

EFFECT OF MOLDING CONDITION ON IMPACT PROPERTY OF GLASS FIBER REINFORCED THERMOPLASTICS USING IN-SITU POLYMERIZABLE POLYAMIDE 6 AS THE MATRIX

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1 Introduction

Fiber reinforced plastics (FRP) have been widely used as a lighter weight alternative to metallic materials. Thermosetting resin, a type of matrix of FRP, is converted into a permanent cross-linked polymer by curing. Therefore, it cannot re-melt anymore even by heating, which makes material recycling and reuse. On the other hand, fiber reinforced thermoplastics (FRTP) use a matrix of non-cross-linked, straight-chain polymer that allow the material to re-melt and be remolded by heating, which means that they can be easily recycled and reused. The application possibility of FRTP as a material that can reduce environmental impact has been investigated in the automotive field. To use FRTP for automobile structural parts, they must be better than metallic materials with respect to specific strength and rigidity, which suggests that a higher strength FRTP must be developed by using continuous fibers and increasing their content. However, such materials cannot be made easily. Thermoplastic resins as a matrix of FRTP are high polymers that remain highly viscous even at a higher temperature than their melting points, so that they need higher temperatures, higher pressures and longer time to allow them to have good adhesion to the fibers, unlike FRP that can be easily molded due to the use of a lower viscosity liquid resin as the matrix. We have been studying how an FRTP containing a larger amount of continuous fibers to obtain higher mechanical properties can be manufactured using a simple apparatus like those applicable for FRP¹⁾⁻³⁾. One approach for this purpose was the evaluation of mechanical properties of the FRTP using in-situ polymerizable polyimide 6, which is obtained by anionic ring-opening polymerization of ϵ -caprolactam,⁴⁾ as the matrix (I-FRTP). As a result, I-FRTP was found to exhibit higher mechanical characteristics⁴⁾. In the case of the common FRTP molding process, after heating and melting the matrix of thermoplastic resin to higher than its melting

point and impregnating it into the fiber material, the mixture must be cooled down to a level where thermal deformation such as warping and twisting can no longer exist before removing it from the mold. If the thermoplastic resin is a crystalline high polymer, the cooling process, if performed too quickly, may lead to insufficient crystallization, which results in the formation of a solid containing a larger non-crystallized portion. As a result, the made FRTP may not have the expected level of mechanical strength and heat resistance that would normally be achieved by such crystalline high polymers.

On the other hand, I-PA6 based on the anionic ring - opening polymerization of ϵ -caprolactam will crystallize at the same time when polymerization occurs at lower temperatures than the melting point of the PA6 crystals, and the subsequent quick cooling can still produce a higher degree of crystallinity than that obtained by cooling the polymer from the beginning of its melted state⁵⁾. If this is the case also for I-FRTP molding, a higher degree of crystallinity of the matrix than C-FRTP can be obtained, which means that higher mechanical strength and heat resistance can be obtained.

This study first evaluated the degree of crystallinity and mechanical strength of a series of I-PA6 resins at different molding temperatures with a view to demonstrating how the molding conditions may affect the degree of crystallinity of I-PA6 and mechanical properties of the plastic material.

Next, the same evaluation was performed for a GFRTTP (I-GFRTTP) consisting of a matrix of I-PA6 and glass fiber reinforcement with a view to demonstrating how the reinforcing fiber may affect the degree of crystallinity of the I-PA6 and how the molding conditions may affect the mechanical properties of I-FRTP. Then, the PA6, once highly polymerized, was remelted and molded into a test sample (C-PA6) to use as a matrix for molding a GFRTTP (C-GFRTTP) by sheet stacking method, in order to obtain

comparison samples for evaluating the mechanical properties.

2 Experiment

2.1 Test Specimens

2.1.1 Matrix Resin and Reinforcement Fiber

The I-PA6 used for this study was obtained by polymerizing a monomer of ϵ -caprolactam using a sodium salt of ϵ -caprolactam as a catalyst for anionic polymerization, and hexamethylene diisocyanate (HMDI) as an activator. As a reference for evaluating I-PA6, a C-PA6 matrix taken from a pellet of UBE Nylon 1015B (Ube Industries Ltd.) and cut into the relevant test sample size was used. Fiber reinforcement used for both the I-GFRTP and C-GFRTP was a textile of glass fiber (WEA22F-BX, Nitto Boseki Co., Ltd.).

2.1.2 Molding of I-PA6 and I-GFRTP

The catalyst for anionic polymerization of ϵ -caprolactam may lose its catalytic function due to the water in the air whereby polymerization may fail. Therefore, to produce I-PA6 and I-GFRTP, it may be necessary to use molding methods that can control the water content in the system, i.e., those using a sealed (airtight) mold, e.g. resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), and infusion method that uses a vacuum bag. This study chose, among these three options, the VARTM method that comprises a simple vacuum pump configuration as a resin injection system for molding both I-PA6 and I-GFRTP. Figure 1 shows an approximate view of the VARTM molding system used for this study.

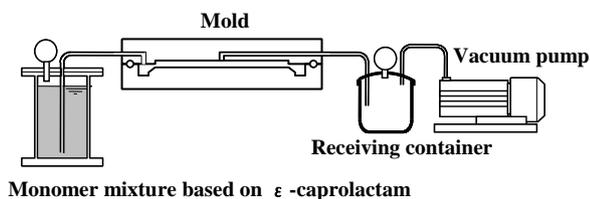


Fig.1 Schematic drawing of VARTM system.

This experiment used different mold temperatures of 140°C, 160°C, 180°C and 200°C in order to investigate the effect of the molding temperature of I-PA6 and I-GFRTP on the degree of crystallinity and mechanical properties of the polymer. For I-PA6 molding, after heating the mold to the required temperature, the mold interior was depressurized to 10Pa by vacuum pump, and then a monomer solution of ϵ -caprolactam was prepared by mixing ϵ -caprolactam maintained at 110°C with catalyst and activator, and finally the monomer was poured in the mold maintained at the specified temperature. Then, the mold and melted matrix therein was kept heated for five minutes by a heat source at the specified temperature. The matrix as molded (I-PA6) was removed from the mold

without cooling. For I-GFRTP molding, 15 sheets of b (width) = 200mm and l (length) = 300mm of glass fiber textile (WEA22F-BX, Nitto Boseki) were stacked in the mold, and then the abovementioned monomer solution was injected. Then, the mold and solution was kept heated for five minutes at the specified temperature by a heat source. Finally, the solid (I-GFRTP) was removed from the mold without cooling. The obtained I-GFRTP plate was good in appearance, showing no defects such as voids or sink marks. The plate contained 42 vol. % (V_f) of glass fiber reinforcement.

2.1.3 Molding C-PA6 and C-GFRTP

The C-PA6 reference matrix is a mold made of polyamide 6, which is highly polymerized in the form of a pellet that is commercially available on the market. This polyamide 6 polymer is still viscous after it is heated to higher than its melting point. Therefore, the material was first processed into sheets, and then the sheets were piled up to the specified dimension of the test sample. Specifically, the pellet was processed into films of 100 μ m thick each by inflation molding. A pile of 33 sheets of this film was processed by using a press machine with a 3 mm spacer to obtain the required thickness of the C-PA6 matrix. The press machine (MHPC-100-500, Meiki Co., Ltd.) used a pressurizing plate heated to 240°C to keep the material heated and pressed at 1MPa for five minutes. While keeping the material pressurized, it was then cooled down to 30°C in five minutes at 42°C/min.

To mold C-GFRTP, 15 sheets each of the abovementioned film material and glass fiber textile (WEA22F-BX, Nitto Boseki) were stacked alternately. Other processes for molding C-GFRTP were the same as those for C-PA6. The obtained C-GFRTP plate was good in appearance, showing no defects such as voids or sink marks. The plate contained 42 vol. % (V_f) of glass fiber reinforcement.

2.2 SEM observation

To evaluate how the resin was impregnated, SEM microscopic sectional observation was made for the I-GFRTP and C-GFRTP as molded. SEM observation test pieces were made by cutting the material into pieces of the specified size and then polishing them using a waterproof abrasive paper and finishing with silica polishing solution. The microscopic cross-sectional observation used a scanning electron microscope (SEM, S-3400N, Hitachi High Technologies) that allows observation under vacuum. To evaluate the bond between glass fiber reinforcement and resin, fracture surfaces made by bending were SEM-observed.

2.3 Measurement of melting heat and crystallization level

As mentioned above, the matrix resin of I-PA6 and I-GFRTP crystallizes while polymerization is occurring. The C-PA6 and C-GFRTP matrix resin crystallizes as it

cools down after it is remelted by heating. To measure the degree of crystallinity immediately after polymerization of I-PA6 and I-GFRTP, and that immediately after molding of C-PA6 and C-GFRTP, a test sample of exactly 10mg taken from the resin part of each test piece was placed on an aluminum pan. Using a differential scanning calorimeter (DSC6220, SII), the melting heat of the crystal was measured in a flow of nitrogen at 40ml/min. To measure the melting heat immediately after molding, the ambient temperature was raised from room temperature to 250°C at a speed of 20°C/min (1st heating). Then, the temperature was decreased to 30°C at a speed of 50°C/min and then raised again to 250°C at a speed 20°C/min (2nd heating). In the transition of the 2nd heating, the melting heat of the crystal formed in the process of cooling after remelting was measured. Using the melting heat measured for each the 1st and 2nd heating, the degree of crystallinity of the crystal formed immediately after molding (1st heating *DC*) and the degree of crystallinity of the crystal formed in the transition of cooling after remelting (2nd heating *DC*) were calculated using equation (1).

$$DC = \left(\frac{\Delta H_m}{\Delta H_m^{100\%}} \right) \times 100 (\%) \quad (1)$$

Where, ΔH_m and $\Delta H_m^{100\%}$ are the theoretical melting heat of the crystal and that of a polymer whose degree of crystallinity is 100%, respectively. This study used a $\Delta H_m^{100\%}$ of 188J/g of polyamide 6 reported by Dole et al.⁶⁾.

2.4 Percentage of unreacted monomer and water absorption

Monomer left unreacted (ϵ -Caprolactam) in the in-situ polymerizable polyimide 6 when polymerized can dissolve readily in water. Therefore, the percentage of unreacted monomer in the I-PA6 and I-GFRTP matrix resin and their water absorption can be measured using the following procedure. Immediately after a plate of 3mm in thickness is molded, cut a rectangular piece of 10mm×60mm from the plate. Dry the piece at 60°C for 24 hours in a depressurized chamber. Measure its weight (M_0) precisely. Then, soak it in hot water of 80°C for 72 hours and measure the weight (M_2) precisely. Then, dry it at 60°C for 72 hours in a vacuum chamber and then measure the weight (M_1). Using these values and equations (2) and (3) respectively, the percentage of unreacted monomer (*Mu*) and water absorption (*Ma*) can be calculated as follows.

$$Mu = \frac{M_0 - M_1}{M_0} \times 100 (\%) \quad (2)$$

$$Ma = \frac{M_2 - M_1}{M_2} \times 100 (\%) \quad (3)$$

2.5 Three-point bending test

To evaluate the bending strength and modulus of elasticity of the polyimide 6 matrix as molded and GFRTP made using the matrix, a three-point bending test as per JIS K 7017 was performed. The specimen was $t=3$ mm in thickness, 15mm in width and $l=100$ mm in length. The span length was 80 mm.

2.6 Izod impact test

To evaluate the impact resistance of the polyimide 6 matrix as molded and GFRTP made using the matrix, the Izod impact test as per JIS K 7110 was performed. The specimen was subjected to an impact given by hitting with a hammer in the direction parallel to the surface of the specimen (edgewise impact). The specimen was a notched specimen. The specimen was $t=12.7$ mm in thickness, 3mm in width and $l=64$ mm in length. The notch was $d=2.54$ mm deep.

3 Results and Discussion

3.1 SEM observation

Cross-sectional views of I-GFRTP and C-GFRTP as molded are shown in Fig. 2. It was found that I-GFRTP and C-GFRTP made by sheet stacking method as well had homogeneous impregnation of the matrix – polyamide 6 – over the entire surface of the glass fiber reinforcement without defects such as voids. ϵ -caprolactam melt, a monomer used as the material of the I-GFRTP matrix resin, impregnated into the fiber reinforcement when it was still in a monomer state of lower viscosity, so satisfactory impregnation can be obtained even in the case of using a long-fiber substrate that contains normally a larger amount of fiber reinforcement, e.g. cloth substrate. Therefore, in-situ polymerizable FRTPs using a monomer of ϵ -caprolactam as the matrix does not need high-temperature and high-pressure molding systems such as the sheet stacking method, as they can be produced using simpler molding systems of lower energy consumption.

3.2 Degree of crystallinity

Figure 3 shows how the degree of crystallinity is affected by molding temperature for I-PA6 and I-GFRTP, and for C-PA6 and C-GFRTP for comparison purpose. Comparing the degree of crystallinity of I-PA6 and I-GFRTP measured immediately after they are molded at 140, 160 and 180°C (i.e., 1st heating *DC*) with that measured after they are cooled and solidified following post-polymerization remelting (i.e., 2nd heating *DC*), it was found that the degree of crystallinity immediately after molding (1st heating *DC*) was higher. One possible reason for this is that the crystal growth speed depends on the molecular weight. That is, crystallization that occurs in the polymerization process grows faster due to the presence of low molecular weight molecules that can move slightly at the beginning of polymerization process, while in the post-polymerization remelting and cooling

(solidification) process, the molecular motion is much slower due to the increase in the number of high molecular weight molecules that slow the crystal growth speed. As a result, the degree of crystallinity after the 2nd heating is lower than that after the 1st heating. For C-PA6 and C-GFRTP, the degree of crystallinity is constant at around 23% for both the 1st heating and 2nd heating. This is probably because the C-PA6 and C-GFRTP matrix resin is already highly polymerized in the molding process, thus the molecular motion does not differ between the 1st and 2nd heating processes, which in turn leads to no change in crystal growth speed. At higher molding temperatures for I-PA6 and I-GFRTP, the degree of crystallinity in the polymerization process (i.e., 1st heating DC) was lower. Generally, crystallization occurs in two stages: generation of crystal nuclei and then growth of crystals. It is known that higher temperatures lead to increased difficulty in generating crystal nuclei⁷⁾. This was likely the case for the I-PA6 and I-GFRTP molding process as evidenced by the finding that crystallization did not grow well at higher molding temperatures.

Comparing between I-PA6 and I-GFRTP, the degree of crystallinity was almost the same, which suggests that it is not affected by the presence of glass fiber reinforcement.

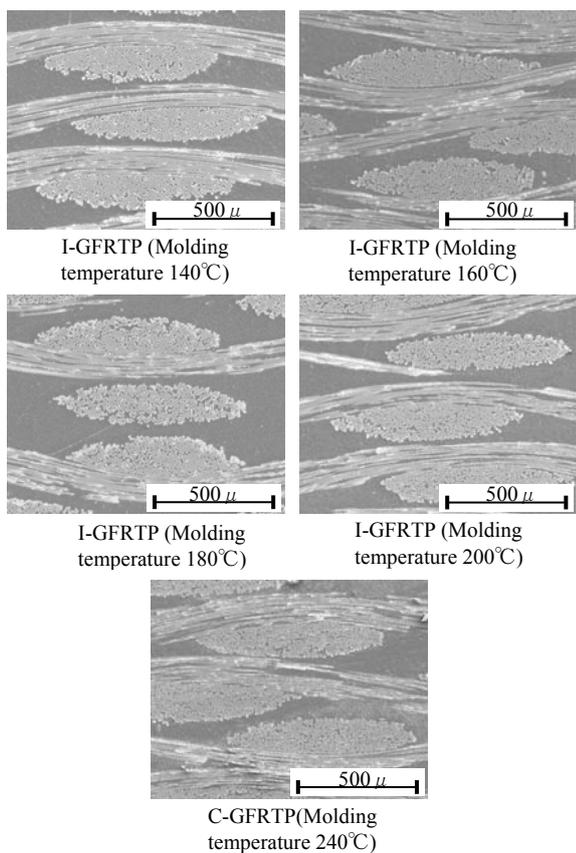


Fig.2 SEM Observation of Cross Sections

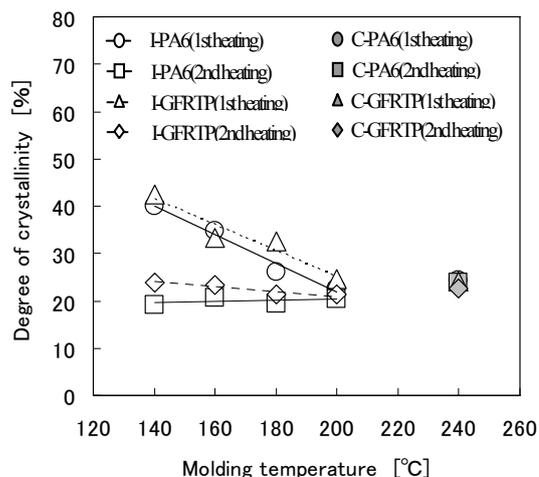


Fig.3 Effect of Molding Temperature on the Degree of Crystallinity for 1st and 2nd Heating for I-PA6 and I-GFRTP

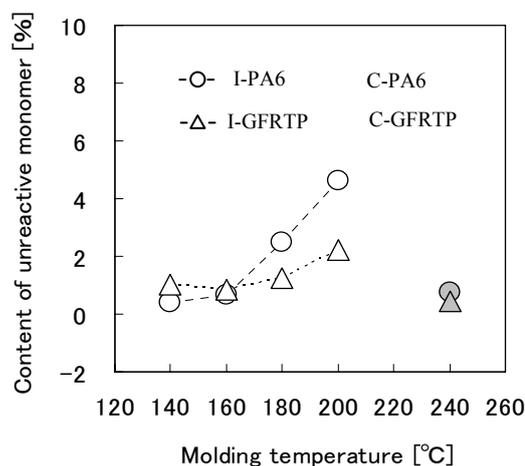


Fig.4 Content of absorption water of I-PA6 and I-GFRTP

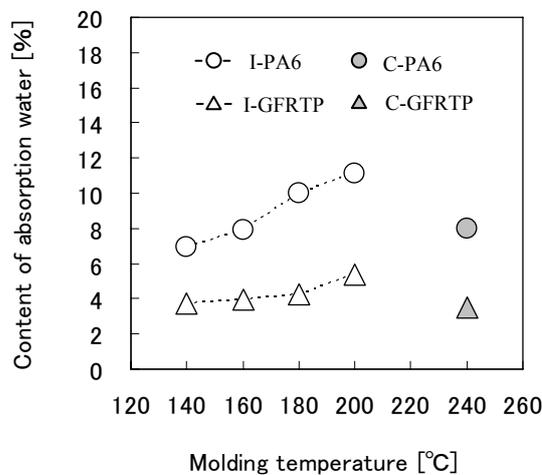


Fig.5 Water absorption of I-PA6 and I-GFRTP

3.3 Content of unreacted monomer and water absorption

For both I-PA6 and I-GFRTP, and C-PA6 and C-GFRTP, Figs. 4 and 5 show the percentage of the monomer left unreacted to the sum of reacted and unreacted monomer (hereinafter called the “content of unreacted monomer”) and water absorption, respectively. As can be seen in these figures, both the content of unreacted monomer and water absorption are smaller in a molding temperature range between 140°C and 160°C for both I-PA6 and I-GFRTP. However, for a molding temperature of 200°C, both the content of unreacted monomer and water absorption are larger for both I-PA6 and I-GFRTP. The reason for the dependency of the content of unreacted monomer and water absorption on the molding temperature is likely that there is an appropriate range of polymerization temperature for ε-caprolactam. That is, the matrix resin molded at a temperature of 140 to 160°C has likely been highly polymerized so that the content of unreacted monomer and water absorption have decreased. I-PA6 and I-GFRTP had no difference in the tendency of either the content of unreacted monomer or water absorption. This indicates that the glass fiber contained in the reinforcement rarely affects the polymerization of the I-PA6 and I-GFRTP matrix resin. The water absorption of C-PA6 and C-GFRTP prepared for the purpose of comparison was approximately the same as that of I-PA6 and I-GFRTP molded at 140 to 160°C. This indicates that I-PA6 and I-GFRTP have approximately the same water absorption as C-PA6 and C-GFRTP made from already polymerized polyamide 6.

3.4 Three-point bending test

Figure 6 shows the bending test results of I-PA6 and I-GFRTP, and C-PA6 and C-GFRTP. This figure tells that, for both I-PA6 and I-GFRTP, both the bending strength and modulus of elasticity for bending become the highest when the molding temperature is 140°C to 160°C. This dependency of the bending strength and modulus of elasticity on the molding temperature likely correlates with the content of unreacted monomer in the matrix (see Fig. 4). That is, I-PA6 and I-GFRTP molded at 180 to 200°C have a larger percentage of monomer left unreacted to the sum of reacted and unreacted monomer contained in the matrix, which leads to insufficient polymerization and resultantly lower mechanical strength.

On the other hand, for C-PA6 that was prepared for the purpose of comparison against I-PA6, both the bending strength and modulus of elasticity for bending were approximately the same as those of I-PA6 molded at 140 to 160°C. Likewise, C-GFRTP was approximately the same as I-GFRTP molded at 140 to 160°C in terms of both the bending strength and modulus of elasticity for bending. Based on these bending test results and fracture surface cross-section SEM observation data, we found that there is

an optimum molding temperature range for in-situ polymerizable polyimide 6; for the subject GFRTP that uses a matrix of in-situ polymerizable polyimide 6, a molding temperature of 140 to 160°C can achieve the same mechanical characteristics as the counterpart GFRTP that uses a matrix of already polymerized polyimide 6.

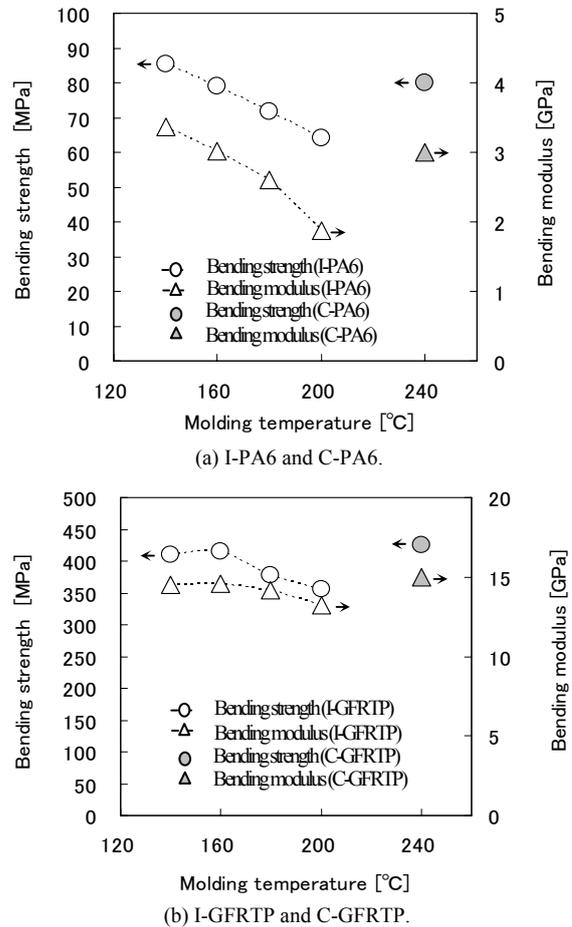


Fig.6 Results of three-point bending tests

3.5 Izod impact test

Figure 7 shows Izod impact test results for I-PA6, C-PA6, I-GFRTP and C-GFRTP. This figure shows that, for I-PA6, the Izod impact strength becomes largest when the matrix is molded at 200°C, and is twice that obtained with a molding temperature of 140 to 160°C; however, for I-GFRTP, the Izod impact strength is rarely affected by the molding temperature within the range of 140 to 200°C, which means that the I-GFRTP’s impact strength does not depend on the molding temperature.

The reason for the independence of the I-GFRTP’s impact strength from the molding temperature is likely that the glass fiber reinforcement is dominant in determining the strength. That is, the impact strength is

determined mainly by the configuration (fiber orientation, and fiber length and diameter) and content of the glass fiber reinforcement.

The C-GFRTP prepared for the purpose of comparison showed the same level of Izod impact strength as I-GFRTP. This finding indicates that GFRTP made using a matrix of in-situ polymerizable polyimide 6 can, irrespective of the molding temperature, show the same level of impact strength as that using a matrix of already polymerized polyimide 6.

4 Conclusion

In order to demonstrate the effect of molding temperature on the crystallinity and mechanical properties of in-situ polymerizable polyimide 6 as polymerized by anionic ring - opening polymerization of ϵ -caprolactam, we evaluated the content of unreacted monomer (percentage of monomer left unreacted to the sum of reacted and unreacted monomer), water absorption and mechanical strength of in-situ polymerizable polyimide 6 molded at various molding temperatures and GFRTP made using a matrix of the abovementioned polyimide 6.

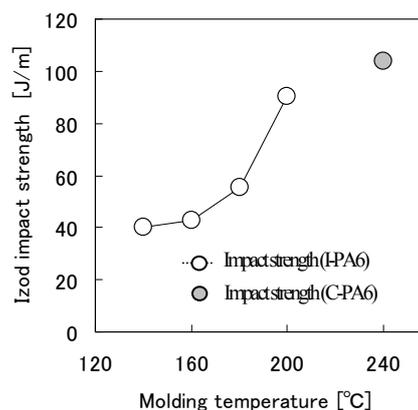
To support our evaluation work, we prepared also test pieces made of already polymerized polyimide 6, and GFRTP made using the already polymerized polyimide 6 as a matrix, and compared them with the in-situ polymerizable polyimide 6-based GFRTP. As a result, we concluded:

1) In-situ polymerizable polyimide 6 crystallizes simultaneously to polymerization, which leads to a higher crystallinity than already polymerized polyimide 6. The crystallinity of the in-situ polymerizable polyimide 6 is independent of the fiber reinforcement contained.

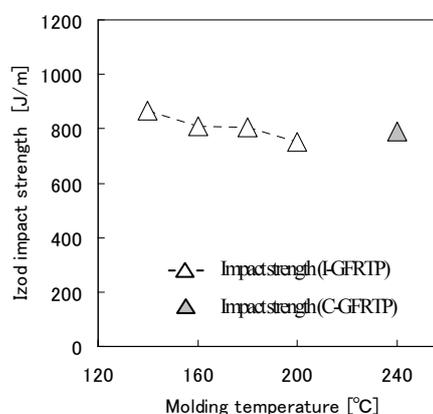
2) In-situ polymerizable polyimide 6 and GFRTP made from a matrix of this in-situ polymerizable polyimide 6 depend highly on the molding temperature to the degree that the crystallinity of the matrix and the mechanical properties of GFRTP vary significantly at different molding temperatures. Molding in-situ polymerizable polyimide 6 at 140 to 160°C, which is about 100°C lower than the molding temperature applicable for already polymerized polyimide 6, will lead to a higher crystallinity and mechanical strength of the GFRTP obtained.

3) In-situ polymerizable polyimide 6-based GFRTP has a higher crystallinity than already polymerized polyimide 6-based GFRTP, nevertheless the both of them are equal in impact strength.

4) Remelting a molding of in-situ polymerizable polyimide 6 will result in the same crystallinity as that of already polymerized polyimide 6. This is the case also for GFRTP; remelting GFRTP made from a matrix of in-situ polymerizable polyimide 6 will result in the same crystallinity as that made from a matrix of already polymerized polyimide 6.



(a) I-PA6 and C-PA6.



(b) I-GFRTP and C-GFRTP.

Fig.7 Results of Izod Impact Tests

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