INFLUENCE OF RECYCLING CONDITION ON THE SCATTER OF CFRP PROPERTIES

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ABSTRACT

Carbon fiber reinforced plastics (CFRP) are increasingly used in some special fields because of their high specific mechanical properties. However, the amount of CFRP wastes are increasing along with the growing global demand of CFRP products. Even though it has proved that recycled carbon fibers (rCF) will not be significantly damaged in mechanical properties by current recycling processes, there are concerns of the stabilities of products made by rCF. In this paper, tensile tests are conducted to investigate the difference of coefficient of variation (CV), which is used to identify the quality variation of rCF, between virgin CF and rCF. A recycling method called superheated steam treatment (SHS treatment) is used to obtain rCF and the processing temperature is 700°C. Polyamide 6 (PA6) and epoxy (EP) are used as matrix in order to investigate the effects of thermoplastic and thermoset on the CV of CFRP bundles. Additionally, a Monte-Carlo simulation is conducted to understand the filament number dependence of CV.

1 INTRODUCTION

The demand of carbon fibers (CF) is increasing annually. Especially carbon fiber reinforced plastics (CFRP) will be applied to mass production automobile in order to decrease energy consumption and reduce global CO_2 emission. Proved by some reports, recycled carbon fibers (rCF) are thought to be theoretically feasible to replace the fresh CF to meet the growing global demand of CFRP products, especially those in automotive industries. However, there is no satisfied method to re-use rCF currently and the landfill capacity is stressed from CFRP wastes. The CFRP wastes are divided into two groups, one is in-plant waste and the other is market waste. In-plant waste is generated during manufacturing process and it occupies 30% of total wastes amount. It is relatively cleaner waste in terms of contamination and degradation of resin. However, there is a concern that the variation in mechanical properties of rCF filament becomes bigger due to the recycling processes, though some researches have proved that current recycling processes are moderate enough to maintain the mechanical properties. A statistic concept of coefficient of variation (CV) is generally used to describe the stability of the product qualities. It is acknowledged that the CV of rCF filament is too large to be accepted by current markets. However, there is a lack of investigations to demonstrate that CV will decrease after rCFs are impregnated by resin.

Some studies have concluded that the CV of composites properties reduces by increasing the filament number of CF [1]. However, only virgin CF are discussed in these papers and the correspondent conclusion cannot help to increase the confidence to re-use rCF. Therefore, the present study intends to expand the CV investigations by investigating rCF bundles.

It is generally acknowledged that "weakest-linking theory" can describe the failure of CF filament and bundles. Based on this theory, the reinforcement fiber will beak at the weakest position. In the case of rCF filament, the unpredicted damage levels and the unpredicted damage locations, a single filament at tension will just break at a random location of a large range of strength values. Therefore, the CV is unexpected high. However, after impregnating the filaments with resins, the rCF filaments will be connected as chains to moderate the single filament failure. Therefore, a chain-model based on Monte-Carlo simulation is given in this paper.

The main recycling methods are divided into three groups, one is mechanical recycling, another is thermal recycling and the other is chemical recycling. The three recycling processes have different characteristics [2], but the specimen size is shortened in all process. In this study, a recycling method called superheated steam (SHS) treatment is used to obtain rCF.

In this paper, tensile test is conducted to investigate the CV of virgin CF and rCF. EP and PA6 are decided as matrix to make specimen with virgin CF to compare carbon fiber reinforced thermosets (CFRTS) and carbon fiber reinforced thermoplastics (CFRTP). The shape of specimen is rectangle tape but the width is so narrow that tensile test is conducted referred to strand tensile test condition. The specimen is called tape-strand in following contents. The processing temperature of SHS treatment, in this study, is 700°C. The detail of SHS treatment is mentioned in section 2.1.2.

2 TAPE-STRAND TENSILE TEST

In this paper, tape-strand tensile test is conducted to investigate the difference between thermoset and thermoplastics, virgin CF and rCF. The specimen made from virgin CF and EP is called CF/ EP, from virgin CF and PA6 is called CF/ PA6, and from rCF and PA6 is called rCF/ PA6 in following contents.

2.1 Materials

2.1.1 virgin CF

In this paper, EP and PA6 are decided as matrix and virgin CF is used as fiber to compare CFRTS and CFRTP. The same type of CF is used to each CFRP specimen.

2.1.1.1 CF/ EP

Unidirectional CF/ EP prepreg sheet was made by Mitsubishi Rayon Co., Ltd. TR50S and EP (#350) are from Mitsubishi Rayon Co., Ltd. The sheet's thickness is 120 μm and the V_f is about 56%.

2.1.1.2 CF/ PA6[3]

Industrial and Technology Center of Fukui Prefecture made unidirectional CF/ PA6 prepreg sheet, using a pneumatic method for spreading tow. In this method, 15000 filaments spreading into 48 mm adhered temporary to both sides of PA6 sheet. TR50S and Diamiron®C from Mitsubishi Plastics, Inc. are used. The sheet's thickness is 44 μm and the V_f is about 54%.

2.1.2 RCF by Superheated Steam treatment (SHS treatment) [4]

SHS is dry steam, which the temperature of it is higher than its boiling temperature. The steam having much energy than ordinary air, composites are uniformly heated and matrix can be rapidly decomposed. Also, The fiber orientation distribution can be kept because only steam contacts with materials.

In this paper, unidirectional CF/ PA6 prepreg sheet mentioned in section 2.1.1.2 was recycled with SHS treatment by Japan Fine Ceramics Center. The processing temperature is 700°C and processing time is 60 minutes. rCF/ PA6 prepreg sheet is called rCF sheet in following contents.

2.2 Molding and Cutting process

Two types of specimens are made, which has different number of filaments, one is 600 and the other is 1000. All specimen is measured its weight by an electronic balance (AUX320, Shimadzu Co.) and calculated filament number from its weight and specific gravity because specimen size is measured less precisely with Vernier micrometer than with an electronic balance. The specific gravity of CF is 0.00182 g/ mm^3, that of EP is 0.0012 g/ mm^3, and that of PA6 is 0.00114 g/ mm^3.

All specimens are tabbed by rectanglar thick papers that referring to Sawada and Shindo[5].

2.2.1 CF/ EP

Because cutter might cut the fiber, CF/ EP prepreg sheet is torn along fiber orientation by hands. Then, tape-strands are measured their weight and their filament numbers are calculated. After that, they are heated and thermoset in Incubator (Kosumosu AT-S13, Isuzu Seisakusho Co., Ltd.), which temperature is 130°C for an hour.

2.2.2 CF/ PA6

The same as CF/ EP, prepreg sheet is torn along fiber orientation by hands at first and tape-strands are measured. Then, using heater (HOT PLATE STIRRER, RSH-1DN, AS ONE Co.), tape-strands are heated for about 5 seconds both faces. It is considered that the tape-strands are rotated to be more circularly in this heating process. However, the heater size being 150 mm x 150 mm, in the terms of the edge of the heater which might hurt fibers, the non-rotated heating process is decided to use.

2.2.3 rCF/ PA6

rCF/ PA6 is made from rCF sheet and PA6, Diamiron®C from Mitsubishi Plastics, Inc. rCF sheet is put between two PA6 films and they are set in the die. Then, they molded in heating and cooling hand press (SINTO Metal Industries Co.) preheated to 250°C, at about 2.5 MPa until the temperature comes to 200°C then changed to about 12 MPa until 220°C. After them cooling, the composite is detached to two parts because the two PA6 films are not adhered to each other. By measuring weight of each parts of composite, V_f of rCF/ PA6 can be calculated.

Due to its low V_f, it is difficult for rCF/ PA6 sheet to be torn by hands, so the sheet is cut with circle cutter (NC-382, ISE office supply Co.) and tape-strands are measured their weight and calculated their filament numbers.

2.3 Tensile test

Tensile test was performed with stroke speed of 1.0 mm/min. A Universal testing machine (AUTOGRAPH AGX-100, Shimadzu Co.) is used to calculate load, and non-contact digital video extensometer (DVE-101/ 201, Shimadzu Co.) is used to measure its strain. The specimens' length is 250 mm, the length between tabs is 150 mm, and gauge length is 50mm.

Tensile modulus was calculated at liner region on stress-strain curve, mostly using strain range from 0.1% to 0.6%, or range of 0.5% if it was not linear from 0.1% to 0.6%.

2.4 Result and discussion

CF/ PA6 and rCF/ PA6 would not be impregnated enough. The tensile strength of CF/ EP is more than twice of CF/ PA6 and rCF/ PA6 (Figure 1). The modulus of CF/ EP is higher than that of CF/ PA6 and rCF/ PA6, which also implies lack of impregnation of resin (Figure 2). So, further study is necessary.

Figure 3 shows that the CV of CF/ EP whose filament number is 600 is smaller than whose filament number is 1000. It suggests that filament number less affects CV of tensile strength than variation of specimen manufacturing affects.

Most CV of Young's modulus are smaller than those of tensile strength, which can indicate that Young's modulus doesn't relate to final state of specimen.

Concerning the specimen which has 600 filaments, CV gets smaller in the order of CF/ EP, CF/ PA6, and rCF/ PA6 (Figure 3). The CV of Young's modulus also shows that CV of rCF/ PA6 is almost the same as or less than that of CF/ EP and CF/ PA6 (Figure 4).

Therefore, rCF will be applied to automotive when types of fibers are clear.

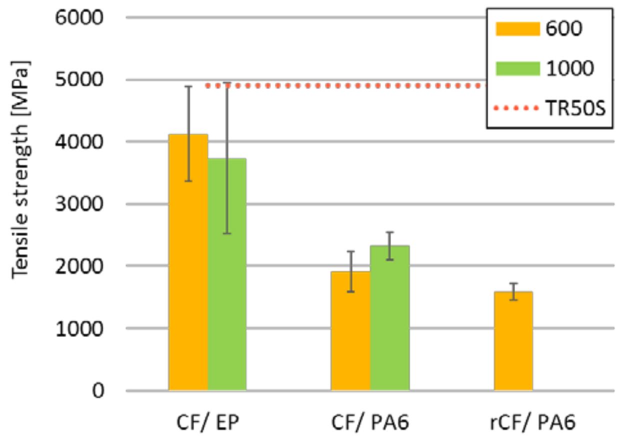

Figure 1: Tensile strength of tape-strands.

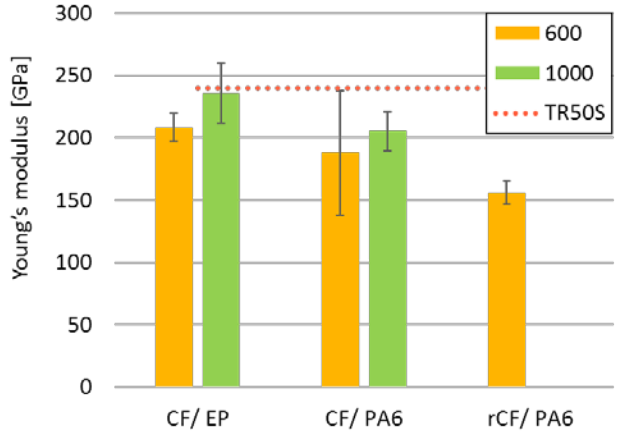

Figure 2: Young's modulus of tape-strands.

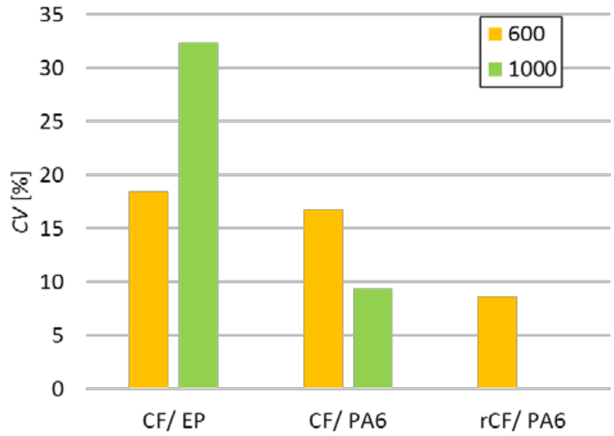

Figure 3: CV of tensile strength of tape-strands.

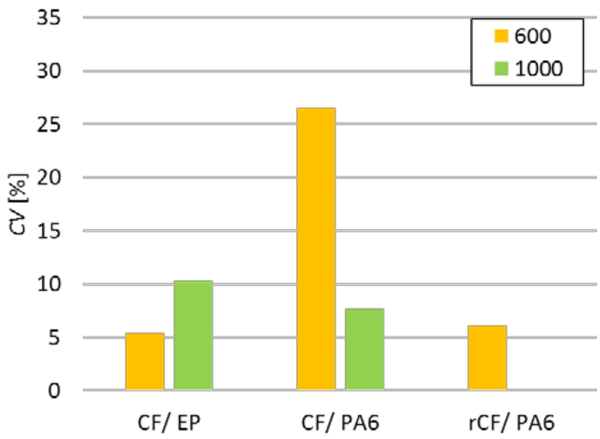

Figure 4: CV of Young's modulus of tape-strands.

3 MONTE CARLO SIMULATION [6]

Monte Carlo simulation is conducted to predict the relation between filament number and CV. In this paper, simulation model proposed by Wada and Fukuda [6] is used.

3.1 Prediction model

3.1.1 Quasi-LLS (local load-sharing) rule

Using quasi-LLS rule by Wada and Fukuda, stress-concentration factors (SCFs) around broken fibers are calculated. This rule predicts lower bound of the strength.

Figure 5 shows SCF in the case of hexagonal-array. In this figure, Kr shows SCF of filament number A, B and C after filament number 1 and 2 are broken in numerical order.

A $Kr = 1 + \frac{1}{6}$

B $Kr = 1 + \frac{1}{6} + \frac{1}{5} \times \frac{7}{6}$

C $Kr = 1 + \frac{1}{5} \times \frac{7}{6}$

Figure 5: Concept of SCF (quasi-LLS rule). [6]

3.1.2 Simulation condition

Strength of each filaments is randomly set by Monte Carlo simulation, using Weibull distribution.

$$x = \alpha[-\ln 1 - F(x)]^{\frac{1}{m}} \tag{1}$$

where x is the strength, m is the shape parameter, α is the scale parameter, and $F(x)$ is Weibull distribution function. It is called x = $STR_{(i,j)}$ and SCF = $SCF_{(i,j)}$ in following contents. Figure 6 shows this model in three dimensions. The letter i means the number of each fiber and j means link number. The figure 7 shows the numbering way of i and j in the cross section of the strands. The link number starts with 1, and ends with a number which equals to tab length divided by a critical length.

In this paper, the simulation is carried out with that the link number is 6, same as the experimental specimen size, critical length is 25 mm, the scale parameter is 1 because it doesn't affect value of CV, and the shape parameters are 3.5, 4.0, 5.0, 5.5, 6.5, 7.0, 7.5, 8.5 and 9.0.

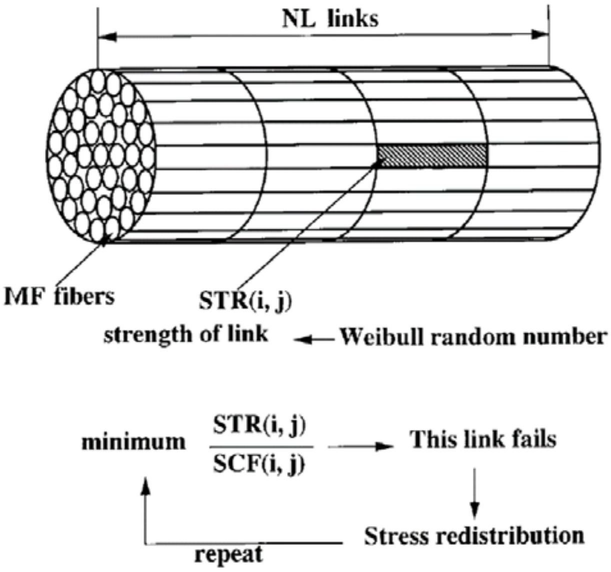

Figure 6: Monte Carlo simulation of three-dimensional model. [6]

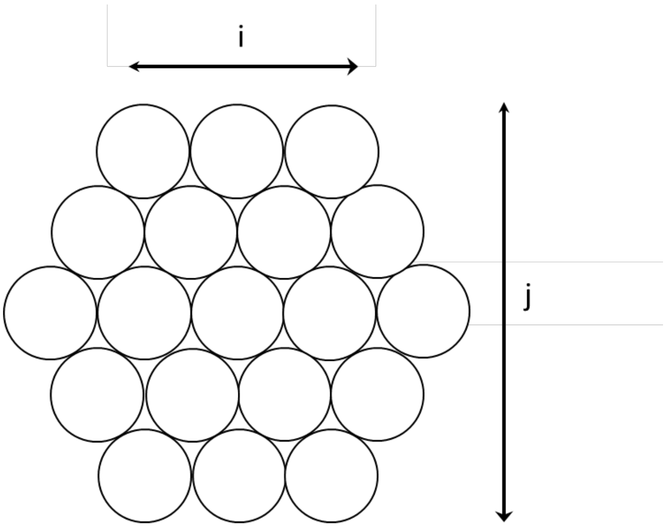

Figure 7: The link number l and the link number of carbon fiber i.

3.1.3 The broken way of a link

In this paper, the hexagonal strands are change to the shape which shown in figure 8 to indicate the arrays for a programming code.

In this case, it is made to share the strength by red fibers in figure 8, when the black fiber is broken but all the white fibers have been already broken. If the red ones are also broken, then green fibers share the strength. The tensile strength is indicated by $\frac{STR_{(i,j)}}{SCF_{(i,j)}}$ and the link will be broken at the smallest point.

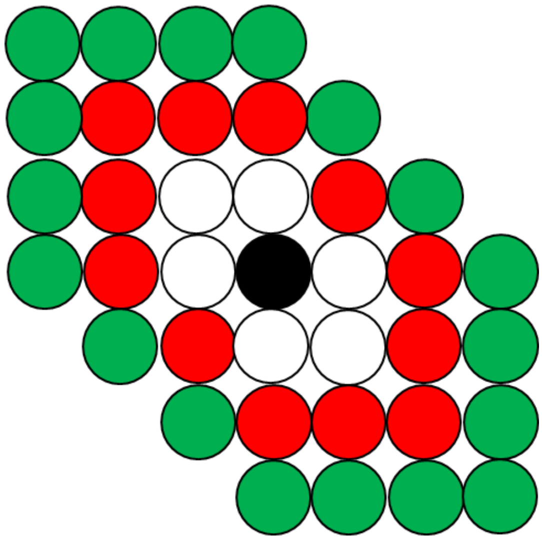

Figure 8: The strands shape of this model.

3.2 Result and discussion

CV decreases when filament number increases, but decreasing rate of CV becomes small when filament number comes above 60 (Figure 7). Therefore, the number of filaments and CV are correlated to each other but the correlation coefficient is closed to 0 when the filament number becomes bigger.

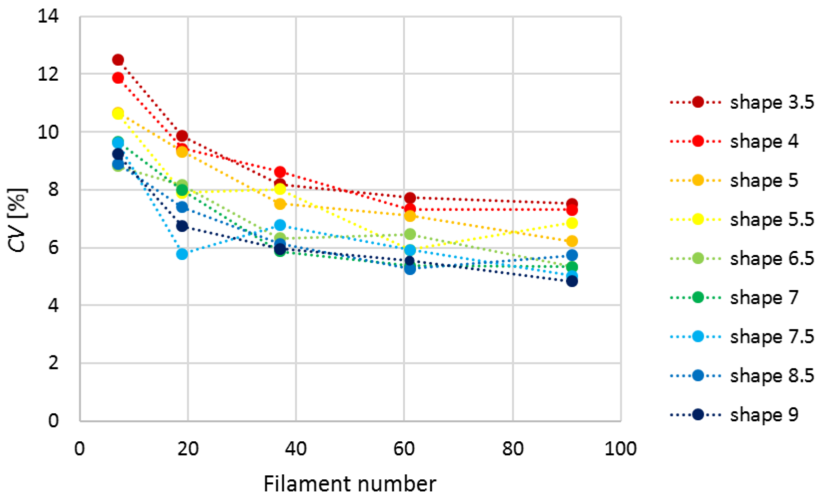

Figure 7: Relation between filament number and CV.

4 COMPARISON BETWEEN EXPERIMENTAL AND SIMULATION RESULTS

The CV of specimen which has 600 filaments must be bigger than that of specimen which has 1000 filaments, but the experimental data does not show it. The experimental error must be dominant than CF and matrix condition.

In this paper, the shape of simulation model is hexagonal but the shape of specimen is rectangle, so it needs to be changed.

5 CONCLUSION

In this paper, three types of specimen are introduced to compare coefficient of variation. The following conclusions are obtained.

- Tape-strand made from rCF shows smaller CV than made from virgin CF.
- Increasing of filament number makes CV smaller but the decreasing rate of CV gets smaller when the filament number comes over 100.

Based on this result, if it has as many filaments as amount using in automotive member, quality variation would be affected more by structural element than by filament itself. It would be useful to predict mechanical properties of rCF composites.

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