Tensile strength of Polypropylene Reinforced by Carbon Fiber Covered with and without Sizing Epoxy Film

Shodai Kitagawa¹, Hideki Kimura¹, Sagiri Takase¹, Naruya Tsuyuki¹, Daisuke Kitahara¹, Anna Takahashi¹, Michael C. Faudree¹, Helmut T. Uchida¹, Akira Tonegawa¹, Masae Kanda¹,², Noriyuki Inoue¹,², Satoru Kaneko³, Tamio Endo⁴, Michelle Salvia⁵ and Yoshitake Nishi¹,⁵*

¹. Tokai University, Hiratsuka, Kanagawa, Japan, 2. Chubu University, Aichi, Japan, 3. KISTEC, Kanagawa, Japan, 4. Sagamihara Surface Lab, Kanagawa, Japan, 5. Ecole Central Lyon, France,

* Corresponding author: e-mail: west@tsc.u-tokai.ac.jp

Tensile strength at each accumulative probability of strength ($P_f$) was obtained for 28mass% carbon fibers (CF) reinforced thermoplastic polypropylene (PP) with and without sizing epoxy film on the fibers prior to making composites (CFRTP) of three cross CF cloth sheets and four PP mats, layer by layer. The sizing film covered on CF apparently improved the tensile strength. Namely, an effect of the sizing epoxy film covered on carbon fiber apparently strengthened the CFRTP. It could be explained by the increasing resistance to pull-out fibers with large friction force because the adhesive sizing film probably increased the interface contact atom pairs of CF and PP. The PP was distorted and twisted polymers more than that of straight polymers of polyethylene, and was probably generated the spontaneous nano-scale rough interface against CF.

Key words: carbon fiber, sizing, polypropylene, NMR, tensile strength

1. INTRODUCTION

The conventional carbon fiber reinforced polymer (CFRP) of epoxy resin matrix with high strength is usually applied to the body of airplanes and blade of wind power generator. Strengthening carbon fiber [1,2] and CFRP [3-9] has been investigated. However, the long-term solidification of Epoxy-CFRP [3-5] is a serious problem to produce them. To shorten the solidification term in production process, thermoplastic polymers are useful, since the solidification term of inexpensive Polypropylene (PP) is tremendously shorter than that of expensive Epoxy. The drop rate of solidification term for PP is less than 1/10 of that for Epoxy. On the other hand, decreasing the strength from Epoxy to PP is caused by easy pull-out fibers. Although carbon fiber (CF) is always wrapped by Epoxy, the initial crystalline heterogeneously nucleates at point contacts of carbon fiber surface prior to the dendrite growth in thermoplastic PP because of its low wettability to CF. Decreasing the strength from Epoxy to PP mainly corresponds to decreasing the contact area from plain to points at CF/polymer interface. If the sites number of nano-scale contact at interface between light PP with rough surface and CF with the sizing polymer may be lower than that without the film, the strengthening CFRTP (carbon fiber reinforced thermoplastic polymer) by covering the sizing polymer can be expected.

Therefore, the purpose of the present work is to evaluate the effects of sizing epoxy film on tensile strength of PP reinforced by 28mass% CF.

2. EXPERIMENTAL PROCEDURE

2.1 The way to remove sizing epoxy film from CF surface

Carbon fibers were generally coated by polymer coating with nano-thickness. To remove the film, the carbon fiber - cloth (6.8 g) was dipped for 20 min in acetone (100 mL, 019-00353: Wako Pure Chemical Industries, Ltd, Osaka) at room temperature, as shown in Figure 1. Since solutes of nano-thickness polymer film coated on CF are eliminated by 20 min-dipping in acetone, the peaks can be detected for acetone solution in proton-NMR (AVANCE500, Neutron Magnetic Resonance, Shimazu, Kyoto).

Fig.1 Schematic drawing of dipping sized carbon fibers in acetone at room temperature.

2.2 Making composite for sample preparation

Specimen fabrication was as follows:
As shown in Figure 2, the 28mass%-carbon fiber reinforced thermoplastic polypropylene (PP-CFRTP) sample was constructed with carbon fiber (TR3110M, Mitsubishi Rayon Ltd. Tokyo) and thermoplastic polymer (Polypropylene: BC06C Novatec, Nissho Ltd. Tokyo) matrix. The sample sizes of length, width and thickness were 80 mm, 10 mm and 2 mm, respectively, as schematically illustrated in Figure 3. Making composites are performed by hot-press (IMC-185A, Imoto Machinery Co., Ltd) under 4.0 MPa at 473 K for 1 min, as shown in Figure 4.

Fig.2 Constructive outline of the prepared CFRTP sample. Black and white sheets correspond to the CF- and PP layers, respectively

Fig.3 Schematic geometry of the CFRTP specimen.

Fig.4 Hot-Press machine (Type IMC-185A).

2.3 Tensile tests

Tensile tests were carried out at room temperature with an Autograph tensile tester (Shimadzu Model AG-10TE). Here, the practical distance between marked points on specimen, chuck length and head speed were 40 mm, 20 mm and 1.0 mm/min, respectively.

To evaluate the fundamental mechanical property, the tensile stress-strain curves of the CFRTP with and without the coated sizing polymer film were obtained by using crosshead displacement and confirmed by using video recording device. Since the PP rods preferably deformed during tensile test, true stress – true strain curves were not adaptable because of the heterogeneous deformation. The joint strength, \( \sigma_b \) (MPa) was obtained by the nominal stress-strain curves.

When the tensile load (N), acceleration of gravity (m/s²) and cross section area (m²) are \( m \), \( g \) and \( S \), respectively. Applying those values, the tensile strength \( \sigma \) (MPa) is expressed by the following equation.

\[
\sigma = \frac{mg}{S}
\]

Evaluating the cumulative probability of strength \( (P_f) \) is a convenient method of quantitatively analyzing experimental values, and is often employed in statistical quality control (QC) in industry. \( P_f \) is expressed by the following equation which is a generalized form of the median-rank method [9]:

\[
P_f = \frac{(i - 0.3)}{(N_s + 0.4)}
\]

Here \( N_s \) and \( i \) are total number of samples and rank order integer of \( \sigma_b \) of each sample, respectively, where \( i \) is from weakest to strongest. In this case, \( N_s = 9 \) hence when \( i \) values are 1, 5, and 9, their corresponding \( P_f \) values are 0.94 and 0.06, respectively.

Samples are characterized by not only tensile test, but also by ESR (electron spin resonance) [10] and NMR (Nuclear magnetic resonance).

3. RESULTS

To evaluate the fundamental mechanical property, the tensile stress-strain curves have been measured in this work for the CFRTP samples with and without the coated sizing polymer film prior to dipping in thermoplastic resin and hot-press. Samples are characterized by tensile test, also by ESR and NMR.

Figure 5 compares the changes in tensile stress and strain at high and low accumulative probabilities of the strength (\( P_f \)) for PP matrix 28mass%-CFRTP with and without the coated sizing polymer film prior to making composites by dipping PP, respectively. It can be recognized that removing the sizing polymer film on CF prior to dipping PP obviously decreases the tensile strength and its stiffness at high and low \( P_f \) of 0.94 and 0.06. Fig. 5(b) shows that the stress slightly drops at 0.03 and 0.04 of tensile strain. They are partly pull-out because of lack of contact sites on eliminated CF.

Furthermore, Figure 6 illustrates tensile strength at each accumulative probability of strength (\( P_f \)) for PP matrix 28mass%-CFRTP with and without the coated sizing polymer film on CF prior to making composites by dipping PP. Removing the sizing polymer film on CF prior to dipping PP decreases the tensile strength at each \( P_f \). Namely, it is confirmed that the sizing polymer film covered on carbon fibers apparently improves the tensile strength and an
effect of the sizing polymer film covered on carbon fiber apparently strengthens.

4. DISCUSSION
4.1 Removing sizing polymer film from CF
Figure 7 shows NMR analysis results of carbon fibers immersed for 10 min and additional 10 min. Immersing for 20 min in acetone mostly annihilates the peak of $^1$H NMR spectrum that the coated nano-thick polymer film on CF can be mostly eliminated. In other words, solutes of nano-thickness polymer film coated on CF are eliminated by 10 min-dipping in acetone and the peaks can be detected by acetone solution in proton-NMR, as shown in Figure 7. Removing the sizing polymer film were performed by dipped the commercial used carbon fiber in acetone at room temperature for 20 min.

4.2 Influence of interface roughness of PP sheet
Since the sizing epoxy film covered on CF apparently improves the tensile strength, an effect of the sizing epoxy film covered on CF apparently strengthens the CFRTP. It could be explained by the increasing the resistance to pull-out fibers with large friction force because the adhesive sizing film probably increases the interface contact atom pairs of CF and PP. The PP was distorted and twisted polymers more than that of straight polymers of polyethylene.

To prevent the CF-pull out from PP, both bonding condition and numbers of contact sites are important for the PP to adhere to the CF at interface. As shown in Fig. 8, although Polyethylene (PE) polymers are constricted by principal chains, PP polymers are side chains of -CH3 as well as principal chains. Thus, the density of PP (~0.90 g/cc) is lower than that of PE (~0.95 g/cc). The low density has been used to be explained by the spontaneous interspace of polymers induced by the side chains. Since the spontaneous interspace of PP is large, it probably decreases the number of contact sites at PP/CF interface. On the other hand, since the epoxy is traditional glue, the covered and wrapped epoxy film on CF easily adhere to PP. Thus, the strengthening the CFRTP by covering the sizing epoxy film can be explained by improvement of resistance to pull-out induced by the interfacial adhesion force of the Epoxy film.

We conclude that the strengthening the CFRTP by covering the sizing epoxy can be explained by the increasing resistance to pull-out fibers with large friction force because the sizing epoxy film increases the interface contact atom pairs of CF and PP at nano-scale rough interface of CF/PP.

5. CONCLUSION
Tensile strength was applied for PP matrix 28mass%-CFRTP with and without sizing polymer film on CF prior to making composites. The sizing film covered on CF apparently improved the tensile strength of the CFRTP. It could be explained by the increasing resistance to pull-out fibers with large friction force because the adhesive sizing film probably increased the interface contact atom pairs of CF and PP, which was distorted and twisted polymers.
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ACKNOWLEDGEMENT
The authors wish to thank Mr. Yasuo Miyamoto (EPMA) and Mr. Yoshiki Oda (NMR) of Tokai University for their useful help. This work was partly supported by the JSPS Core-to-Core Program, A. Advanced Research Networks, “International research core on smart layered materials and structures for energy saving”.

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(Received January 7, 2018; Accepted April 5, 2018; Published Online June 1, 2018)