RECYCLING OF MARKET CFRP/CFRTP WASTE FOR MASS PRODUCTION APPLICATION

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1. Introduction

In the current world, the energy consumption and greenhouse gases emission have attracted considerable attention, since both of them have become imperative problems bothering all the scientists around the world [1]. About 1/3 of energy supply is consumed in transportation sector for moving people and goods from one place to another [2]. And the way people love cars makes the energy consumption even worse if the car companies had not lightened the car structures or had not developed the technologies of the engines. Hence, a lot of materials have been tested to realize the lightening purpose [3]. Carbon fibers are proved to be capable of metal replacement for car structures. Their high strength and stiffness with their light weight make them largely applied ranging from sports goods to aircraft structures in the form of CFRP (Carbon Fiber Reinforced Plastics) [4]-[9]. With the increasing replacement of metal, the demand of carbon fibers has been increasing dramatically [10]-[13]. Till now, the amount of the waste of carbon fibers from the in-plant cut-offs and the end-of-life products have increased to the point threatening the land capacity, and the endless life of the carbon fibers makes the situation even worse. So, a lot of attention and effort have been devoted to reclaim the carbon fibers [14]-[17]. However, in the form of CFRTS (Carbon Fiber Reinforced Thermosetting resin), the difficulties and the cost of removing the matrix are high, even though how promising the mechanical properties of CFRTS are [18]. On the other hand, CFRTP (Carbon Fiber Reinforced Theroplasics) are more suitable to push not only the carbon fibers but also the matrix into recycling loop. Because the thermoplasics are so thermo-sensitive that they can be simply removed for second use and can leave the carbon fibers with delightful properties [18] [19].

In this paper we will discuss the effect of the compression molding on the mechanical properties of CFRTP in the case of polyamides 6 (PA6) as the matrix. Polyamides (PA) are semi-crystalline polymers with good mechanical properties, especially the particularly good tough and fatigue properties and sliding and wear characteristics, but simultaneously with the moisture absorption affects the properties of the final products.

In the specimens forming, we think that not the fully impregnated substrates but the semi-impregnated ones will be made just by heat and cool forming. So we imagine that applying the compression molding can improve the impregnation ratio and the mechanical properties of the composites. Even though the flow stage in compression molding is very small, it will still affect the fibers orientation and segregation to some extents [20]. The molding parameters of this experiment will be discussed, but the optimal molding parameters, T-P-t (Temperature-Pressure-time), have been discussed in the paper of Mr. Hasegawa [21]. In this paper, we name the specimen before compression molding is “SUBSTRATE”, that after it is “PLATE”.

2. Materials

2.1 Preparation of the specimens

PA6 was used as matrix material and the carbon fibers used in this experiment as shown in Fig. 1 were derived from tennis rackets, of which the thermosetting resin was removed by depolymerisation under ambient pressures and 190 degrees Celsius while K₃PO₄ nH₂O used as catalyst and diethylene glycol monomethyl ether (DGMM) [22].

We mixed the PA6 fibers and recycled carbon fibers, as shown in Fig. 2, to make the “card web” as shown
in Fig. 3 by a carding machine.

2.2 Molding methods

2.2.1 Heat and cool forming

20 laminates of card webs as shown in Fig. 4 are fed to form substrates by heat and cool forming. The molding parameters are shown in Fig. 5. Two substrates as shown in Fig. 6 are prepared.

2.2.2 Compression molding

To save the production time, one of the substrates was melt outside of the mold by using the hot plate or the infrared heater. Then, the melted substrate was immediately transferred into the compression mold and formed within 1 minute. The plate is shown in Fig. 7.

3. Experiment

3.1 Three point bending test

A Shimadzu Autograph AGS-X was operated in three point bending test to determine the flexural strength and flexural modulus by the span to thickness ratio of 16:1 and at the speed of 1.5 mm/min. The dimensions parameters are shown in Table. 1.

3.2 Izod Impact Test

We prepared specimens with the size shown in Table. 2. The specimens are separated by compression molding or not into 2 groups, 20 pieces of each. 10 pieces of one group were waiting to be struck at the edge of the specimen and the other 10 were to be struck at the flat face respectively by the Izod test machine.

We performed the experiment to let the pendulum strike the vertical cantilever specimens at a velocity of 1.5 m/s. The specimens of one group were griped upright to the pendulum with the wider faces and those of the other group were done with the narrower faces.

3.3 SEM and optical microscopy

Morphologies of composites were investigated by means of scanning electron microscopy (SEM) and optical microscopy.

3.4 Calculation of volume fraction

In order to investigate the volume fraction of the fibers, an ash oven was used to remove the matrix, PA6, at 400 degrees Celsius for 30 min and at 450 degrees Celsius for sequent 30 min. Before the burning, the specimens were cut into the size of 30 mm * 25 mm. The residual materials as shown in Fig. 8 were carbon fibers in main proportion and little scale of resin. The volume fraction of carbon fibers and that of voids are calculated by the equations shown in (1)-(3), in which the \( m \) and the \( Vf \) represent the mass and the volume fraction of the constituents respectively and the \( V_C \) represents the volume of the composite specimen.

\[
V_{f_{CF}} = \frac{m_{CF}}{\rho_{CF}V_C} 
\]

\[
V_{f_{PA6}} = \frac{m_{PA6}}{\rho_{PA6}V_C} 
\]

\[
V_{f_{voids}} = 1 - (V_{f_{CF}} + V_{f_{PA6}}) 
\]

3.5 CF Length distribution

The length of the carbon fibers sprayed on a piece of white paper was investigated by the optical microscopy. The fiber length distribution and the mean fiber length were therefore determined.

4. Results and Discussion

4.1 Three point bending test

The flexural strength, strain and modulus are given in Fig. 9-11. The positive effect of the compression molding process on the composites can be confirmed by 20% and 12% increases of flexural strength and modulus respectively. It can be seen in Fig. 12-13 that the energy absorption during the Izod impact test obviously improved with the maximum stress increased together with the failure strain. The result can be contributed by the improvement of the adhesion between fibers and matrix, and the removal of the voids induced from 20% to 2%, shown in Table. 3. When the compression force was conducted, the closely touched interfaces have efficiently transferred the load from the matrix phase to the carbon fiber phase. Therefore the hardness of the composites has been improved by the increased impregnation ratio. Therefore, it is comprehensible that the flexural properties could have increased more significantly if we had made the void free plate.

4.2 Izod impact test

The results of Izod impact test were recorded in Tables. 4 and 5, and a little change was recognized. We predict that the impact energy should have been absorbed much higher, because the compression
molding was believed to be able to improve the impregnation extent of the plate. Therefore the transition of the load could be more perfectly realized and a larger scale of energy absorption can be performed by carbon fibers borne the main load and pulled out of the composites. Making the deviation of the results into account, we cannot say that the impact properties have been improved. We think the reasons of the disappointing results are related to the left voids, the increased ends of fibers and a little water absorption. And this leads us to think that the impact energy absorption can be increased considerably by removing the voids out of the composites.

4.3 SEM and optical microscopy

Given by the SEM as shown in Figs. 14-15, the significant improvement of the interfacial bond between the fibers and the matrix after compression molding can be confirmed. Comparing the SEM morphologies of impact fracture surfaces of substrate and plate, we can see that the gaps between matrix and fibers in substrate are much more than those in the plate. Additionally, in the substrate, the extrusive parts of carbon fibers are not perfectly covered by the matrix and the deformation of the fracture surface of matrix is very small, which is contrary to those shown in the SEM of the plate.

It can be seen in Fig. 16-19 that the voids in the composite decreased with the application of compression molding. A considerable impregnation improvement has been realized and consequently developed the carbon fibers to be the main role in the load bearing stage.

And the same result can be clearly confirmed by the 3D morphology formed by the optical microscopy. The hollows in Fig. 20 that represent the voids in the composite tremendously decreased after compression molding, which is proved by the relatively smooth surface of the composite, which was shown in Fig. 21. Therefore, the positive influence of the compression molding is proved.

4.4 The fiber length distribution

Given by Table. 6, the mean length of carbon fibers seems unexpectedly increased after compression molding. The existed inconstant length discrepancy of the fibers in raw material, card webs, which have been stacked with 20 laminates to form substrates, can contribute an effort to explain the unexpected phenomenon. Additionally, the experiment errors inevitably happened during the length measurement by choosing fibers to measure with human’s eyes. However, the ignorable effect of the compression molding on the length distribution of the carbon fibers can be confirmed by the slight difference shown in Fig. 22. The maximum length of the carbon fibers was little negatively influenced by the compression molding. Above all, we can say that the effect of the compression molding on the length of the carbon fibers can be ignored.

5 Conclusion

The aim of this paper is to make higher performance CFRP that can be used as automotive parts by using discontinuous recycled carbon fibers and to investigate the possibility of the mass production by using this method. The mechanical properties were measured by three point bending test and by Izod impact test, while the morphologies of the carbon fibers from the substrate and the plate were observed by SEM and optical microscopy, before which an ash oven had been used to remove the matrix. At the same time the length of the carbon fibers were measured under the optical microscopy to make clear the effect of the compression molding on the length of fibers.

By conducting the compression molding, the flexural properties have been improved significantly. However, the results of Izod impact test show the depressive effect of the voids, which is observed by the volume fraction calculation and the morphology investigations. But we can still expect that the impact energy absorption can be improved significantly if we can make the void-free plate. The compression molding is still suitable to eliminate the voids and to increase the impregnation ratio of the composites, because the length distribution of the carbon fibers, which directly influences the mechanical properties of the CFRTP composites, is gently changed.

Above all, we are led to the direction in which we should make void free composites and adjust the carbon fiber content and the molding parameters. It is meaningless to use more carbon fibers while improvement of the mechanical properties is difficultly recognized. And the optimal T-P-t parameters will be investigated in further study: higher pressure and longer time would be applied in the compression molding to make sure the impregnation ratio and the voids elimination. However we cannot just devote the time and energy cost to get perfect material, we must investigate the optimal point in the molding parameters and processes to suit the mass production in the future.

6 Acknowledgment

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hyper composite technology" since 2008fy. Additionally, the recycled carbon fiber was supplied by Hitachi Chemical Co., Ltd.. Authors would like to express sincerely appreciation to them who have provided valuable information and useful discussions.

Reference


Table 1 The size of the specimens for three point bending test.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (mm)</th>
<th>Width (mm)</th>
<th>Span (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>3.6</td>
<td>49.8</td>
<td>56.0</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>49.6</td>
<td>45.0</td>
</tr>
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</table>
### Table 2  The size of the specimens for Izod test.

<table>
<thead>
<tr>
<th></th>
<th>Width (mm)</th>
<th>Length (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>10.0</td>
<td>70.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Plate</td>
<td>10.0</td>
<td>70.0</td>
<td>2.9</td>
</tr>
</tbody>
</table>

### Table 3  The volume fractions of the carbon fibers and of the voids.

<table>
<thead>
<tr>
<th></th>
<th>Wf of CFs (%)</th>
<th>Vf of CFs (%)</th>
<th>Vf of Voids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>52</td>
<td>43</td>
<td>20</td>
</tr>
<tr>
<td>Plate</td>
<td>50</td>
<td>51</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table 4  The results of Izod impact test struck at the flat face.

<table>
<thead>
<tr>
<th></th>
<th>Total energy (J)</th>
<th>Impact strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate-flat</td>
<td>0.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Plate-flat</td>
<td>0.4</td>
<td>14.6</td>
</tr>
</tbody>
</table>

### Table 5  The results of Izod impact test struck at the edge.

<table>
<thead>
<tr>
<th></th>
<th>Total energy (J)</th>
<th>Impact strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate-edge</td>
<td>0.5</td>
<td>15.8</td>
</tr>
<tr>
<td>Plate-edge</td>
<td>0.4</td>
<td>14.2</td>
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</table>

### Table 6  The length investigation of the carbon fibers before and after compression molding.

<table>
<thead>
<tr>
<th></th>
<th>maximum (μm)</th>
<th>minimum (μm)</th>
<th>mean length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>13,735</td>
<td>57</td>
<td>1,799</td>
</tr>
<tr>
<td>After</td>
<td>11,652</td>
<td>54</td>
<td>2,279</td>
</tr>
</tbody>
</table>

Fig. 1  A picture of recycled carbon fibers after resin removal.

Fig. 2  A picture of PA6 and recycled carbon fibers.

Fig. 3  A picture of obtained card web surface.

Fig. 4  A picture of card web laminates.
Fig. 5  The parameters of heat and cool forming.

Fig. 6  Substrate before fed into compression molding.

Fig. 7  Plate formed by compression molding.

Fig. 8  A picture of the residues of CFRP after burning.

Fig. 9  The result of flexural strength of before and after compression molding.

Fig. 10  The result of flexural strain of before and after compression molding.
The result of flexural modulus of before and after compression molding.

Stress-strain curves of substrate.

Stress-strain curves of plate.

A picture of scanning-electron microscopy of fracture surface of the substrate.

A picture of scanning-electron microscopy of fracture surface of the plate.

A picture of optical microscopy of the substrate.
Fig. 17  A picture of optical microscopy of the substrate.

Fig. 18  A picture of optical microscopy of the plate.

Fig. 19  A picture of optical microscopy of the plate.

Fig. 20  The 3D scanning of the substrate.

Fig. 21  The 3D scanning of the plate.

Fig. 22  The length distribution of carbon fibers.