Possibility of Repeated Recycling of CFRTP for Mass Production Automotive Application

Masachika Yamane*, Isamu Ohsawa, Kiyoshi Uzawa, Tsuyoshi Matsuo and Jun Takahashi

School of Engineering, Department of Systems Innovation, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 JAPAN
**yamane@sys.t.u-tokyo.ac.jp*

Keywords: CFRTP, Recycling, In-plant waste, Market waste

Abstract

Fiber reinforced thermoplastics (FRTPs) are attractive because they have the possibility of drastic cost reduction by their manufacturability, such as high-cycle molding, secondary-formability and weld jointing. Hence there are a lot of research concerning preform and manufacturing technologies. However, if FRTPs are to be applied to mass production automobile as expected, we have to clarify their possibility of repeated recycling. In this study, CF/PP is used to investigate the influence factors on the mechanical properties of repeated recycled materials. We especially focused on the degradation of resin due to thermal history and the change of the fiber length due to recycling process.

1 Introduction

Recently many technologies have been developed to solve the problem of global warming and exhaustion of energy resources. Requirement for fuel efficiency has been especially increasing for automobiles, which are consuming more than half of total oil demand. In our laboratory, we are aiming to contribute to construct the sustainable world, through weight lightening of automobiles by using CFRP which have high specific strength and stiffness. CFRP are expected to be alternative material in the next generation, but now mass production automobiles can't fully adopt CFRP, because they have problems in respects of cost, mass productivity, and recyclability.

In terms of mass productivity, we can solve this problem by replacing thermosetting matrix resin (as represented by epoxy resin of conventional CFRP) to thermoplastic resin which has short cycle manufacturing time. In this paper, we focused on the recyclability under the assumption that the thermoplastic-CFRP (CFRTP) will be used in mass production automobile in the future.

2 Demand forecasting and waste problems of CFRP

2.1 "in-plant waste" and "market waste"

In the manufacturing process of CFRP, various wastes that are not used in the products will be generated. Considerable amount of waste, such as fraction of the material, molded defective parts, NG parts, and test piece for quality assurance, are generated before CFRP products are on the market. In the case of thermosetting CFRP, an especially large amount of waste can account for 30 to 50 % of usage. These wastes could become high quality recycled materials, because the identity of the material is clear and there is no environmental degradation. Hereinafter we refer to this as “in-plant waste”. On the other hand, once CFRP products are on the market and with environmental degradation, to distinguish the materials from "in-plant waste", we refer to this as “market waste”. In the case of thermosetting-CFRP, “market waste” is processed by landfill as industrial waste. Figure 1 shows conceptual diagram of “in-plant waste” and “market waste”.

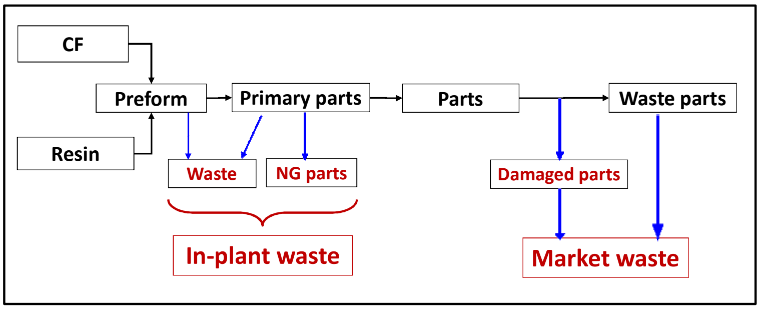

Figure 1. Conceptual diagram of “in-plant waste” and “market waste”.

2.2 Demand forecasting of CFRP

Figure 2 shows the trends of global carbon fiber market demand. Until 1990's carbon fiber was mainly used in sporting goods such as tennis rackets and golf club shafts, but rarely used in aircraft and automobile industries. Since 2000, in aircraft, CFRP has been adopted in the primary structural member of the Airbus A380. In the Boeing 787 entered service recently, CFRP came to be used up to 50% of the aircraft structure. So it is expected that the demand of CFRP will increase sharply after 2010.

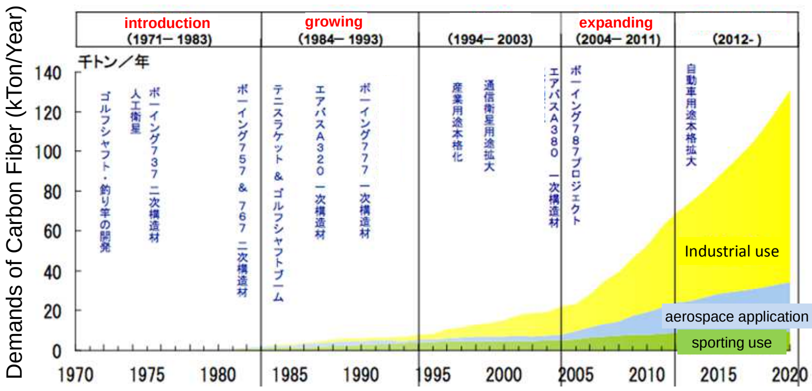

Figure 2. The trends of global carbon fiber market demand. [1]

Table 1 shows an estimated result of the world future potential demand of CF for each application. We focused on wind turbine blade and commercial aircraft as typical application which accept cost and long molding cycle time of thermosetting CFRP. Current demands for these applications are several thousand tons. And future demand for these applications will stop around hundreds of thousand tons. On the other hand, in order to solve the problem of productivity (molding cycle) and recyclability, which are required for the material for passenger automobiles and trucks, research and development of CFRTP has been carried out in the world. Assuming that CFRP-car production line will replace 10 to 20 % of the renewed automobiles production line (estimated at 1/7 of the annual production), CF demand will become 1-2 million tons in 2030, as shown in Figure 3. In that case, the effective use of “in-plant waste” will become necessary immediately. And after their usage in the market, advanced repeated recycling technology of “market waste” will be necessary in the future.

Table 1. World carbon fiber potential demand by application. [2]

	unit	passenger automobile	Truck	wind turbine blade	commercial airplane (L)
world stock	10^3	70,0000@2010 100,0000@2030 130,0000@2050	28,0000@2010 39,0000@2030 50,0000@2050	120@2010 1,000@2030 1,500@2050	15@2010 30@2030 45@2050
world annual production	10^3	58,000@2010 75,000@2030 100,000@2050	19,000@2010 30,000@2030 40,000@2050	25@2010 50@2030 60@2050	0.6@2010 1.2@2030 1.8@2050
CF demand per product	ton	0.1	0.4	4	25
world annual CF demand	10^3 tons per year	5,800@2010 7,500@2030 10,000@2050	8,000@2010 12,000@2030 16,000@2050	100@2010 200@2030 240@2050	15@2010 30@2030 45@2050

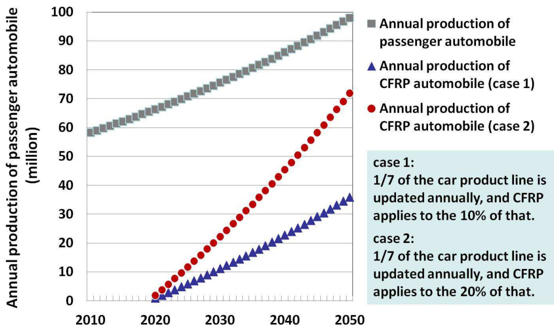

Figure 3. Prediction of the steel and CFRP-car production volume in the world. [2]

3 Recycling of “in-plant waste” in case of CFRTP

3.1 Materials and Recycling process

The materials used in this study have been developed in Japanese METI-NEDO project "Development of sustainable hyper composite technology". Figure 4 shows the production process of CFRTP prepreg sheet under development. This CFRTP prepreg consists of CF mat with uniformly dispersed monofilaments and acid-modified PP (polypropylene) impregnated by double belt pressing machine. The fiber volume fraction (Vf) is 20%. Via the press molding process shown in Figure 5, CFRTP parts are produced.

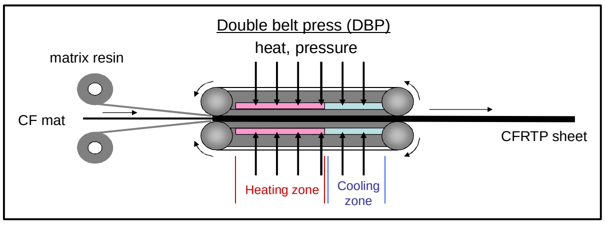

Figure 4. Production process of CFRTP sheet. [3]

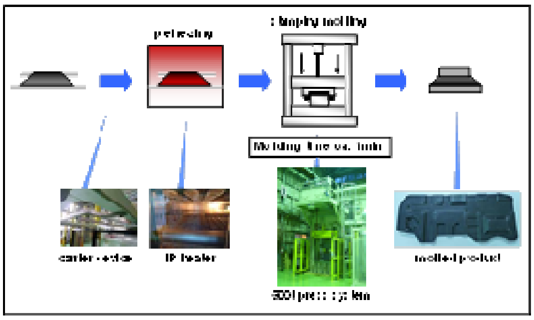

Figure 5. Press molding process. [3]

Figure 6 shows a recycling process of “in-plant waste” in case of CFRTP. These materials are assumed as NG parts (short-shot or defective products). After crushing them by using low speed crushing machine, these pieces are molded into a form of plates by using the heating and cooling press machine. In addition, after heated and melted in Infrared (IR) heater, they are re-molded by using the press molding machine. Here is the first step of the recycling process.

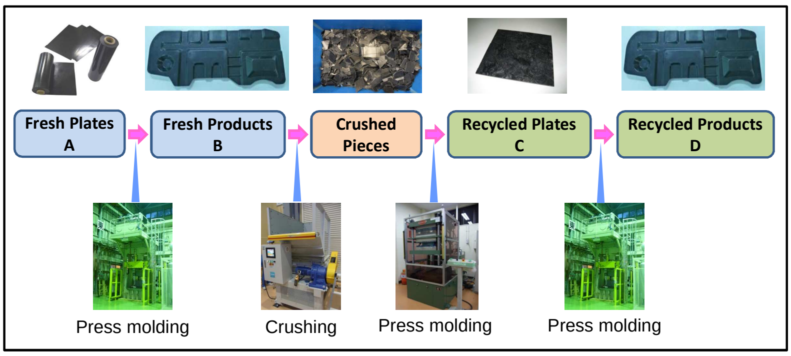

Figure 6. Recycling process of “in-plant waste” in case of CFRTP.

3.2 Process conditions

3.2.1 Press molding of fresh materials

3 mm thickness plates for measuring the mechanical properties assumed as products made by "fresh materials" are molded by using the press molding machine (300 tons press machine TMP2-300 manufactured by Kawasaki Hydromechanics Corp.). Table 2 shows the conditions of press molding.

Table 2. Conditions of press molding for products by using fresh materials.

Material heating temperature	200 Celsius
Tool temperature	120 Celsius
Molding pressure	18 MPa
Holding time	60 sec.

3.2.2 Crushing of products made by fresh materials

To keep fiber length relatively longer and reduce thermal influence during high-speed crushing, we adopted the super low-speed crushing machine (MSHT-800 manufactured by MATSUI MFG. CO., LTD) which can produce relatively large crushed pieces. This machine can suppress the generation of shattered powder and fragments of crushed pieces compared to conventional models with high crushing speed. It is a special crushing machine developed in order to crush relatively soft plastic products such as drums, bumpers and gasoline tanks which are easy to melt by friction heat. The conditions of crushing are that the blade diameter is 320 mm, the blade width is 70 mm, the number of blades is four, the pitch of blade is 251 mm and the rotation rate is 5.6 rpm. Approximate crushing size is determined by the pitch of the blades. Since it has no mesh like a conventional crusher, dispersion of size is small.

3.2.3 Molding of recycled plates made by crushed pieces (Plates recycling)

Crushed pieces obtained in the previous section are charged in a mold for flat plate predetermined amount of crushed pieces, and molded by using the heating and cooling press machine (AWFA-20 manufactured by SHINTO Metal Industries Corporation). Since this press machine is equipped with a heating platen and a cooling platen, we can heat up or cool down so that the temperature of platen can be kept constant, and the molding cycle time can be relatively short. The pressure of molding is kept as low as possible until materials are heated to melt because the crushed pieces are three-dimensional shapes. Table 3 shows the condition of press molding for recycled plates from crushed pieces.

Table 3. Conditions of press molding for recycled plates by using crushed pieces.

	Molding temperature	Molding pressure	Holding time
	Celsius	MPa	min.
Preliminary heating	210	0.3	5
Heating and melting	210	3	2
Cooling and solidification	Below 80	3	15

3.2.4 Molding of recycled products (Press molding of recycled plates)

Recycled plates obtained in the previous section are molded into 3 mm thickness plate by using the press molding machine. These plates are assumed as recycled products. The condition of press molding is the same as the case of molding by using fresh materials. (See Table 2)

4 Results and discussion

4.1 Flexural test

We also measured the properties of the plate before press molding in order to understand the change in the properties at each stage of the recycling process as shown in Figure 6. We carried out the three-point flexural tests using the INSTRON type universal testing machine (AUTOGRAPH AGS-X manufactured by Shimadzu Corporation) in accordance with JIS K 7074. Table 4 shows the symbols of the test specimen (see also Figure 6). The results of the flexural strength and modulus of these materials are shown in Figures 7 and 8 respectively.

Table 4. The symbols of the test specimen.

Symbol	Used materials	Recycling stage
A	CF and polypropylene being used in the developing CF/PP	before press molding
B	CF and polypropylene being used in the developing CF/PP	after press molding
C	in-plant waste of the developing CF/PP	before press molding
D	in-plant waste of the developing CF/PP	after press molding

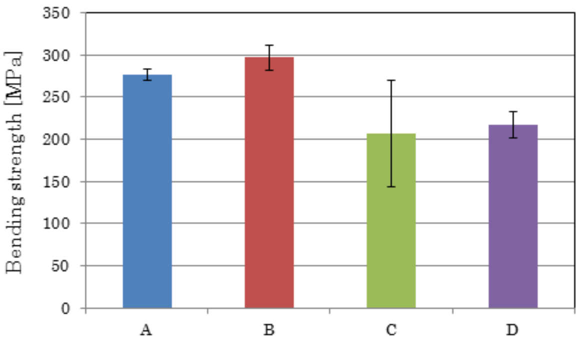

Figure 7. Experimental results (flexural strength).

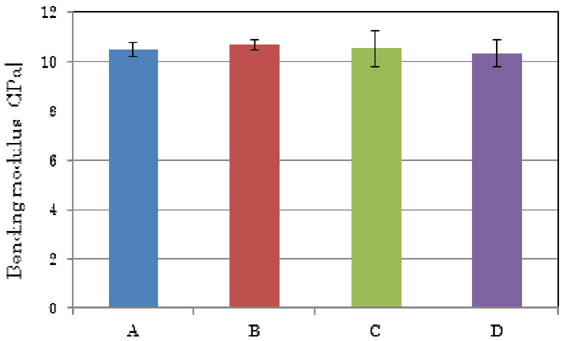

Figure 8. Experimental results (flexural modulus).

As shown in Figure 7, flexural strength of the press molded recycled material "D" declines to 73% of that of the press molded fresh material "B", while flexural modulus of fresh materials and recycled materials are almost the same as shown in Figure 8. These results also show us that the variation of the properties has decreased by performing a press molding in especially in the case of recycled materials. The reason may be both the low molding pressure of the materials before press molding and the existence of resin-rich part or void between crushed pieces.

4.2 Impact test

We conducted Izod impact test (flatwise) using instrumented Izod impact test machine (Dynatup POE2000e manufactured by INSTRON corporation) in accordance with JIS K 7110. Izod impact energy absorption is obtained from equation (1).

$$a_{iu} = \frac{U}{bh} \times 10^3 \quad (1)$$

where a_{iu} is Izod impact energy absorption [kJ/m^2], U is total absorbed energy [J], h is thickness of test specimen [mm], and b is width of test specimen [mm] respectively.

Figure 9 shows the results of the Izod impact energy absorption of the prepared materials. The Izod impact energy absorption value of the material "A" is the highest, and those of the material "B", "C" and "D" are almost the same. The reason may be the change of fiber length by press molding which will discuss in the next section.

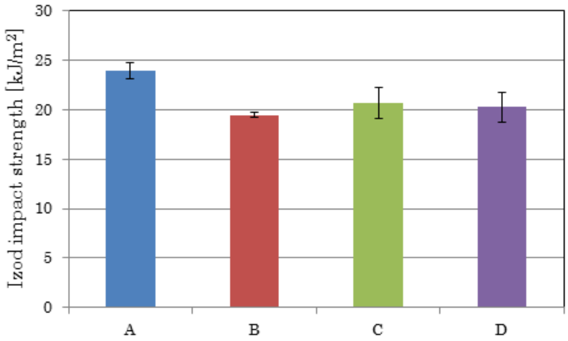

Figure 9. Experimental results (Izod impact energy absorption).

4.3 Distribution of reinforcing fiber length

Before performing the above experiment, we assumed that the most significant deterioration factor in the recycling process was heating process by IR-heater just before press molding, where resin was heated over the melting point under oxygen atmosphere. However, by comparing the experimental results between the materials "C" and "D" (or "A" and "B") in Figures 7 to 9, such thermal deterioration could not be found. It may because the developed polypropylene has very good heat resistance. The other possibilities of the reason of the flexural strength's decrease by recycling are shortening of fiber length and disturbance of the fiber linearity. Among them, disturbance of the fiber linearity did not observed.

Therefore we measured fiber length distribution for each process in order to clarify the reason of the flexural strength's decrease by recycling. The specimens of each recycling stage are burned to remove resin. Then we measured the length of 300 carbon fibers of each specimens by using the digital optical microscope (VHX-1000 manufactured by KEYENCE CORPORATION). Figures 10 to 14 show fiber length distributions of each recycling stage, and Figure15 shows average fiber lengths respectively.

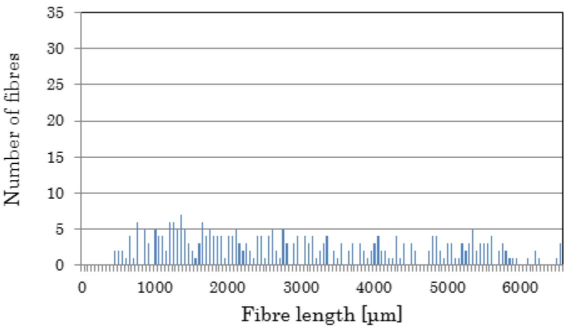

Figure 10. Fiber length distribution of the material "A".

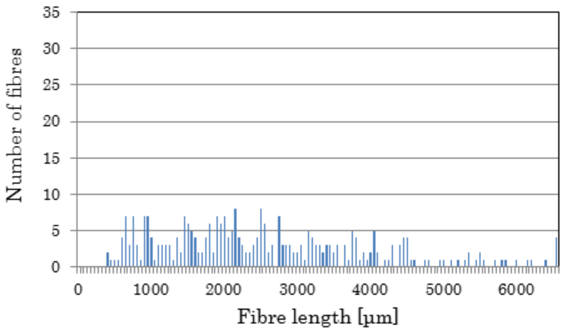

Figure 11. Fiber length distribution of the material "B".

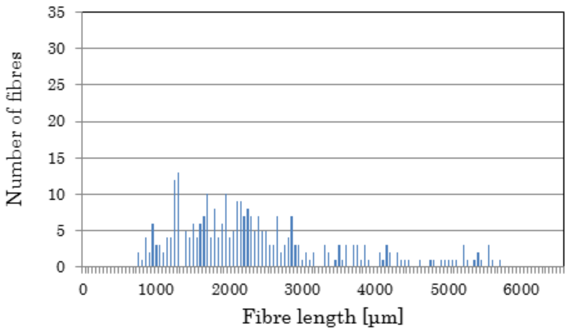

Figure12. Fiber length distribution of crushed pieces.

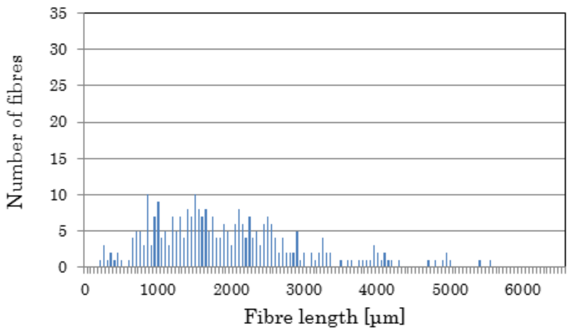

Figure13. Fiber length distribution of the material "C".

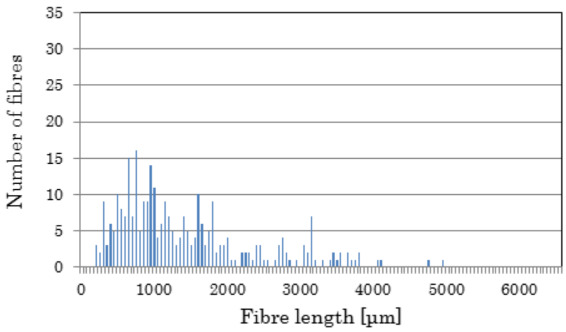

Figure14. Fiber length distribution of the material "D".

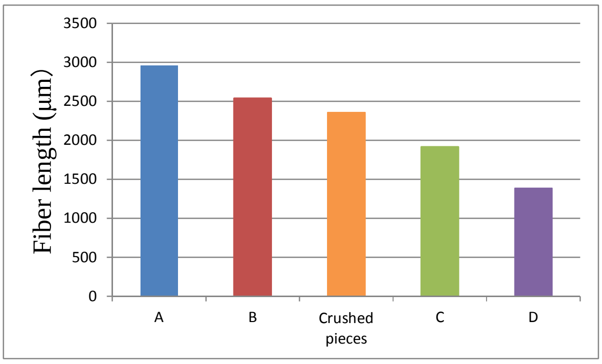

Figure15. Average fiber length of each recycling stage.

As shown in Figures 10 to 14, longer fibers are broken during the recycling process and the distribution shifts to shorter range. It may be because longer fibers are selectively-broken at press molding since longer fibers have more crossover points between fibers than shorter fibers. Figure15 shows that there is not a large difference between the average fiber length of crushed pieces and that of the material "B". Therefore, it can be said that the average fiber length doesn't become shorter by crushing if the size of the crushing cutter is sufficiently large, while the fibers become shorter by press molding.

4.4 The relationship between mechanical properties and distribution of fiber length

From the results described above, flexural strength decrease in the recycle process is mainly related to fiber length becoming shorter, and it happens during not crushing but press molding process. On the other hand, the flexural modulus and the impact energy absorption are not affected, even though the average fiber length in the recycled materials is short.

Generally, composite material with long fiber is able to absorb a large amount of impact energy compared to the short fiber one because of the energy for fiber pullout is increased. But in this study, the correlation between the impact energy absorption and fiber length was small. This is a very interesting result and can be presumed as not the "pulled out fiber" but "fiber breakage" becomes predominant.

As for the CFRTP used in this study, due to the very high interfacial bonding strength between fiber and matrix resin, "fiber breakage" fracture mode is frequently observed when broken by impact. When the material had broken down with "fiber fracture", we can consider that the influence of fiber length is slight, because the fiber volume fraction is the dominant factor of the properties.

5 Conclusions

CFRPs are promising material for automotive weight reduction. It is expected that demands for CFRTPs will increase in the future, and it will cause some problems that can't be solved by conventional recycling technologies. We discussed about recycling methods enabled by our thermoplastic material. Here are some conclusions.

1) We think that the waste to be increasing rapidly based on the prediction of future demand, should be classified as “in-plant waste” and “market waste”. That is to say, “in-plant waste” whose composition is clear, has a possibility to become a high-quality recycled material with no environmental degradation. On the contrary “market waste” is poor quality material with deterioration.
2) We have proposed a method of recycling technique called “plate-recycling method” meaning recycled as a material for press molding. We confirmed that the thermal degradation of the matrix resin caused by heating under an oxygen atmosphere by infrared heater during press molding is small.
3) The influence on the flexural modulus and the impact energy absorption is small though the high pressure of the press molding shortens the fiber during the recycling process.
4) Flexural strength is affected significantly by reinforcing fiber length. It is difficult to make recycled materials with strength of the fresh material level by using only recycled materials. Therefore there is a need to take into account hybrid configuration with fresh material.
5) In the case of repeated recycling of “market waste”, it is necessary to consider the influence of environmental degradation due to the aging of matrix polymer. In future work, in the same manner as in this case, in a hybrid configuration with fresh material, it is possible to manufacture recycled material which has the performance comparable to fresh material.

Acknowledgments

This work belongs to Japanese METI-NEDO project "Development of sustainable hyper composite technology" since 2008fy. We appreciate that the materials and the molded products used in this study were provided from Toray Industries Inc. In addition, authors would like to express sincerely appreciation to all project members who have provided valuable information and useful discussions.

References

[1] M. Kamiura, 3rd. IT-2010 Strategy Seminar (Carbon Fiber Reinforced Plastics), JAPAN, (2008).

[2] J. Takahashi, *Development trend of Thermoplastic CFRP for mass-produced automobiles,* “*CFRTP from Hamamatsu*, Shizuoka, JAPAN, (2012).

[3] M. Honma, A. Tsuchiya, N. Hirano, T. Hashimoto, *Novel carbon fiber reinforced stampable thermoplastic sheet with high strength,* in “ICCM 18, KOREA, (2011).