NEW GMT MATERIAL SUITABLE FOR VARIOUS POLYMERS AND HIGH GLASS FIBER CONTENT

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Abstract

As a kind of long fiber reinforced thermoplastic, a new Glass Mat Thermoplastic (GMT)-like material is introduced. It is designed to be suitable for various polymers and high glass fiber (GF) content, which might be a promising attempt to overcome the limit of conventional GMT material (PP grade and maximum 40 wt. % GF). The concept is based on a multi-layered hybrid structure consisting of several thin GF sub-layers and polymer films having an inherently high viscosity. They are then needle matted all together. The capability of higher GF content was derived from the porosity changes under pressure and the cross-sectional view after impregnation. It was finally confirmed by measurement of flexural properties up to 70 wt. % of GF content in PP grade. Moreover, PA6 grade was investigated to show the other capability of multi-layered hybrid mat for various polymers.

1. Introduction

1.1 Conventional GMT in long fiber reinforced thermoplastics

Since 1972, after the first market launch in USA, the conventional Glass Mat Thermoplastic (GMT) has acted as a pioneer of long fiber reinforced thermoplastic materials for lightweight design in automotive application. However, after 2002, it faced the stagnancy in the market compared to the newly grown Long Fiber reinforced Thermoplastic-Direct compounding (LFT-D) and LFT-Pellet shape (LFT-P) material [1][2]. The most important benefit of GMT among them is an excellent impact resistance due to its longer fiber length (25 mm and 37 mm in general) which is mostly preserved in molded parts. The benefit of LFT-D and LFT-P is the variety of polymers and its flowability due to relatively short fiber length which is unavoidably reduced during the compounding and/or injection process [3][4].

The manufacturing process of conventional GMT consists of two clearly separated steps. The first step is the chop/needle mat line to produce a pure GF needle mat from multi-end rovings consisting of 40 sub-bundles in which each sub-bundle is composed of 100 fibers in case of 2,400 TEX (g/km) standard grade. In general, the rovings are chopped into the mixture of 25 and 37 mm length, scattered in plane as evenly as possible, and subsequently needle-matted to e.g. 1,000 g/m^2 areal density [5]. These are determined by considering the handling of needle mats, the manufacturing cost, and the impregnation quality in the second step using double steel-belt press to make a consolidated GMT sheet. But, the impregnation of GF needle mat with molten resin is very difficult due to the inherently high viscosity of thermoplastics which could not be suitably overcome even by increasing either temperature or shear rate. In case of PP resin, it is therefore required to significantly reduce the viscosity in a chemical way, e.g. by using peroxides (controlled rheology) [6]. Moreover, the needling configuration can be optimized in order to improve the impregnation. For example, the PP/GF19 vol. % (40 wt. %) conventional GMT could be processed into a consolidated sheet of 4 mm thickness with 2 layers of GF needle mat having an areal density of 1,000 g/m^2 and 3 layers of the lowered viscosity PP from the extruder as schematized in **Figure 1**. Of course, by reheating it in convection oven, the consolidated GMT sheet becomes ready-to-mold again.

1.2 The concept of multi-layered hybrid mat for new GMT

As described in Section 1.1, the impregnation of conventional GMT is based on the lowered viscosity technology, which depends on the type of polymer. Anyway, it is still questionable why the conventional GMT is commercially limited to only PP matrix and to maximum 40 wt. % of GF content [5], which is a relatively low content (merely 19 vol. %) if the basic aim of fiber reinforced composites is considered.

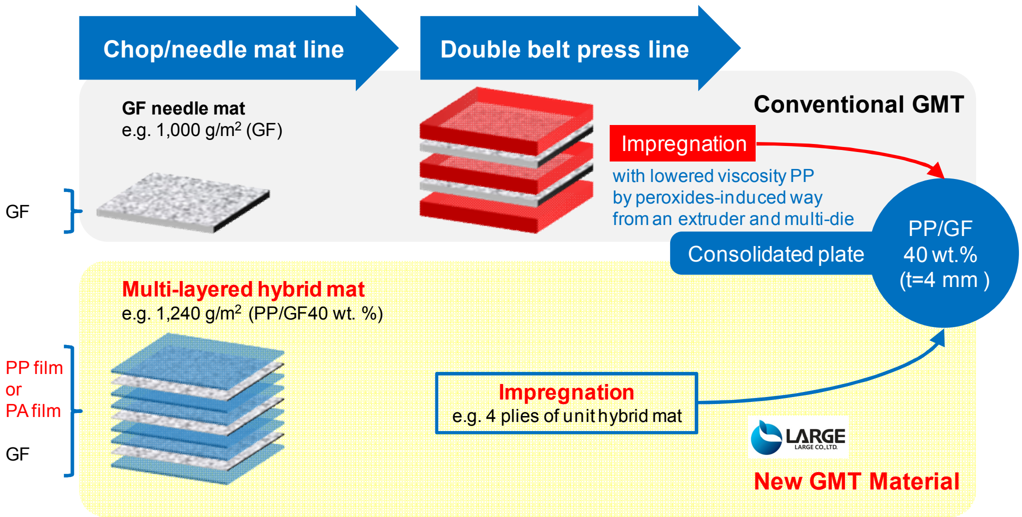

Figure 1. Comparison between conventional GMT and the concept of multi-layered hybrid mat

Therefore, as schematized in **Figure 1**, the concept of multi-layered hybrid mat was invented to realize a new GMT material, which is suitable for various polymers and high GF content. It is manufactured in the chop/needle mat line by chopping of multi-end GF rovings, inter-positioning polymer films, and then needle matting. It is desirable to use the same specific GF grade which has already been verified in the chop/needle mat line of conventional GMT for a long time. However, it is essentially possible to use all kinds of thermoplastic films, without reducing its melt viscosity for the following impregnation step such as in double belt press line. In case of PP/GF19 vol. % (40 wt. %) hybrid mat, the unit needle mat was designed to have 1,240 g/m^2 areal density consisting of 3 sub-layers of GF having an areal density of 165 g/m^2 (minimized thickness for impregnation) and 6 PP films with a thickness of 136 μm as shown in **Figure 1**. The unit thickness will be 1 mm in case of a fully impregnated and consolidated plate. Another benefit of hybrid mat compared to conventional GMT is the thinner unit thickness suitable for thin and large parts such as hood, roof, and door panels in automotive applications. They are normally thinner than 2 mm and better to be hybrid molded with continuous fiber reinforced thermoplastic as local reinforcement [7].

2. Impregnation

2.1 Porosity measurement for permeability

In most cases, the impregnation of fiber reinforcement with molten resin is accompanied by pressurization (ΔP) which is aimed to increase volumetric flux (v or superficial velocity) on the basis of Darcy's law. But it can also decrease the permeability (K), exactly the porosity (ε) in it, due to the compaction of reinforcement. Meanwhile, it is obvious in Darcy's law that conventional GMT is fundamentally based on the lowered viscosity (η), in the same way as thermoset resins, by peroxide induced chemical way in PP resin. But the concept of multi-layered hybrid mat is based on the efficiently minimized unit thickness (h) of the reinforcement and therefore it is independent of resin viscosity.

$$v = -\frac{K\Delta P}{\eta h} \tag{1}$$

The porosity change in fiber reinforcement due to pressure at room temperature can be calculated from the entire-thickness change, which was done for several plies of multi-layered hybrid mat as displayed in **Figure 2**. The thickness at a given pressure consists of air, fiber, and polymer portions as shown in **Figure 3**. The portions of fiber and polymer can be separated by the information of a fully impregnated and consolidated plate on the assumption that both are not compressed by pressurization. But, this does not influence the proper estimation of the porosity in fiber reinforcement which will be impregnated or replaced with polymer, because it returns lower values (underestimated porosity in fiber reinforcement).

Figure 2. The plies of PP/GF19 vol. % (40 wt. %) hybrid mat

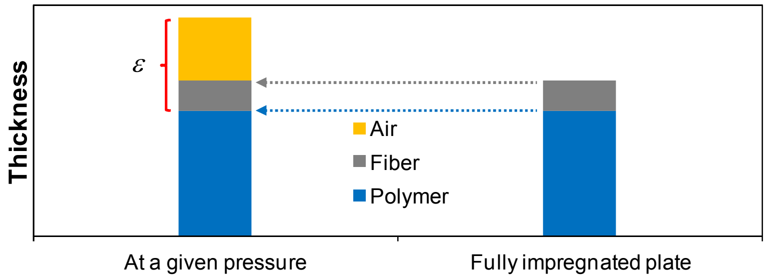

Figure 3. Porosity in reinforcement from entire thickness measurement and information of a fully impregnated plate

Prior to compression tests, the baseline was set up to 140 bar without any sample between the rigid disks of 135 mm diameter to compensate the intrinsic displacement of the measurement setup by pressurization, which has the almost perfect linear fit of 99.9 % R^2 and is roughly 1.5 mm displacement at 100 bar. Then the 3 plies of PP/GF19 vol. % (40 wt. %) hybrid mat were 3 times pressurized with the speed of 3 mm/min as shown in **Figure 4** and **Figure 5**.

From the overall thickness changes (see **Figure 5**), the two representative porosities in the fiber reinforcement could be calculated as 58 % at 20 bar in the first run and 37 % at 100 bar (average of runs) as summarized in **Figure 6** for PP/GF19 vol. % (40 wt. %) hybrid mat. The porosity of 37 % can be treated as the lowest porosity of this hybrid mat, which is obviously higher than theoretical values for very well aligned fibers (9.3 % by hexagonal model and 21.5 % by square model).

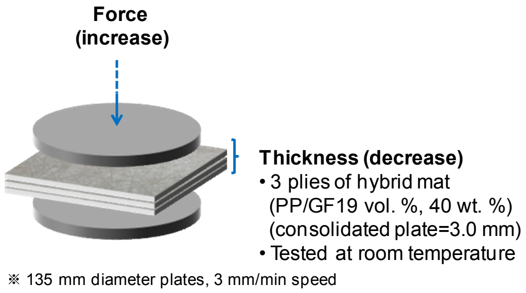

Figure 4. Thickness measurement for porosity in reinforcement of the hybrid mat

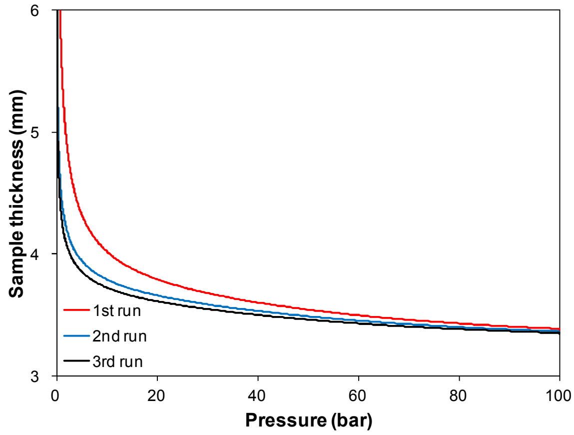

Figure 5. Thickness change by pressure on PP/GF19 vol. % (40 wt. %) hybrid mat

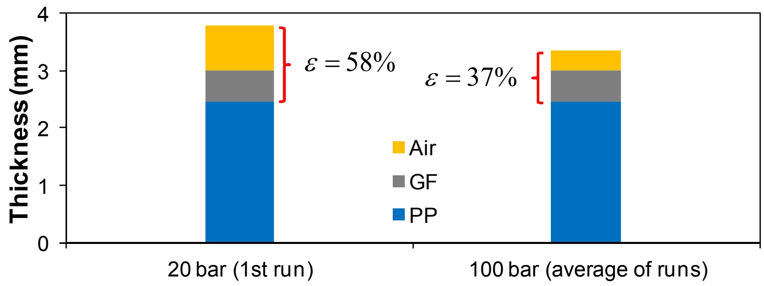

Figure 6. The representative porosities on PP/GF19 vol. % (40 wt. %) hybrid mat

In the case of a porosity of 58 % at 20 bar in the first run, the portion of air is equivalent to only 31 % of the whole PP in PP/GF19 vol. % (40 wt. %) hybrid mat. This implicates that the remaining 69 % of PP might not be involved in the following impregnation. This corresponds to the cross sectional view of an impregnated plate in **Figure 7**. It shows islandlike sub-bundles which are normally composed of 100 fibers.

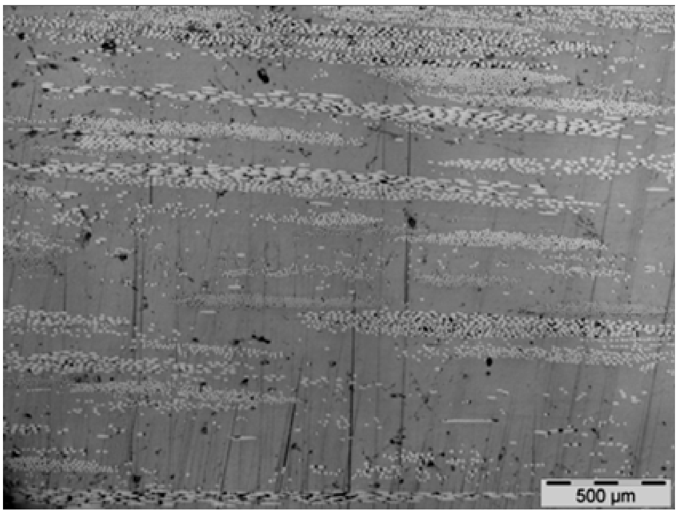

Figure 7. Cross sectional view of impregnated PP/GF19 vol. % (40 wt. %) mat

2.2 Capability of higher GF content

If the amount of polymer in multi-layered hybrid mats was reduced evenly in each film, it would be possible to make the hybrid mats with a higher GF content of up to 42 vol. % as schematized in **Figure 8**. Due to the concept of multi-layered hybrid mat consisting of several GF sub-layers having the desirable areal density (**Table 1**) for impregnation, the impregnation behavior would not be influenced significantly by the amount of polymer.

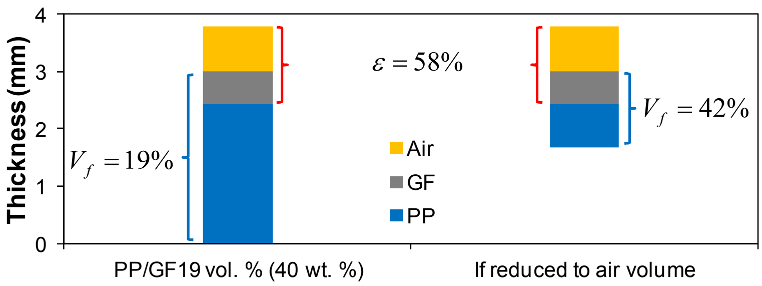

Figure 8. The capability of higher GF content if the amount of PP was reduced to air volume

Figure 9 shows another cross sectional view of an impregnated plate consisting of PP/GF45 vol. % (70 wt. %) hybrid mats, which no longer shows islands of sub-bundles. In order to identify the capability of higher GF content in multi-layered hybrid mat, the mechanical properties should be measured and compared with theoretical values calculated by the rule of mixtures. It is described in Section 3.2.

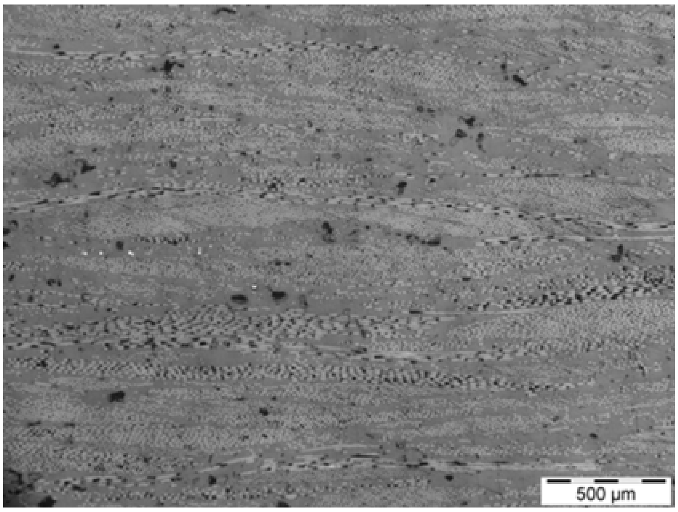

Figure 9. Cross sectional view of impregnated PP/GF45 vol. % (70 wt. %) mat

Unit Hybrid Mat	Areal density	Thickness	GF sub-layers
PP/GF19 vol. % (40 wt. %)	1,240 g/m^2	1.00 mm	165 g/m^2 × 3 EA
PP/GF45 vol. % (70 wt. %)	1,055 g/m^2	0.63 mm	148 g/m^2 × 5 EA

Table 1. The specification of PP/GF multi-layered hybrid mat

3. Performance

3.1 Test method and statistical analysis

Several plies of multi-layered hybrid mat are placed into the compression mold and impregnated at a given temperature for 5 min at 10 bar and then 5 min at 30 bar to make a consolidated plate of 340 mm width and 480 mm length. From this plate, specimens for a three-point bending test are extracted with the size of 25 mm width and the recommended length as class II in ISO 14125 [8]. All test sets respectively consisted of 7 or 8 specimens according to the positions in the plate and bending directions (upper or bottom side). After the three-point bending test, the outlier verification in each set is performed with 95 % probability. Furthermore, the statistical comparisons are done by a two-factor ANOVA without replication (position) or a single-factor ANOVA (bending direction) with 95 % confidence level, so that when the resultant P-value is higher than 5 %, there is no significant difference between the test sets. After considering all P-values on both positions and bending directions, the representative properties are carefully determined and, if necessary, the behavior characteristics will be discussed in detail.

3.2 PP/GF grades of higher GF content

First of all, to verify the concept of multi-layered hybrid mat for easy impregnation, the flexural property of PP/GF19 vol. % (40 wt. %) hybrid mat (**Table 1**) was compared with conventional GMT RD40 (5.5 GPa modulus, 137 MPa strength) which has also 40 wt. % GF content and considered as the maximum reinforcement in conventional GMT [5]. The 4 plies of PP/GF19 vol. % (40 wt. %) hybrid mat were impregnated at 200℃ and the other parameters are same as outlined in Section 3.1. After statistical analysis, the representative values of the flexural properties were determined as follows, modulus of 7.0 GPa, strength of 174 MPa, and strain of 3.5 %, which is over 25 % enhancement in both flexural modulus and strength compared to the conventional GMT RD40. As expected in Section 2.2, the multi-layered hybrid mat has the strong capability to have a higher GF content without any significant change in impregnation behavior. This was gradually confirmed with PP/GF32 vol. % (57 wt. %) and PP/GF45 vol. % (70 wt. %) hybrid mats. PP/GF32 vol. % (57 wt. %) hybrid mat has 1,230 g/m^2 areal density of unit needle mat and its thickness will be 0.85 mm after full impregnation (the unit needle mat consists of 5 sub-layers of GF having an areal density of 141 g/m^2). It was impregnated at 200℃ using 5 plies and the other parameters are same as outlined in Section 3.1. After statistical analysis, the representative values of the flexural properties were determined as 10.1 GPa for modulus, 210 MPa for strength, and 2.9 % for strain. Finally, PP/GF45 vol. % (70 wt. %) hybrid mat (**Table 1**) was impregnated at 200℃ using 6 plies and the other parameters are same as outlined in Section 3.1. After statistical analysis, the representative values of the flexural properties for PP/GF45 vol. % (70 wt. %) hybrid mat were determined as 14.1 GPa for modulus, 215 MPa for strength, and 2.1 % for strain.

As shown in **Figure 10**, the flexural modulus of PP/GF multi-layered hybrid mats follows the tendency of “the rule of mixtures” according to the GF content. The red dotted line is an elastic modulus theoretically calculated in the case of isotropic layup (0/90/±45˚) with continuous fiber reinforced material [9][10]. Therefore, this could be the absolute evidence that the concept of multi-layered hybrid mat is excellent for impregnation quality and independent of GF content in impregnation behavior. The referred elastic modulus of PP and GF is 1.7 GPa and 80.5 GPa, respectively [11][12].

$$E_{(0/90/\pm 45°)} \cong \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \tag{2}$$

where E_{11} is the longitudinal modulus (iso-strain) and E_{22} is the transverse modulus (iso-stress) at a given GF volume content.

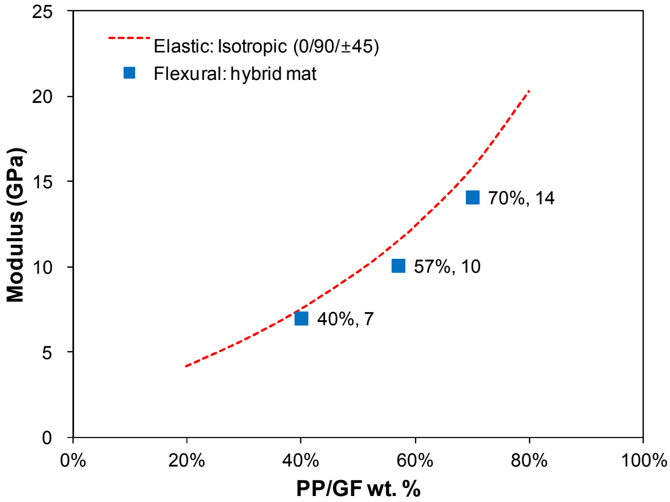

Figure 10. Flexural modulus of PP/GF hybrid mats with GF weight content

Furthermore, the flexural modulus linearly increases with GF volume content having an almost perfect fit of 99.5 % R^2, such as 1.4 and 2.0 times compared with PP/GF19 vol. % (40 wt. %) hybrid mat, while the flexural strain linearly decreases (99.3 % R^2). Therefore, it could be concluded that the flexural strength does not increase with the GF content due to the lack of strain. The other characteristic value of PP/GF hybrid mat which is the ratio of real flexural strength to flexural modulus-based strength (modulus times strain) was determined as 72 %. This can be used as the degree of bias on flexural stress from initial to break stage.

3.3 PA/GF grade and isotropy check in mat

The isotropy check in multi-layered hybrid mat was done with PA6/GF37 vol. % (58 wt. %) grade, whose areal density of unit needle mat is 1,080 g/m^2 and its thickness will be 0.64 mm after full impregnation (the unit needle mat consists of 4 sub-layers of GF having an areal density of 156 g/m^2). The 6 plies of multi-layered hybrid mat were impregnated at 250℃ and the other parameters are same as outlined in Section 3.1. After statistical analysis in/between MD (machine direction) and TD (transverse direction), it could be concluded that there is no significant difference with 95 % confidence level. Therefore, the overall representative flexural properties for PA6/GF37 vol. % (58 wt. %) hybrid mat could be determined as 13.6 GPa for modulus, 369 MPa for strength, and 3.3 % for strain. That is isotropic enough so that the other directions such as ±45° must not be checked. The ratio of real flexural strength to flexural modulus-based strength was determined as 83 % for PA6/GF37 vol. (58 wt. %) hybrid mat, which is a higher ratio and has a longer strain than PP grade. This could be a guideline why PA6 grade is better for strength dominant applications.

4. Conclusion

The concept of multi-layered hybrid mat is a good approach for easy impregnation of long fiber reinforced thermoplastic materials, which is based on the efficiently minimized unit thickness of the reinforcement. Furthermore, it is suitable for various polymers and high GF content without any significant change in impregnation behavior. **Figure 11** shows the position of the flexural modulus of multi-layered hybrid mats, which is newly explored region compared to the time of conventional GMT.

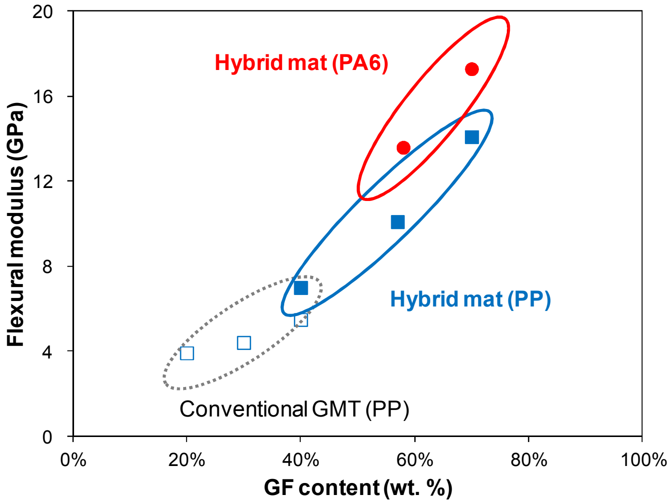

Figure 11. The position of the flexural modulus of multi-layered hybrid mats

Acknowledgement

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