DEVELOPMENT AND EVALUATION OF MECHANICAL PROPERTIES OF POLYETHERSULFONE / ELECTRON CURABLE RESIN SYSTEM FOR NEW AFP PROCESS OF CFRP

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ABSTRACT

The authors have been investigating the applicability of automated fiber placement (AFP) process using carbon fiber-reinforced thermoplastics (CFRTP) to the main propulsion tank molding for the purpose of cost reduction and mass-production of rocket tank. Since polyether sulfone (PES), one of super engineering plastics, has a high viscosity even at elevated temperatures above its melting point hindering the impregnation of the resin into reinforcing fiber bundle, authors devised a new method that includes reducing the melt viscosity of PES by mixing electron beam (EB)-curable monomers and regaining the original thermal and mechanical performance by EB irradiation after tape lay-up. Specifically, triallyl isocyanurate having allyl groups and polyamide 6 having aliphatic chains that generate radicals by EB irradiation were kneaded into PES. The melt viscosity and the tensile strength after EB irradiation of this modified PES were evaluated. As a result, it was confirmed that this system can realize the desired function.

Keywords: CFRTP, AFP, EB-curable monomer mixture
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1. INTRODUCTION

As satellites are becoming more important, it is necessary to reduce rocket costs and launch more satellites [1]. In order to realize this system, it is desired to realize mass production of reusable rocket components. Among these components, the main propulsion tank is a pressure vessel with a simple shape, so it can be expected to be reused and mass-produced. Since the tank is a pressure vessel and needs to be lightweight, carbon fiber reinforced thermosetting resin (CFRTS) is often used and it is manufactured by filament winding (FW) in recent research [2, 3]. On the other hand, since CFRTS requires curing after the FW, it is necessary to heat the entire tank structure, which needs a huge amount of time and space for manufacturing. In addition, thermosetting resins are generally brittle, which causes cracks and decrease of airtightness due to cycle between room and extremely low temperature: A separate liner is required for CFRTS tank to keep the airtightness, although the liner increases weight of rocket. Furthermore, when resin cracks occur in CFRTS, it is necessary to replace the tank itself or repair it by cutting fibers with a patch or the like before reuse in order to reuse the tank. From these issues, the authors are investigating the applicability of carbon fiber reinforced thermoplastic (CFRTP), which has super engineering plastics such as PEEK and PES as the matrix, to rockets in the tank.

In addition to FW, auto fiber placement (AFP) is used to automatically stack fuel tanks and other curved surfaces using a robot [4, 5]. Currently, in the molding of CFRTP using super engineering plastics by AFP, prepregs whose resin already impregnate into fibers are used [6]. However, there are the following problems for practical use. Firstly, since super engineering plastics have a high melting point, a very high temperature is required to fuse the CFRTP prepreg. Moreover, in order to mold this at high speed, a high-power heat source (laser) for instantly heating the prepreg is required. On the other hand, since the laser has directivity and the surface temperature of the material changes with a slight change in the incident angle [7, 8], strict temperature control of the fused surface is difficult. Secondly, in order to prevent peeling or improve the strength between layers of the fused part after fusion, it is necessary to appropriate temperature history during consolidation and cooling in CFRTP [8, 9]. Here, residual stress is generated by rapid cooling from high temperature during fusion. In order to remove the residual stress, it is necessary to take measures such as slowing down the molding speed and annealing. In addition, when using a crystalline thermoplastic resin, the change in crystallinity depending on the cooling rate may affect the mechanical properties of the tank. Finally, since the gaps between the tapes after laminating continue to remain [4, 10], strict robot control is required for the CFRTP prepreg, which has high viscosity and is not easily deformed. In addition, when a thick prepreg is used, heat will not be easily transferred in the out-of-plane direction, and the out-of-plane swell due to lamination will also increase.

Most of the difficulties in AFP molding in CFRTP shown above are due to the thermal behavior of super engineering plastics. In other words, high temperature is required to melt the thermoplastic resin to reduce its viscosity sufficiently. Therefore, in order to solve this problem, it is sufficient to develop a resin system having a function of melting a resin having good mechanical properties at a low temperature at the time of molding and recovering the original mechanical properties after molding. Therefore, the authors consider the following ideas for resin systems and molding processes (Figure 1).

1. An electron beam (EB)-curable monomer is mixed with PES, which is relatively soluble in solvents (monomer) among super engineering plastics. Through this process, it is expected that the viscosity of the modified PES becomes sufficiently low at a temperature lower than the molding temperature of PES itself.

2. The spread carbon fiber tow, which is easily impregnated even with a high-viscosity resin, is impregnated with the modified PES during AFP process.

3. By irradiating an EB at any time during molding, the monomer in PES is started to polymerize and becomes a polymer. Here, the timing of polymerization can be arbitrarily selected by using an EB without using a polymerization initiator such as a curing agent or a catalyst. By this curing process, the decrease in viscosity of PES due to the monomer is suppressed, and the mechanical and thermal properties of PES itself are restored to some extent.

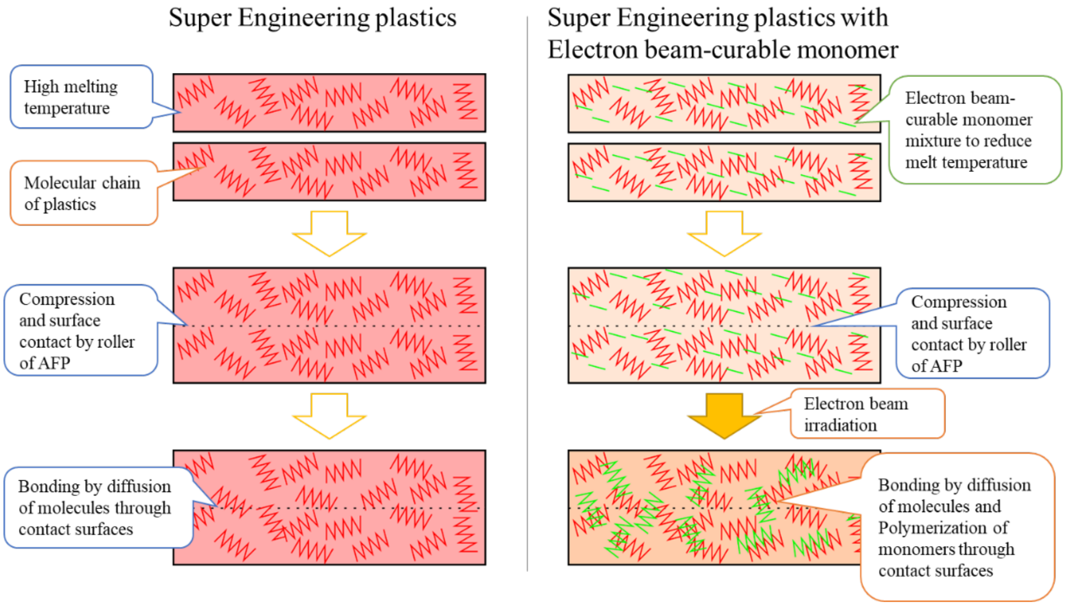

Figure 1. Schematic diagram of expected resin bonding mechanism of low temperature AFP using EB-curable monomer and super engineering plastic

The interaction between the PES with this EB-curable monomer and the Thin-ply laminate using spread fiber tow gives the following four advantages. Firstly, since the modified PES can be molded at low temperature, it can be applied to a heat source with low energy. In addition, since the tow is laminated and cured at a low temperature, the thermal residual stress that causes resin cracking in the extremely low temperature tank is reduced. The use of non-crystalline PES eliminates the need for strict cooling rate control. Secondly, since the EB penetrates substances, it is not necessary to end the polymerization with a single irradiation, and it is possible to gradually carry out the polymerization on the spot while performing AFP. That is, since a new ply is laminated on the semi-cured laminated ply, not only diffusion of thermoplastic resins but also cross-linking of monomers can be expected on the fusion surface. Thirdly, by using the spread CF tow, the tank has thin layers. It is expected that the mechanical properties are improved by reducing the waviness of the fiber, the leakage of LH_2 is reduced by reducing the occurrence of cracks, and the linerless will be accompanied by this. Furthermore, it is a possibility that the EB irradiation device can be miniaturized. Finally, since it is not necessary to use an expensive prepreg, the molding cost is reduced.

On the other hand, to realize this process, it is necessary to prepare a resin system having the above mechanical and thermal properties as the first place. Therefore, in this study, authors searched for and prepared a resin system using PES to lower the melting point with a monomer which can manipulate the melt viscosity with an EB. In addition, the modified PES was evaluated the mechanical and thermal properties through tensile test and complex viscosity measurement test, respectively.

2. MATERIALS AND SPECIMEN PREPARATION

2.1 Materials

The specimen used in this study consists of PES (Sumika Excel # 5003P, Sumitomo Chemical Co., Ltd.), triallyl isocyanurate (TAIC: Nihon Kasei Co., Ltd.) and polyamide 6 (PA6: Amylan® CM1001, Toray Industries, Inc.). PES is a non-crystalline super engineering plastic with a glass transition point of 230 °C and is easily soluble in solvents. TAIC is often used for resin modification by EB [11, 12]. It is a liquid at room temperature and plays a role in reducing the viscosity of PES. In addition, it is a stable monomer even when exposed to a high temperature mixing process with PES. PA6 has an aliphatic molecular part and generates radicals when irradiated with an EB [13-16]. When this chemically binds to TAIC, authors expected that PES and PA6 recover their mechanical properties by losing the role of TAIC as a lubricant. Here, since TAIC is a monomer having three allyl groups, it may undergo three-dimensional cross-linking and exhibit thermosetting properties: In order to show thermoplasticity, it is necessary to have bifunctionality. However, since the first goal this time is to confirm the existence of a system that controls the melting temperature by EB irradiation, authors used this as a monomer having an allyl group as the first step and thermoplasticity of the monomer is ignored this time. The development of this monomer is a future subject.

2.2 Preparation of films

First, PES and TAIC were stirred with a mixer in the room temperature to uniformly wet the TAIC with the PES powder. Next, the PES powder and PA6 pellets were thoroughly mixed and put into a twin-screw kneader to obtain PES/TAIC/PA6 pellets. The temperature of the inlet and die section of the kneader was set to 250 °C, and the temperatures of other section were set to 240 °C. The rotation speed of the screws was set to about 100 rpm. The mixture coming out of the die was cut with a pelletizer. Here, the mixing ratio of PES, TAIC, and PA6 was set as 7: 3: 3 in this study. This ratio was determined by preliminary studies as the amount of TAIC sufficiently attached to the PES particle surface in the manufacturing method described above, and then the same amount of PA6 as TAIC was mixed.

The pellets were heated and compressed to obtain a film with a thickness of about 0.1 mm for mechanical and thermal evaluations. PES/TAIC/PA6 pellets are made into a film by heat compression with a hot press (NSF-37HH0, Kondo Metal Industry Co., Ltd.). Here, the pellet was first heated with no load for 2 minutes, and then heated and compressed for 1 minute with a cylinder load of 10 kN. In addition, Kapton tape was used as a spacer to bring the plate thickness to 0.1 mm. The film after molding is shown in Figure 2. Unlike PES alone (light brown transparent) and PES / TAIC, it was an opaque cream color. This suggests that part of PA6 may be phase-separated inside the film. In addition, the brown unevenness extended radially, suggesting that the kneading at the time of pelletization was insufficient and the laminates had a heterogeneity. Here, steam was emitted from the film as in the case of PES/TAIC when unloading was performed after film molding. Since there was almost no increase or decrease in weight, this effect was ignored this time. In addition, in order to confirm whether PA6 introduced as a radical generator functions, films from which PA6 were removed was also prepared.

Figure 2. Typical image of film made of PES/TAIC/PA6

2.3 Conditions of EB irradiation

EBC-300 (NHV Corporation) was used to irradiate the film with an EB. The atmosphere inside the irradiation chamber is replaced with nitrogen. In this study, the film was placed in a polyethylene bag with air to simulate actual molding conditions. Further, when the modified PES is applied to the actual AFP, each layer itself inhibits the transmission of the EB, so that the film close to the EB source receives a large amount of the EB: It is considered that the EB is blocked by the new layer in the old layer and the irradiation dose is reduced. Therefore, by stacking 10 films at the same time and putting them in a bag, the difference in mechanical properties depending on the amount of EB transmission under the same irradiation conditions was evaluated. Figure 3 shows the positional relationship between the source, back, and film.

The conditions for EB irradiation were an acceleration voltage of 300 kV and three conditions of irradiation doses of 100, 500, and 1000 kGy to ensure the reaction between PA6 and TAIC. In addition to the film under normal irradiation conditions of 500 kGy, CF/PA6 prepreg film with a thickness of 0.04 mm and a fiber volume content of 54% was also prepared and set on the radiation source side as a mask to simulate the effect of the upper layer on the EB transmittance of the lower layer. Table 3 shows the combination of the type of film to be tested and the EB irradiation conditions. Table 1 shows a table summarizing the above EB irradiation conditions. Here, Ply No. indicates the number of films stacked from the radiation source side among the 10 films: e.g., Ply No. 2 represents the second film from the radiation source side.

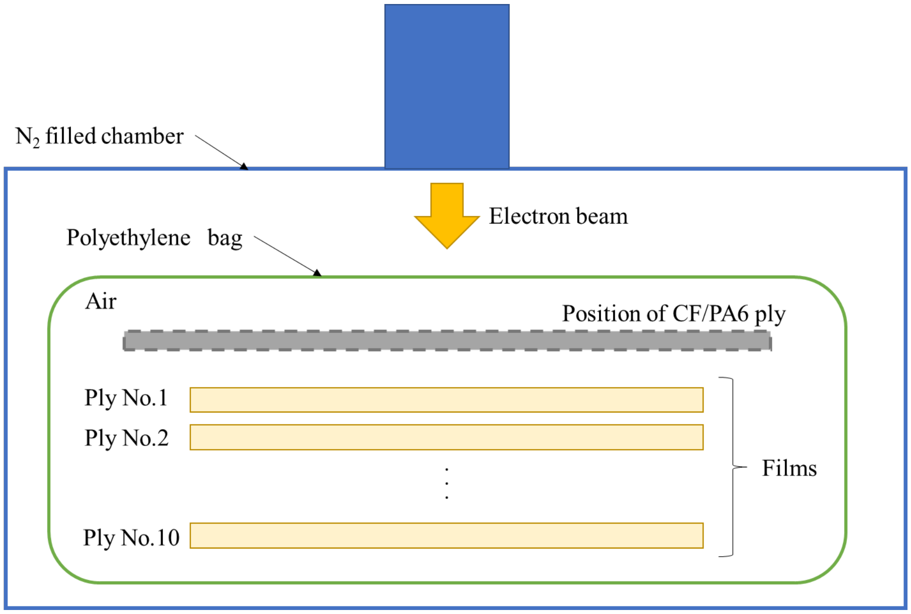

Figure 3. Schematic diagram of the position of films during EB irradiation

Table 1. List of combinations of materials and conditions of EB irradiation

Material	**Mix ratio**	**Electron accelerating voltage (kV)**	**Electron dose (kGy)**	**Ply No.**
PES	-	-	-	-
PES:TAIC	7:3	-	-	-
PES:TAIC	7:3	300	100	2
PES:TAIC:PA6	7:3:3	-	-	-
PES:TAIC:PA6	7:3:3	300	100	2
PES:TAIC:PA6	7:3:3	300	500	2
PES:TAIC:PA6	7:3:3	300	1000	2
PES:TAIC:PA6	7:3:3	300	1000	4
PES:TAIC:PA6	7:3:3	300	1000	6
PES:TAIC:PA6	7:3:3	300	1000	8
PES:TAIC:PA6_CFmask	7:3:3	300	500	2

3. EXPERIMENTATION

3.1 Complex viscosity measurement

Complex viscosity by frequency dispersion using a rheometer (MCR302 manufactured by Anton Paar Co., Ltd.) to evaluate the viscosity of PES and PES/TAIC/PA6 using a film before EB irradiation. The film was laminated on the disposable dish to a thickness of about 0.5 mm. The film was once fused at a high temperature, and then the temperature was lowered and the complex viscosity at a predetermined temperature was measured. Figure 4 shows the appearance of the inside of the constant temperature chamber. From the results of preliminary experiments, the temperature range of PES was set as 250 to 300 °C, and the temperature range of PES/TAIC/PA6 was set as 130 to 220 °C.

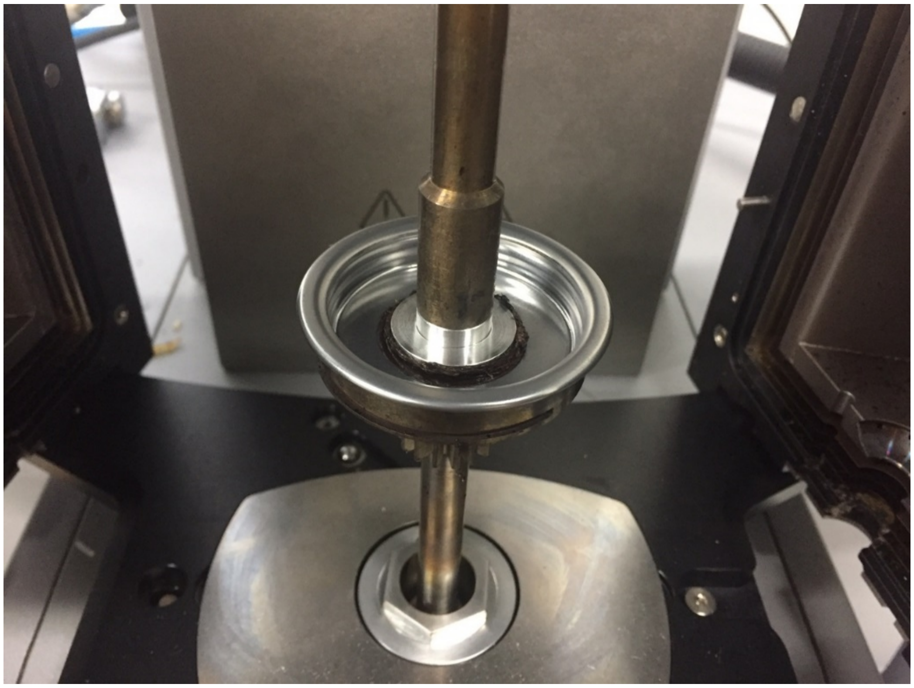

Figure 4. Set up of complex viscosity measurement

3.2 Tensile test

Tensile test was performed to evaluate the change in mechanical properties before and after EB irradiation of films. As shown in Figure 5, the film was punched onto a dumbbell shape specimen which had a parallel part:5 mm wide and 35 mm long. The tabs at both ends of the specimen were gripped, and a load was applied using a universal testing machine (AG-5kN Xplus, Shimadzu Corporation). The test speed was 5 mm/minute, and the number of specimens was 5 per condition. For comparison, a tensile test was also conducted on the PES single film and the PES/TAIC film (weight ratio of PES:TAIC was 7:3).

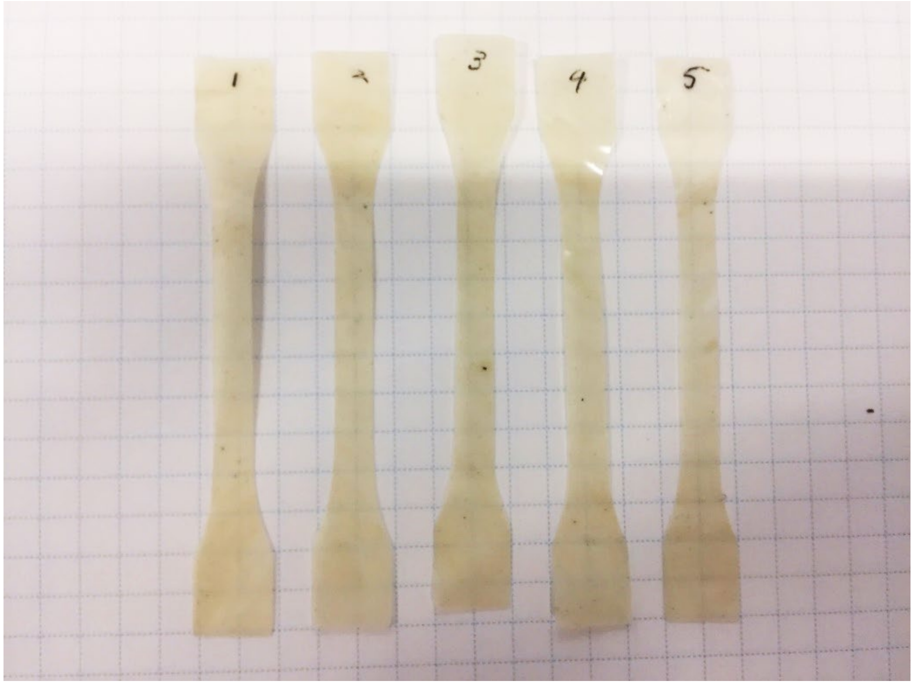

Figure 5. Image pf specimens made of PES/TAIC/PA6 films

4. RESULTS AND DISCUSSION

4.1 Effect of TAIC on the decrease in viscosity of PES/TAIC/PA6

Figure 6 and Figure 7 show the complex viscosity measurement results of PES and PES/TAIC/PA6, respectively. The complex viscosity decreases with increasing temperature and angular frequency in both figures. When compared at an angular frequency of 0.1 rad/sec, PES/TAIC/PA6 maintains the same viscosity at 80 °C lower than PES and becomes lower when each frequency increases. Comparing 250 °C of PES and 220°C of PES/TAIC/PA6, the complex viscosity is two orders of magnitude lower. In fact, since PES is a solid before the glass transition point at 220 °C, it can be said that the viscosity could be extremely reduced by mixing TAIC and PA6 with PES.

On the other hand, in PES/TAIC/PA6, TAIC may volatilize during measurement. Therefore, it is necessary to consider the validity of the results and the acquisition method in the future regarding the acquisition of the viscosity itself, which needs to be measured over time by rotation measurement.

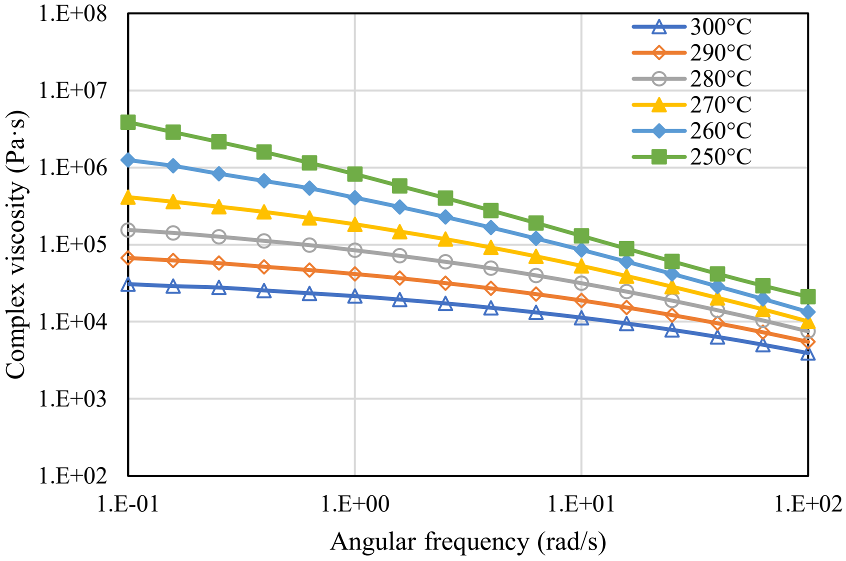

Figure 6. Relationship between angular frequency and complex viscosity of PES at each temperature

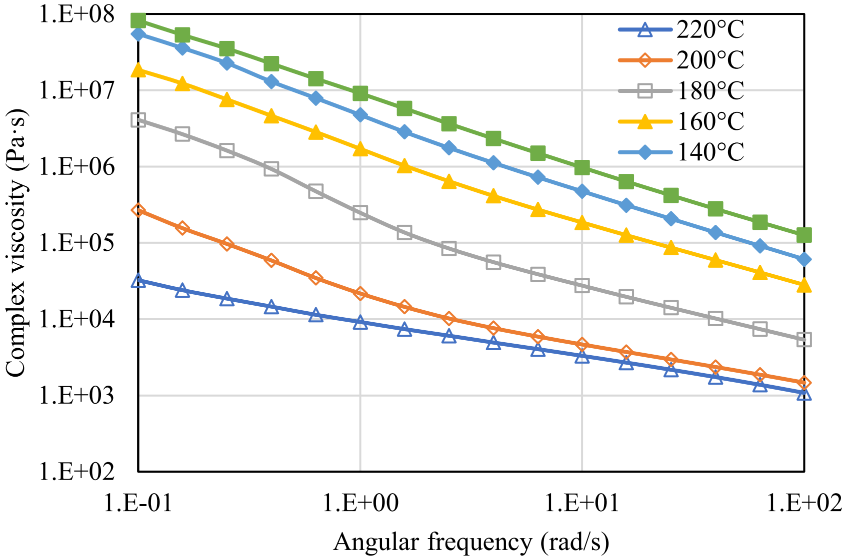

Figure 7. Relationship between angular frequency and complex viscosity of PES/TAIC/PA6 at each temperature

4.2 Effect of EB irradiation on tensile strength

Figure 8 shows the average tensile strength of specimens. The specific value of the strength is written at the bottom of each bar graph. As shown in Table 3, the name of each test piece consists of the composition of the resin, the EB irradiation conditions (when irradiating with an EB), and Ply No.

The strength of PES was 78 MPa, which was the highest among specimens. The specimen of PES/TAIC did not show any significant change before and after EB irradiation. Therefore, it can be said that there was almost no effect of EB irradiation on mechanical properties. On the other hand, in specimens of PES/TAIC/PA6, the average value of strength of 100 kGy, 500 kGy, and 1 MGy were clearly improved compared to that of specimens before irradiation. It is considered that PA6 and TAIC in PES reacted by the electron beam and then the fluidity of the liquid TAIC at room temperature disappeared, so that the strength of PES/TAIC/PA6 was increased compared to before the EB irradiation. In addition, since the strength did not increase uniformly as the EB irradiation dose increases, there may be an optimum irradiation dose.

Focusing on specimens with an EB irradiation dose of 1 MGy, the strength tended to decrease as the Ply No. increases, except for Ply No. 8. This tendency consistent with the tendency of the relative dose of the EB to decrease with the ply thickness and indicate that the strength changes depending on the energy of the EB. That is, it is considered that the relative dose of the EB promotes the binding of TAIC/PA6, which leads to the improvement of the strength of PES/TAIC/PA6. The reason why the strength of Ply No. 8 was higher than that of Ply No. 6 will be investigated later.

In the specimen with an EB irradiation dose of 500 kGy, the specimen covered with a CF/PA6 thin ply prepreg mask had a decrease in intensity of about 22% compared to the specimen without the mask. The specific weight of the prepreg, PES, and PA6 were about 1.53, 1.4, 1.2, respectively: The specific gravity of PA6 is about 80% of that of prepreg, and the difference in specific gravity is 20%. On the other hand, the thickness of prepreg (0.04mm) was 40% of the film. Thus, the energy absorption effect of the EB by the CF/PA6 prepreg is higher than that of the film itself. This is because CF has graphite crystal structures, and it seems that the effect of easily trapping EB was exhibited. Therefore, in order to actually perform AFP of CFRTP and give an EB cross-linking effect to the fusion interface, it is necessary to consider the thickness of the new CFRTP tow between the radiation source and the fusion surface.

Figure 9 shows the results of observing the fracture surface of a specimen (irradiated PES/TAIC/PA6 with an EB of 1 MGy and 300 kV) obtained from 5000x with a field emission scanning electron microscope (FE-SEM, JSM-7100F, JEOL RESONANCE Co., Ltd.). Here, the acceleration voltage of the FE-SEM was 2 kV, and a small amount of gold was deposited on the surface. Many small particles were found on the surface, and it was presumed that PA6 was phase-separated. In addition, the particles and the base metal were partially bonded. Therefore, the mechanism of the change in strength before and after EB irradiation is inferred as follows. First, since PES and PA6 are phase-separated in PES, the strength is low before EB irradiation. After that, it is considered that the strength was recovered by the increase of elastic modulus of the particles by cross-linking between PA6/TAIC by performing EB irradiation, and then by slightly improving the PES/PA6 interface by cross-linking TAIC and PA6 in PES. On the other hand, the strength of PES/TAIC/PA6 was all lower than that of PES. This is because that the strength of

PA6 is lower than that of PES itself, and that the amount of PA6 and TAIC was more than the amount of PES. In addition, the PA6 particles in PES may role the starting point of cracks before plastic deformation of specimen, resulting in a decrease in strength. In this time, a large amount of PA6 and TAIC was added to reduce the viscosity. However, it is necessary to change the amount and type of additives to PES in order to improve the mechanical properties in the future work.

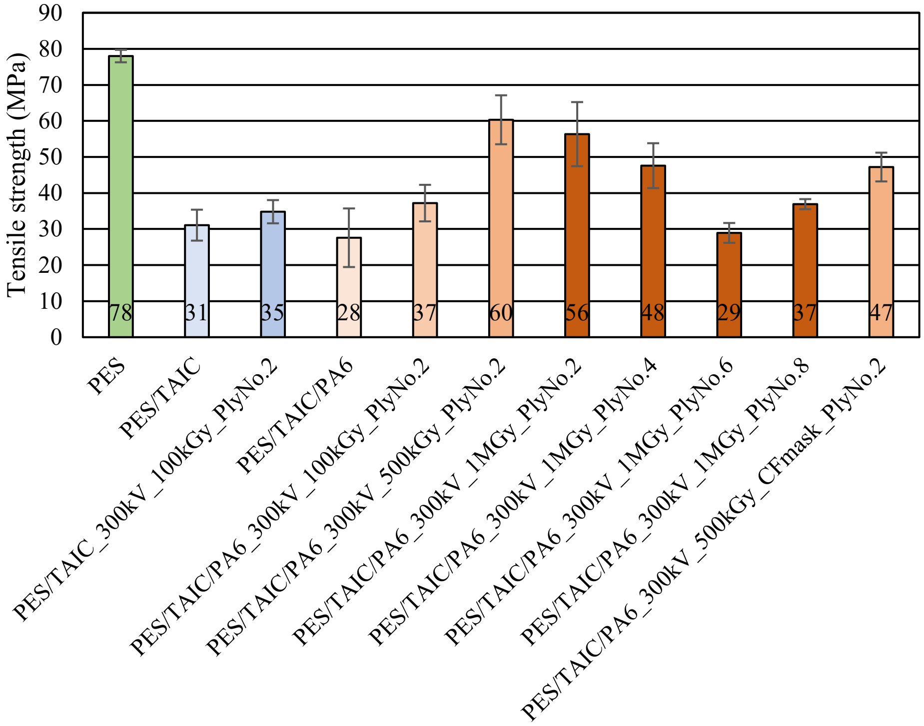

Figure 8. Comparison of average value of tensile strength and its standard deviation of each specimen.

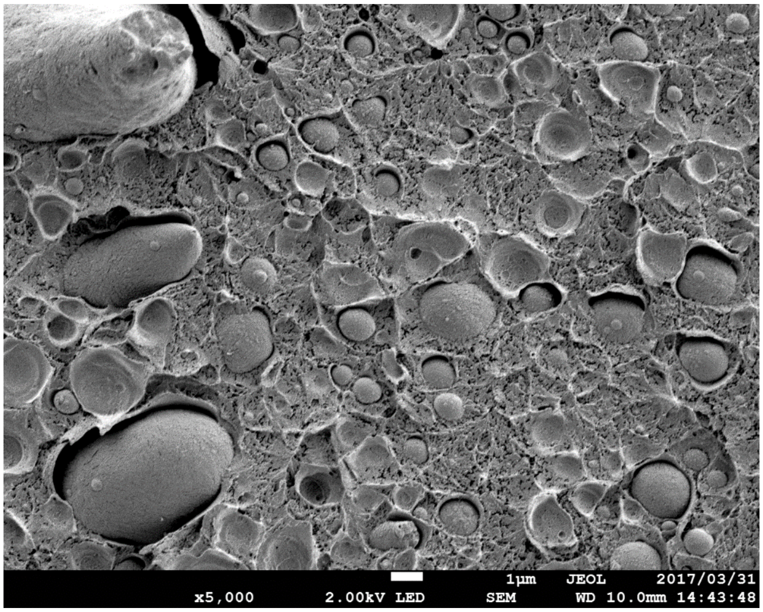

Figure 9. Observation image of the typical fracture surface of PES/TAIC/PA6 specimen after 1 MGy, 300 kV EB irradiation in the region with many PA6 particles.

5. CONCLUSIONS

In this study, the authors investigated the applicability of CFRTP using PES, which is a super engineering plastic, in the molding of the main propulsion tank in order to reduce the cost and mass-produce rocket tanks. Since PES has a high viscosity even if it is a liquid, authors devised a method to reduce the melt viscosity of PES by mixing monomers and restore the melt viscosity and mechanical properties by EB irradiation after molding. As a result of the experiment, although the strength of PES / Electron curable resin system was lower than that of PES, two functions could be realized by mixing TAIC and PA6 with PES as a first step: the viscosity was lower than that of PES and the strength was recovered by EB irradiation. The decrease in strength is considered to be due to the separation of the particles of PA6 in PES. In the future, authors improve the system by changing the type and amount of the mixture.

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