better compatibility with the base resin than that of R-TPO.

Molding Conditions

Two types of screws were used in a standard injection-molding unit. One was a "*low-shear*" design for LGFTP and the other was a "*conventional*" design. The former is a modified screw and nozzle designed by us as shown in Table I. This modified screw was made using deep channels at all zones, reduced compression ratio, and expanded compression zones. The check ring has a wide clearance and the nozzle diameter was enlarged.

Table I: Molding conditions

Molding Condition		1	2
Screw Design		Modified	Standard
Check Ring		Modified	Standard
Nozzle		Modified	Standard
Injection Speed (1^{st})	ml/s	66	66
Backpressure	MPa	0	7.4
Barrel Temperature	^{o}C	250	250
Mold Temperature	^{o}C	50	50

Test Method

Testing methods typically used to assess impact performance of plastic materials are Izod impact (JIS), Gardner impact (ASTM), and Dart impact (custom). These results are shown in Table II, which also lists other material properties that were evaluated.

Table II: Test Method

Test Conducted or Property Measured	Standard or Conditions Followed
Tensile Strength	JIS K7113
Flexural Modulus	JIS K7203
Izod Impact Strength	JIS K7110
Gardner Impact	ASTM D5420 • Weight = 2 kg • Diameter of Weight = 15.9 mm • Diameter of Support = 16.3 mm • Specimen Size = 150 x 150 x 3 mm • E50 = 50% failure energy (J)
Dart Impact (Falling Weight)	Chisso • Weight = 2 kg • R = 40 mm • Diameter of Support = 100 mm • Specimen Size = 150 x 150 x 3 mm • E50 = 50% failure energy (J)

Results & Discussion

The *A Type* (outlined in Table III and Figure 2) consists of a modified matrix polymer made from a combination of HSPP and R-TPO. The mix ratio of HSPP and R-TPO at 75:25 has the optimum property balance with Izod impact still in the high steady range and tensile strength just beginning its decline with increasing R-TPO content. The tensile strength does increase a small amount at HSPP content greater than 75%, but with a substantial drop in impact strength. "*Current-1*" is a rigid type of LFGPP[1] while "*Current-2*" is an impact type of LFGPP[2]. The newly developed HSPP/R-TPO (75:25) material shows better impact and strength balance than that of both current grades. One effective method to study the composite is to assess the surface after fracture. The SEM photo outlined in Figure 3 shows the fracture surface of *Type A*. One can see some glass fibers of few hundred micrometers in length, overlapped glass fibers, and breakage of fibers at the surface.

Table III: Physical properties of various glass-filled content for A-Type polymer under Molding Condition 1

Test	**Matrix**	**HSPP/R-TPO GF**					
	Ratio HSPP/R-TPO	*100*	*75*	*50*	*0*	Current 1	Current 1
		0	*25*	*50*	*100*	Rigid	Impact
	% GF Content	*48*	*48*	*48*	*48*	*48*	*48*
Tensile Strength	MPa	192	181	151	110	197	170
Flexural Modulus	MPa	9680	8350	7800	7030	9600	8000
Izod Impact Strength	KJ/m^2	108	122	158	160	96	110
Gardner Impact (E50)	J	11.8	19.6	>19.6	>19.6	7.8	11.8
Dart Impact (E50)	J	15.7	31.4	35.3	>35.3	7.9	15.7

Table IV: Physical properties of various glass-filled content for A-Type polymer under Molding Condition 1

Test	**Matrix**	**HSPP/R-TPO 75/25**				**Current-1**	**Current-2**
	GF Content	20	30	40	48	40	40
Tensile Strength	MPa	95	128	160	181	181	145
Flexural Modulus	MPa	3520	5070	7030	8350	7800	6250
Izod Impact Strength	KJ/m^2	50	74	110	122	80	83
Gardner Impact (E50)	J	9.8	13.7	17.6	19.6	5.9	9.8
Dart Impact (E50)	J	23.5	21.6	31.4	31.4	7.8	13.7

Next we took this 75:25 ratio of HSPP/R-TPO and studied the effect of glass-fiber content on the physical properties. Physical property balances are best when the GF content is over 40% in this HSPP/R-TPO ratio, as shown in Table IV.

And next the effect of fiber lengths and physical properties were studied. We prepared specimens by two types of molding conditions. These condition changes involved different shear stress at the metering zone. These two molding conditions resulted in two different fiber lengths (outlined in Table V), which are 3.4-mm and 1.3-mm fiber length for *A-Type* material using *Molding Condition 1 and 2*. Physical properties of *A-Type* have fallen off due to dependence on fiber length. The *B-Type* material, the 3.2mm fiber length results in an Izod impact value of $100kJ/m^2$ and the 1.2mm fiber length results in an impressive Izod impact value of $83KJ/m^{2.}$ *B type* uses impact modifiers rather than R-TPO, exhibits much less dependence on fiber length than the HSPP/R-TPO "*A-Type.*" There is some

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[1] Chisso formulation
[2] Chisso formulation

reduction in tensile strength and a more pronounced reduction in flexural modulus. The impact performance, however, is much less dependent on fiber length comparable to the *A-Type*. Figure 4 shows a TEM photo of the PP matrix for the *B-Type* material. The dark segments in the photo are the impact modifier. As you can see, there are many small-sized soft segments in the matrix. These soft segments absorb impact energy and reduce interfacial tension between the matrix and the glass fiber.

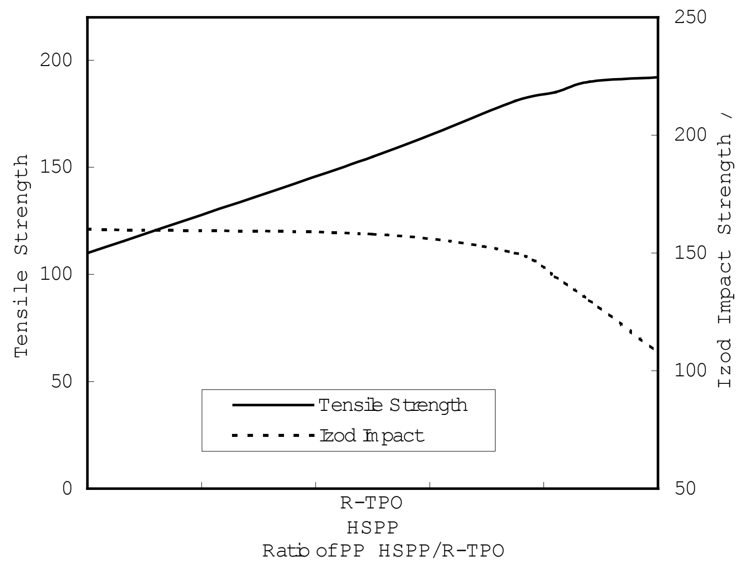

Figure 2: Relationship between polymer ratios and tensile strength / Izod impact at 40% GF

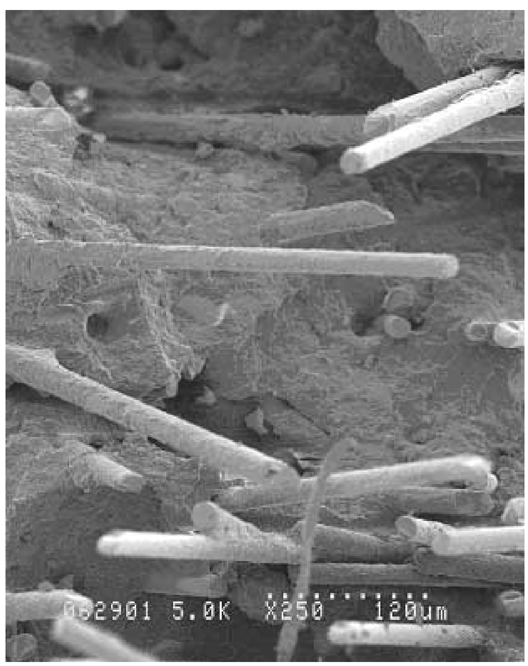

Figure 3: SEM photo for fracture face of A-Type material

Table V: Relationship between physical properties and fiber length

Test		***A-Type***	***B-Type***

Matrix		HSPP/R-TPO 75/25		HSPP/Impact Modifier	
% GF Content		*40*	*40*	*40*	*40*
Molding Condition		*1*	*2*	*1*	*2*
Average Fiber Length	mm	3.4	1.3	3.2	1.2
Tensile Strength	MPa	160	128	135	123
Flexural Modulus	KJ/m^2	7030	6730	6100	5680
Izod Impact Strength	J	110	45	100	83
Gardner Impact (E50)	J	17.6	9.8	15.7	13.7
Dart Impact (E50)	J	31.4	15.7	31.4	29.4

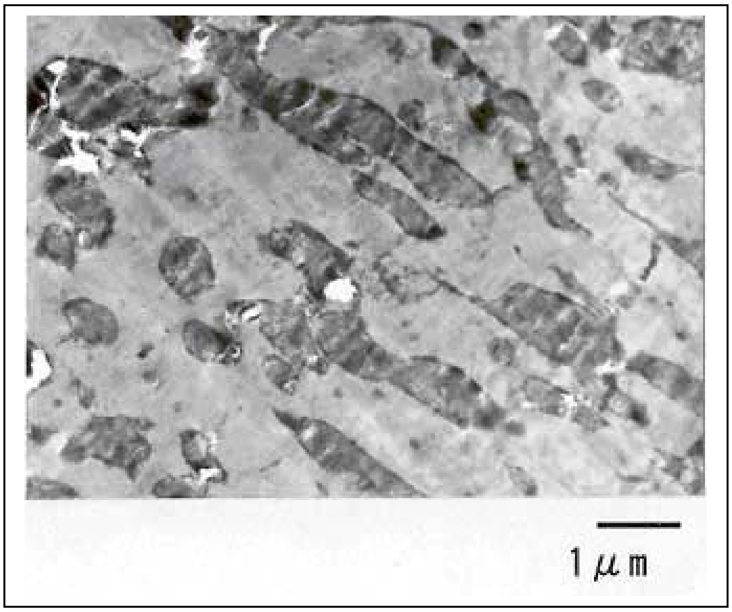

Figure 4: TEM photo for B-Type material (using R_UO_4 dye)

Study of Injection Molding Conditions

Retention of glass-fiber length is not only effective for impact strength but also tensile strength. Therefore, we felt it was important to define how to prevent fiber breakage during molding. A study of screw configuration and molding conditions of our laboratory-scale machine is shown in Table VI. The screw lead, check ring, and nozzle were investigated. Our modified screw has the ability to maintain fiber length 2x or greater than the conventional screw. Adjustment of molding condition such as Injection speed and backpressure are also very effective, as shown in Table VI.

Table VI: Physical property vs. screw configuration, and molding condition (GF40% A type)

Parameter								
Screw		Standard			Modified-1	same as left	same as left	same as left
Check Ring		Standard	Standard	Modified-2	same as left	same as left	same as left	same as left
Nozzle		Standard	Modified-3	same as left	same as left	same as left	same as left	same as left
Injection Speed	ml/s	66	66	66	66	33	66	66
Backpressure	MPa	7.4	0	0	0	0	7.4	0
Barrel Temperature	^{o}C	250	250	250	250	250	250	280
Fiber Length in Part	mm	1.3	2.1	2.3	3.4	3.6	1.9	3.8
Tensile Strength	MPa	128	140	142	160	172	148	162
Flexural Modulus	MPa	6730	6980	6880	7030	7060	7035	6970
Izod Impact Strength	KJ/m^2	45	82	88	110	114	82	130
Modified-1 = Deep channel, wide compression zone, low compression ratio Modified-2= Wide clearance, long stroke Modified-3 = Enlarged nozzle diameter						Machine size = 160 t clamping force		

The study included calculation of shear stress generated during metering and injection by using CAE. The relationships between shear stress and resin temperature at each lead of screw for our laboratory-scale machine are shown in Figure 5, and Table VII and VIII. The conventionally designed screw has a peak of shear stress at 13 lead, which is the compression zone. But, the modified screw does not have this typical peak. The temperature is also lower than that of the conventional screw due to the deep channel depth and low shear at each lead. Therefore where a modified screw is used, we recommended setting a slightly higher barrel temperature.

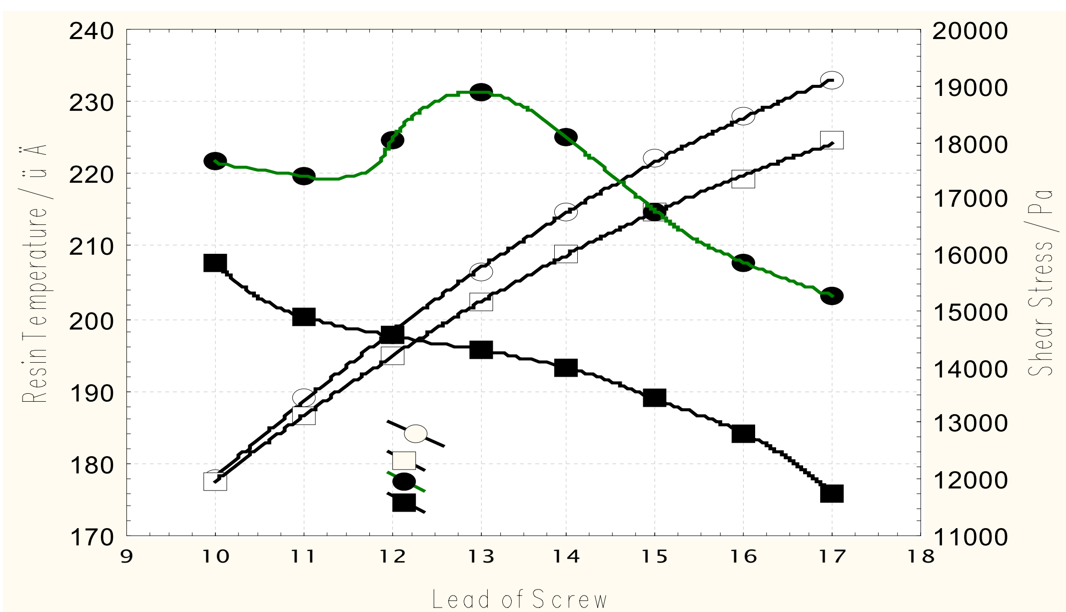

Figure 5: CAE results for metering analysis

Table VII: CAE analysis conditions for metering and injection

Analysis Conditions	
Software	Screwflow
Material	GF 40% A Type
Screw Diameter	50 mm
L/D Ratio	17
Metering Condition	50 rpm, 250 ^{o}C, 9.8 ml/s
Injection Speed	66 ml/sec

Table VIII: CAE results for shear stress of injection at nozzle

Shear Stress (Pa) at Nozzle		
Nozzle Diameter	3 mm	6 mm
Max.	852,459	307,873
Min.	1203	1098

Conclusions

This study demonstrates that fiber length and fiber content are important parameters affecting tensile strength and impact values of the material. Overlapping fiber, fiber pullout, and interfacial tension between the fiber and matrix also will affect impact strength but were not part of this study. Through this study, two new types of high impact grade LGFPP were developed. As was shown, properties are very dependent on fiber length and GF content within the matrix. B Type, which has a minutely dispersed impact modifier in PP matrix, is almost independent of fiber length, but has inferior flexural modulus compared to A Type. A study of molding conditions is also important to learn how to prevent fiber breakage. Proper molding and processing conditions are paramount to retaining both modulus and impact strength. Combining these technologies will enable the usage of LGFPP to expand and be used in new applications.

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