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Reactive extrusion mechanism, mechanical and tribological behavior of fiber reinforced polyamide 66 with added carbodiimide

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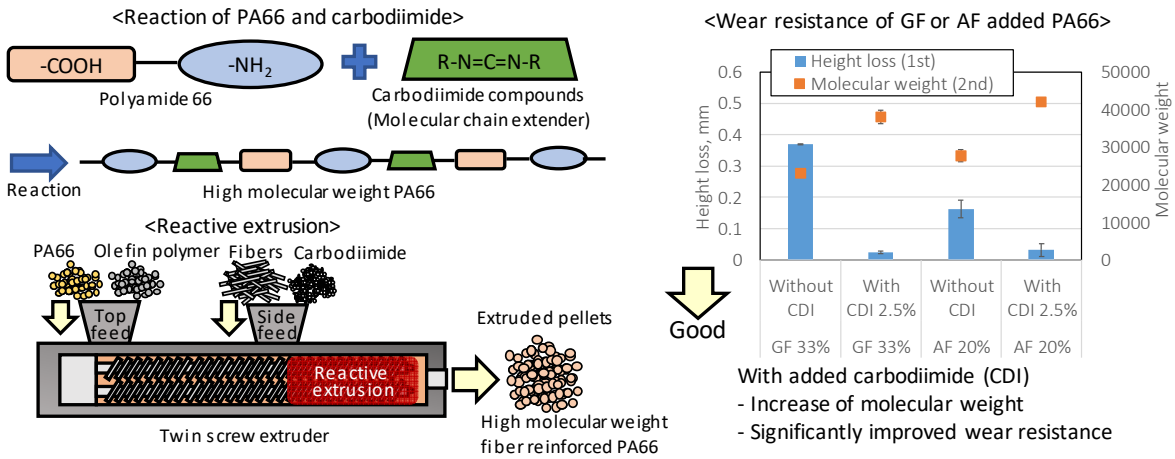
Graphical abstract (Attached in a separate file)



Highlights

• Addition of carbodiimide compounds to fiber reinforced polyamide 66 can increase the molecular weight and improve the toughness.

• Using aromatic carbodiimide can control the reaction velocity, allowing the carbodiimide to remain partially unreacted in the extruded pellets.

• The wear resistance of reinforced polyamide 66 materials could be improved significantly by the addition of carbodiimide.

• A synergistic improvement in toughness was obtained by adding both carbodiimide and a maleic anhydride modified olefin polymer.

ABSTRACT

In this study, the reactive extrusion mechanism of fiber-reinforced polyamide 66 materials with added carbodiimide was clarified, and the mechanical and tribological properties of the materials were evaluated. Increasing the molecular weight of resin is one of the methods that has been proposed to improve the wear resistance and toughness of fiber-reinforced materials. This study proposes a reactive extrusion method using poly-carbodiimide compounds. The effects of the feeding position of the poly-carbodiimide compounds in the twin screw extruder, type of carbodiimide compounds, and proportion of carbodiimide compounds on the

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extrusion reaction and static mechanical properties were elucidated. The toughness of the glass fiber-reinforced polyamide 66 was improved by the increase in molecular weight of the polyamide 66 related to the addition of the carbodiimide compounds. The wear resistance properties were significantly improved by the addition of carbodiimide compounds for both glass fiber-reinforced polyamide 66 and aramid fiber-reinforced polyamide 66 materials. In addition, a synergistic improvement in the toughness was also observed with the addition of both carbodiimide compounds and a maleic anhydride modified olefin polymer to the glass fiber-reinforced polyamide 66 material. The results of this study will be beneficial for improving the mechanical and tribological properties of extruded resins.

Keywords: Polyamide, Reinforcement fiber, Carbodiimide, Wear, Toughness, Extrusion

1. Introduction

Polyamide has strong mechanical properties and good wear resistance owing to its semi-crystalline molecular structure with hydrogen bonding [1-4]. The polyamide 66 (hereinafter PA66) material has especially high wear resistance and a balance of strength, toughness, and heat resistance properties [5,6]. In addition, the cost of the material is much lower than other kinds of polyamide such as polyamide 46, polyamide 11, and any type of aromatic polyamide. Given its excellent properties, PA66 is a widely used material for machine parts in automobiles and for industrial machines such as gears [7-12], bearing retainers [13], rollers [14], and housings [15]. Recently, the demand for downsizing automobiles and industrial machines and an increasing focus on environmental concerns have led to an increasing demand for a reduction in the size and weight of parts and for the ability to apply higher stresses to plastic parts [6,16,17]. As a result, improvements in the mechanical properties of resin materials are necessary. Adding reinforcement fibers, such as glass fibers (GF), carbon fibers (CF) and aramid fibers (AF) is a common method to improve mechanical properties such as the static tensile or bending strength and moduli of polyamide material [5,6,16,18-22]. However, adding reinforcement fibers can induce some negative effects. For example, when a fiber-reinforced material is used for sliding parts such as resin gears, increased wear of the resin may occur. Zhou et al. [21] found that the wear rate of polyamide 6/polyphenylene sulfide-CF composites in adhesive wear mode tended to increase with increasing CF content in the chromium steel ball when sliding on a composite disk. Gordon et al. [22] noted that the wear amount of AF reinforced polyamide 46 increased with the amount of added AF in dry sliding-rolling conditions against an identical polymer material using twin-disc testing machine.

In addition, when plastic parts are fabricated by an injection molding process with a metallic insert, crack initiation at the interface and breakage caused by thermal shock must be considered. Injection molding with inserted metal is an effective method for producing plastic–metal hybrid parts [17,23,24]. However, the plastic parts are subject to stress from the inserted metal parts as a result of the different coefficients of linear expansion for the metal and plastic materials in the area where the metal and plastic parts are in contact, particularly when the edge of the metal is sharp. Therefore, when a cyclic thermal stress is applied (heating and cooling are repeated in the long-term use of plastic parts), cracks related to the shrinkage or expansion may be initiated and propagate in the plastic parts around the inserted metal parts. This can cause the plastic parts to break [23].

Moreover, the effect of this failure mode appears to be much more severe when fiber-reinforced resin materials are used. Indeed, the toughness (expressed by the elongation at breaking) and breakage energy are decreased compared to those of unreinforced plastic material [21], which facilitates the propagation of cracks. Therefore, the effects of the failure of plastic parts with inserted metal should be seriously considered when using fiber-reinforced composite materials for metal-inserted plastic parts.

Increasing the molecular weight of the resin is one of the methods for improving the wear resistance and toughness of fiber-reinforced PA66. Kurokawa et al. [20] reported that the fatigue life of resin gears composed of CF-reinforced polyamide 12 material could be improved by increasing the molecular weight of the polyamide 12. Furthermore, in the authors' previous research, the durability of unreinforced PA66 gears used as the reducer in an automobile electric power steering system was increased with increasing molecular weight of the resin [25].

There are several processes for increasing the molecular weight of fiber-reinforced PA66, and extruding reinforcement fibers in high molecular weight PA66 is one possible method. However, extruding some fillers including fibers in high molecular weight resin is difficult because the melting viscosity of high molecular weight PA resin is increased; therefore, the extruding torque becomes much higher and the effect of degradation of PA resin due to extra heat becomes also much higher [26]. Furthermore, fabricating a continuous strand of extruded composite will become difficult when extruding a high-viscosity resin reinforced with fibers. In addition, the solid-state post-condensation of molded compact is another way to increase the molecular weight of PA66 composite; however, this process is time-consuming and thus expensive [27].

Given these points, this study focused on a reactive extrusion method using a molecular chain extender, which is a relatively simple and inexpensive way to increase the molecular weight of PA [28]. This technology is aiming at the increase of molecular weight by linking molecular chains with the fast reaction between amino or carboxyl end group in PA and molecular chain extender, during the extrusion process. In previous research, various types of additives such as caprolactam, oxazoline, epoxide, ethylene and maleic anhydride (EMA), and diisocyanate were included as the molecular chain extender [27-29]. S.C.Ozmen reported that relative viscosity of PA66 was increased and mechanical properties were improved especially when using the EMA as the molecular chain extender [28].

In this study, the carbodiimide compounds were used as the new molecular chain extenders to increase the molecular weight of fiber-reinforced PA66 material. Carbodiimide compounds contain a -N=C=N- functional group, and are highly reactive with chemical groups such as -COOH or $-NH_2$ [30,31]. Carbodiimide compounds are generally used as additives for plastic materials, such as polyesters and polylactic acid, to prevent hydrolysis [32-34]. It was assumed that fiber-reinforced PA66 with a high molecular weight could be obtained easily because PA66 contains -COOH and $-NH_2$ functional groups, which should be able to react with the carbodiimide group during the extrusion and injection molding process. In addition, using the reactive extrusion method with poly-carbodiimide compounds, it was assumed that reinforcement fibers could be extruded in the resin with a much lower viscosity, and after extruding the fibers, the molecular weight would be increased during the injection molding process, in which it should be much more efficient to obtain the high molecular weight PA66 reinforced with fibers compared to other methods. However, there are few studies on the reaction

mechanism of carbodiimide-added fiber-reinforced PA66 material, and there has been little discussion of the mechanical properties and wear resistance of carbodiimide-added fiber-reinforced PA66. Therefore, in this study, the effects of each parameter in the extrusion reaction process, e.g., the feeding position of poly-carbodiimide compounds in the twin screw extruder, the amounts of added carbodiimide compounds, and the surrounding structure of the poly-carbodiimide group, were investigated. In addition, the mechanical properties and wear resistance of the carbodiimide-added fiber-reinforced PA66 material were also analyzed.

2. Experimental

2.1 Materials

Commercially available raw materials were extruded to fabricate pellets (granules). Test specimens were then fabricated through injection molding of the pellets. Unreinforced PA66 pellet material was used as the raw PA66 material. The molecular weight of PA66 was normal (the viscosity number measured by the relative viscosity method according to standard ISO 307 was 145 ml/g). Strands of GF were cut to the desired size for use (fiber diameter: 6.5 μm, length: 3 mm). GF chopped strands were treated with an agent containing binder resin and amino silane coupling agents. AF-reinforced materials were also evaluated. Strands of AF were also cut to size (fiber diameter: 12 μm, length: 3 mm) and treated with agents. Two different types of carbodiimide compounds were used: aliphatic poly-carbodiimide and aromatic poly-carbodiimide. The main chemical structures of these carbodiimide compounds analyzed with the matrix assisted laser desorption/ionization-mass spectrometry (MADI-MS) are presented in Fig. 1 and Fig. 2. MALDI-MS analysis was performed with using the tetrahydrofuran (THF) solvent, and using the dithranol as the matrix of the measurement. Part of the carbodiimide group in the aliphatic poly-carbodiimide compounds was changed to the urea functional group with the reaction with water, and some terminals of molecules were isocyanate group. In addition, part of the aromatic poly-carbodiimide compounds also contained the isocyanate group in addition to the diisopropylphenyl group. The number average molecular weight of poly-aromatic carbodiimide is 15,000 g/mol. In addition, several types of olefin polymers, chemically modified by a functional group such as a maleic anhydride group (-MAH) or glycidyl methacrylate group (-GMA), were also applied. These olefin polymers are known to act as an impact modifier to improve the impact resistance properties. Extrusion of each raw material was carried out with the compositions and feeding positions listed in Table 1 using a twin-screw extruder (TEM-26SX, Toshiba Machine Co., Ltd.). PA66 was fed in the top feed (i.e., feeding from the root of the barrel of the twin screw extruder), while fibers were fed in the side feed (i.e., feeding from the middle of the barrel of the twin screw extruder). After extrusion, injection molding was carried out with an injection molding machine (ROBOSHOT® S-2000i 100B, FANUC CORPORATION), and test specimens were prepared.

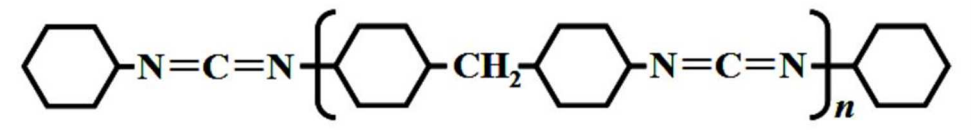

Fig. 1 Chemical structure of aliphatic poly-carbodiimide compounds

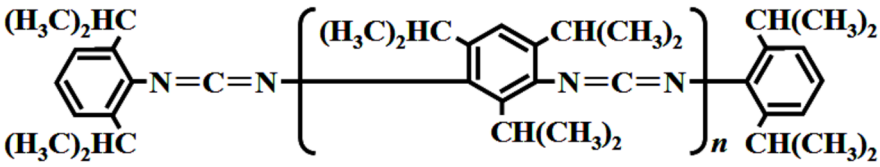

Fig. 2 Chemical structure of aromatic poly-carbodiimide compounds

Table 1. Composition of fabricated materials

No.	PA66	Reinforcement fiber		Carbodiimide compounds			Olefin polymer		
	Level of molecular weight	Type	Amount	Type	Amount	Feeding position of twin screw extruder	Type	Amount	Feeding position of twin screw extruder
1	Normal	GF	33.3 wt%	-	-	-	-		-
2	Normal	GF	33.3 wt%	Aliphatic	2 wt%	Side feed	-		-
3	Normal	GF	33.3 wt%	Aromatic	1 wt%	Top feed	-		-
4	Normal	GF	33.3 wt%	Aromatic	2 wt%	Top feed	-		-
5	Normal	GF	33.3 wt%	Aromatic	3 wt%	Top feed	-		-
6	Normal	GF	33.3 wt%	Aromatic	1.5 wt%	Side feed	-		-
7	Normal	GF	33.3 wt%	Aromatic	2 wt%	Side feed	-		-
8	Normal	GF	33.3 wt%	Aromatic	2.5 wt%	Side feed	-		-
9	Normal	GF	33.3 wt%	Aromatic	3 wt%	Side feed	-		-
10	Normal	AF	20 wt%	-	-	-	-		-
11	High	AF	20 wt%	-	-	-			
12	Normal	AF	20 wt%	Aromatic	2.5 wt%	Side feed	-		-
13	Normal	GF	33.3 wt%	-	-	-	-MAH modification	10 wt%	Top feed
14	Normal	GF	33.3 wt%	Aliphatic	2 wt%	Side feed	-MAH modification	10 wt%	Top feed
15	Normal	GF	33.3 wt%	Aliphatic	2 wt%	Side feed	-GMA modification	10 wt%	Top feed
16	Normal	GF	33.3 wt%	-	-	-	No modification	10 wt%	Top feed
17	Normal	GF	33.3 wt%	Aliphatic	2 wt%	Side feed	No modification	10 wt%	Top feed

2.2 Analysis methods

The number average molecular weights of the pellets and molded test specimens were measured using the relative viscosity method with a formic acid solvent at 25°C, according to standard ISO307. Obtained viscosity number was converted to the number average molecular weight by using the pre-prepared calibration curve, which was obtained with the gel permeation chromatography (GPC) method of reference PA66 material using the HFIP (Hexafluoro-2-propanol) solvent. In addition, the extent of carbodiimide reaction in each process was measured by Fourier transform infrared spectroscopy (FT-IR), as shown in Fig. 3. First, the surface of the pellets or molded test specimens was sliced to a thickness of 50–100 μm using a microtome. Then, the thickness of the samples was made uniform using a hand press machine, and the thicknesses of the sliced samples were measured with a micrometer. Then, using an FT-IR transmission method with a KBr tablet, the absorbance (peak strength), A, of the peak corresponding to the carbodiimide group (-N=C=N-) was measured at approximately 2160 cm^{-1}. The amount of carbodiimide in each sample, C, was then calculated using the Lambert–Beer law: $A = \varepsilon Lc$, where ε is the molar absorption index, and L is the thickness of the sample. Thus, the molar adsorption index, ε, for each carbodiimide compound was calculated based on the slope of the calibration curve created by measuring the peak strength, A, of carbodiimide samples with different concentrations. Fig.4 presents the example of FT-IR chart of the GF reinforced-PA66 with added aromatic poly-carbodiimide in this measurement method. In addition to the peaks related to the polyamide, typical peak of carbodiimide group in 2,160 cm^{-1} was detected.

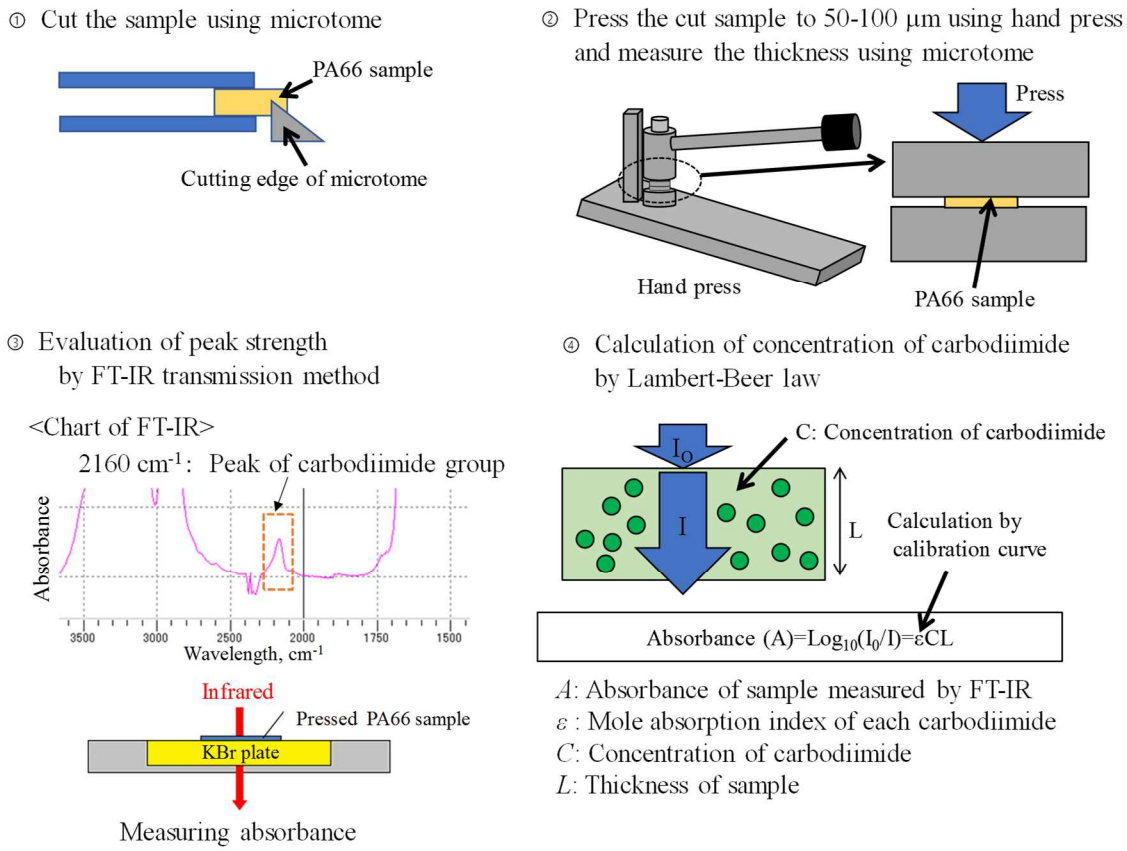

Fig. 3 Method for measurement of the extent of carbodiimide reaction

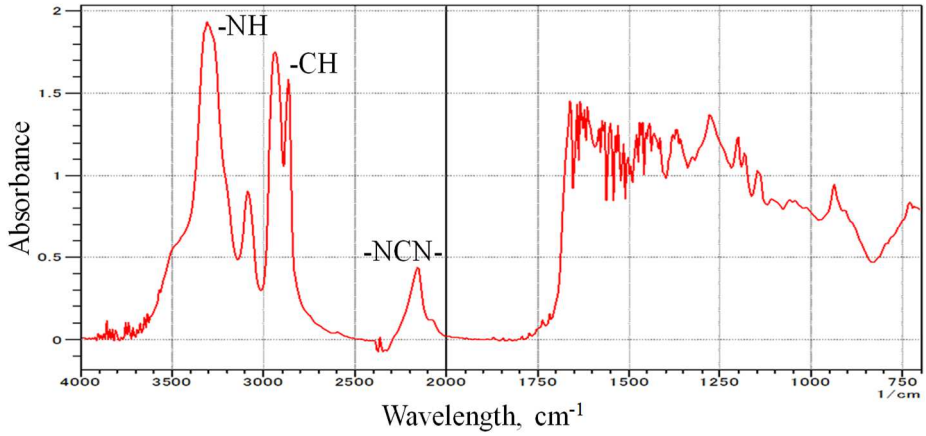

Fig. 4 FT-IR chart of PA66 with added aromatic poly-carbodiimide

2.3 Experimental and observation methods

The tensile mechanical properties of specimens were measured at room temperature following standard ISO527; Table 2 lists the tensile test conditions. The tribological properties were evaluated through sliding tests under grease-lubricated conditions using a rotating composite ring in contact with four fixed steel cylinders, as shown in Fig. 5. With this test, it is possible to obtain high contact pressures, similar to those estimated in real worm gears or rollers (greater than 50 MPa). The increase in the sliding surface temperature can be reduced by introducing intermittent sliding, in which rotation and stopping periods are alternated [25]. Sliding tests were carried out under conditions lubricated with a barium complex grease; Table 3 lists the test conditions. The weight and height of composite ring specimens were measured before and after the test. The sliding surface was observed using an optical microscope and scanning electron microscopy (SEM) after the sliding test. In addition to the sliding test, a notched Charpy strength test was performed following standard ISO 179 for the composite material with added olefin polymer; Table 4 lists the test conditions. Furthermore, the size and distribution of the olefin polymer in the molded samples were confirmed by SEM observation of the fracture surfaces of test specimens No. 13 and 16 after the Charpy impact testing. The olefin polymer was dissolved with toluene by submerging the specimen for 24 h; the remaining hole was considered to be the mark of the olefin polymer. This procedure was employed because it was impossible to distinguish the olefin polymer and polyamide with either microscopic observation or elemental analysis using X-rays.

Table 2 Test conditions for the tensile tests

Tensile test specimens	Shape	150 mm×10 mm×4 mm
Test conditions	Tensile speed	5 mm/s
	Temperature	25 °C
Measured data		- Tensile strength -Tensile elongation at breakage -Tensile breakage energy

Table 3 Test conditions for the sliding tests

Steel cylinder	Diameter	3.5 mm
	Material	Bearing steel (Heat treated)
	Young's modulus	205 GPa
Composite ring (JIS K 7218)	Outer diameter	25.6 mm
	Inner diameter	20 mm
	Height	12 mm
Test conditions	Sliding speed	1 m/s
	Rotation speed	790 rpm
	Normal load	220 N
	Testing time	240 min. intermittent process (10 s sliding and 20 s stopping)
	Temperature	25 °C
	Lubrication	Barium complex grease

Table 4 Test conditions for the Charpy impact tests

Impact test specimens	Shape	80 mm×10 mm×4 mm
Test conditions	Speed	3.8 m/s
	Temperature	25 °C
Measured data		Charpy impact strength

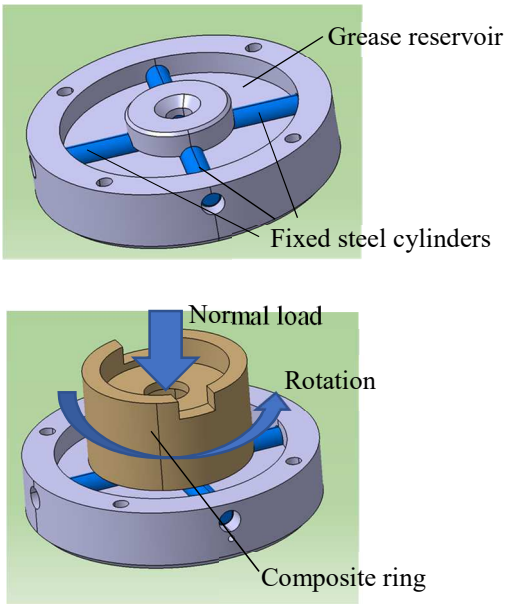

Fig. 5 Schematic view of the steel cylinders-composite ring sliding test

3. Results and discussion

3.1 Effects of the structure surrounding the carbodiimide group on the reaction velocity and mechanism

Fig. 6 shows the variation in the number average molecular weight for each process (sample No. 2, No. 7, and No. 8). A higher molecular weight was obtained for both the pellets and molded samples compared to the raw PA66 material by adding carbodiimide compounds. When the aliphatic poly-carbodiimide compounds were used, very high molecular weights of the extruded pellets were obtained; however, the molecular weight decreased after the injection molding process. In addition, the amount of carbodiimide remaining in the pellet conditions was less than 0.05%, compared to the 2% initially added; here, the remaining carbodiimide is defined not as the amount of functional group itself, but as the converted amount as carbodiimide compounds. This demonstrates that the reaction velocity of the carbodiimide compounds was very high. Therefore, the added carbodiimide compounds were almost exhausted through reactions during the extrusion of pellets, and the effects of decomposition reactions became significant during injection molding. On the other hand, when aromatic poly-carbodiimide compounds were used, the reaction velocity was much lower compared to that for the aliphatic carbodiimide. It was then possible to obtain 0.6–0.9% unreacted carbodiimide remaining, compared to the 2–2.5% initially added. This was because the reaction between the carbodiimide groups and the functional groups in the polyamide was delayed because the poly-aromatic carbodiimide compounds contain isopropyl groups, which created steric hindrance near the carbodiimide group; the reaction was also hindered by resonance stabilization related to the double bonds in the molecular structure. Therefore, the remaining unreacted carbodiimide reacted during the injection molding process in preference to the decomposition reaction; thus, the molecular weight of the molded samples was ultimately increased.

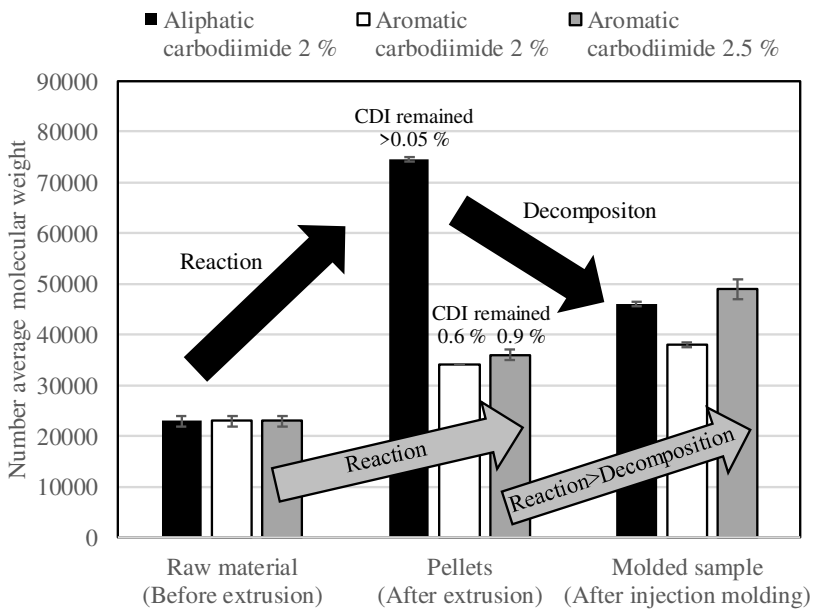

Fig. 6 Variation in the molecular weight for each process

(CDI: Carbodiimide compound)

3.2 Effects of the carbodiimide feeding position in the twin screw extruder and the amount of carbodiimide added

Fig. 7 shows the tensile breakage energy for samples with varying amounts of aromatic poly-carbodiimide added (Sample No. 1, 3–9) with different feeding positions. The tensile breakage energy is the integral of the stress–strain curve obtained in the tensile test, and serves as a barometer for the toughness of composites. When aromatic carbodiimide compounds were fed from the side feeder, the tensile breakage energy was greater for each amount of carbodiimide added compared to top feeding. In addition, for side-feeding of the carbodiimide compounds, the maximum tensile breakage energy was obtained when 2.5 wt.% carbodiimide was added. This can be explained by the following reasons. (1) There was a correlation between the molecular weight of molded samples and the tensile elongation at breaking, as shown in Fig. 8. (2) When 2.5 wt.% carbodiimide was added, the molecular weight of the molded samples was highest. (3) The effect of the amount of added carbodiimide on the tensile strength was weak compared to the tensile elongation at breakage, as shown in Figs. 8 and 9, and thus the contribution of the tensile elongation at breakage was more significant than the effect of the tensile breakage energy. Fig. 10 shows the relationship between the amounts of remaining carbodiimide in the pellet and the tensile breakage energy. Regardless of the feeding position and amount of carbodiimide compound added, the tensile breakage energy increased with increasing remaining carbodiimide in the pellet. With top feeding of the carbodiimide compounds, the reaction time inside the twin screw extruder was long, and the effect of exhausting the carbodiimide became significant. In contrast, with side feeding of the carbodiimide compounds, the reaction time inside the twin screw extruder was short. It is thus possible that unreacted carbodiimide remained in the pellets, and in the subsequent injection molding process, much higher molecular weights of the molded samples were obtained through additional reaction.

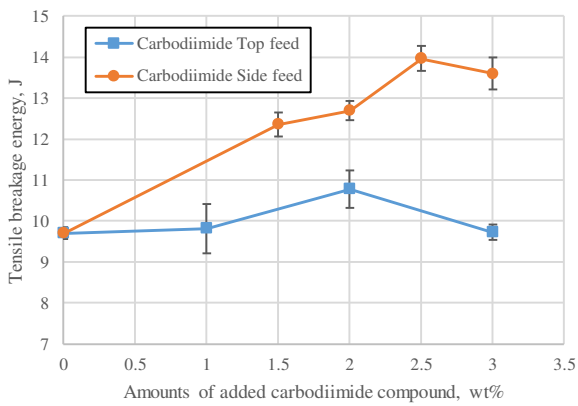

Fig. 7 Relationship between the amount of added carbodiimide compound and the tensile breakage energy

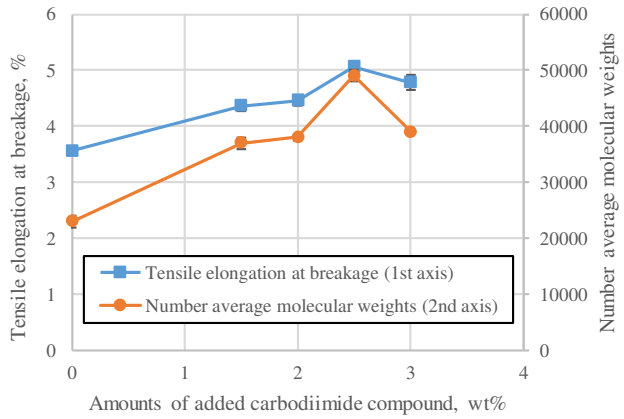

Fig. 8 Tensile elongation at breakage
and number average molecular weights for varying amounts of added carbodiimide compound

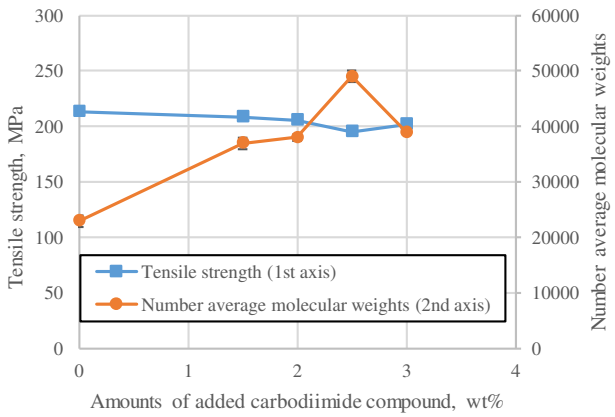

Fig. 9 Tensile strengths and number average molecular weights
for varying amounts of added carbodiimide compound

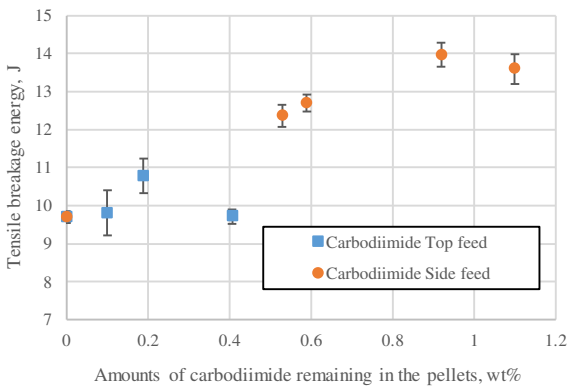

Fig. 10 Relationship between the amounts of carbodiimide remaining
in the pellets and the tensile breakage energy

3.3 Wear resistance of GF-reinforced PA66

Fig. 11 shows the height loss of composite specimens after the sliding tests and the molecular weight of specimens for various GF-reinforced PA66 materials. A low height loss value indicates good wear resistance. The wear of the composite is significantly decreased with the addition of carbodiimide compounds. Fig. 12 shows an optical microscope image of the sliding surface of the specimen without carbodiimide added (Sample No. 1) after the sliding test. Peeling of the composite material related to high contact pressure wear was observed on the sliding surface. Fig. 13 shows an SEM image of the surface of the same sample (No. 1). Peeling of the resin, exposure and dropping off of the fibers, and agglomeration of broken fibers can be observed. In contrast, Fig. 14 shows the sliding surface of a material with added carbodiimide compounds (Sample No. 8). Peeling of the sliding surface was limited to a small area, compared to the material without added carbodiimide. In addition to these observations, the color of the grease, which was originally white, had changed to gray after the test. Fig.15 shows the wear debris inside the grease, which was obtained with the centrifugation and heating of the grease after sliding test. The presence of fibers can be observed. In addition, Fig.16 presents that elements related to GF (Si, Ca) and carbon steel (Fe) were detected in subsequent with SEM-EDX analysis of the wear debris.

Thus, it was confirmed that addition of carbodiimide compounds to GF-reinforced PA66 composites can increase the molecular weight, and it can contribute to decrease the wear of composites. This is related to the fact that the toughness of composite was increased as presented in the results of tensile test, and the initiation and the propagation of the cracks by sliding were prevented.

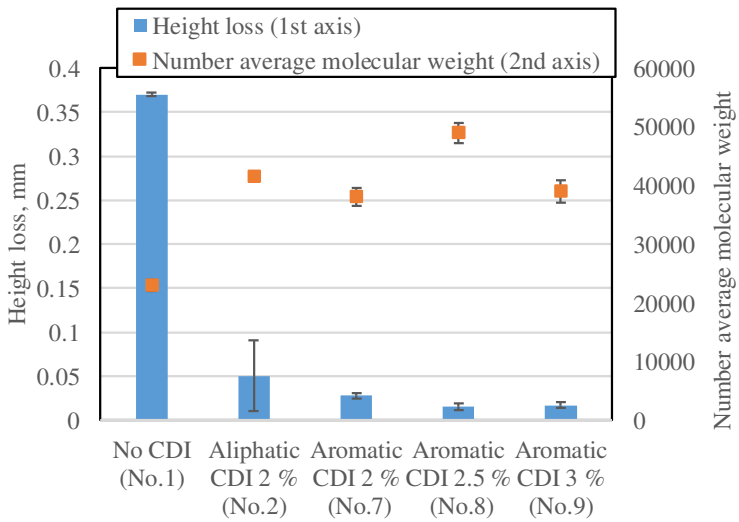

Fig. 11 Height loss after the sliding test and number average molecular weight in each sample

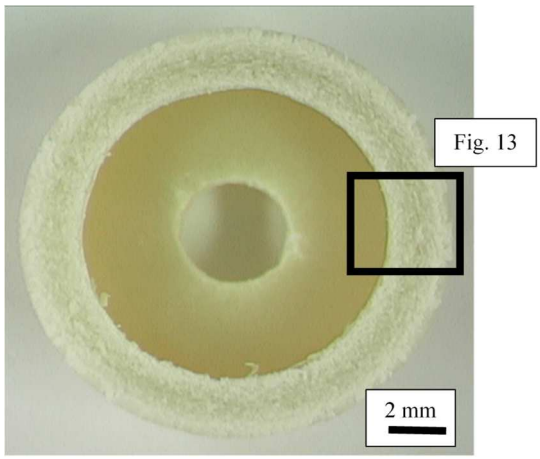

Fig. 12 Optical microscope image of the sliding surface
of the material without added carbodiimide (sample No. 1)

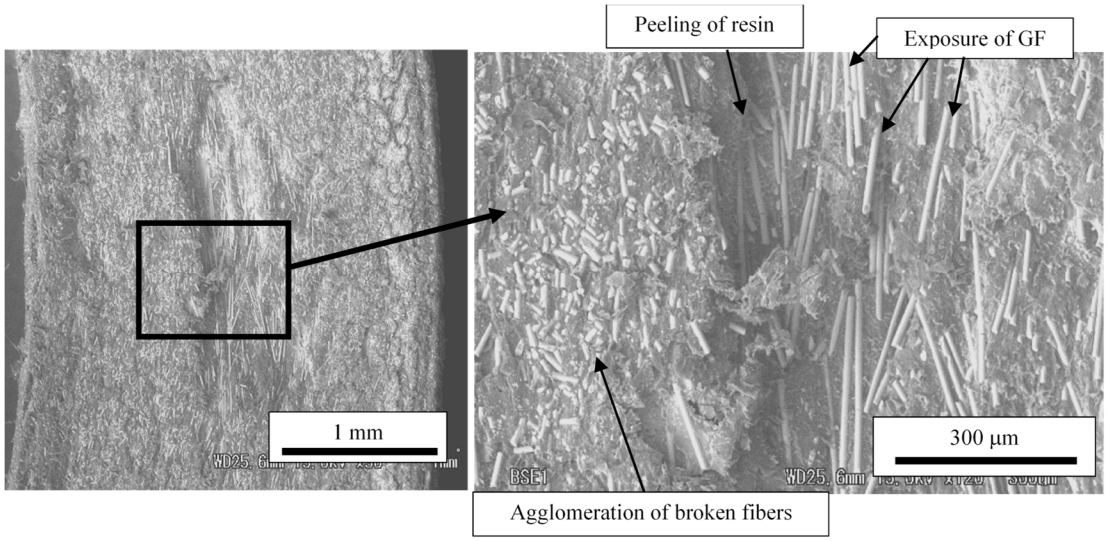

Fig. 13 SEM images of the sliding surface of the material without added carbodiimide (sample No. 1)

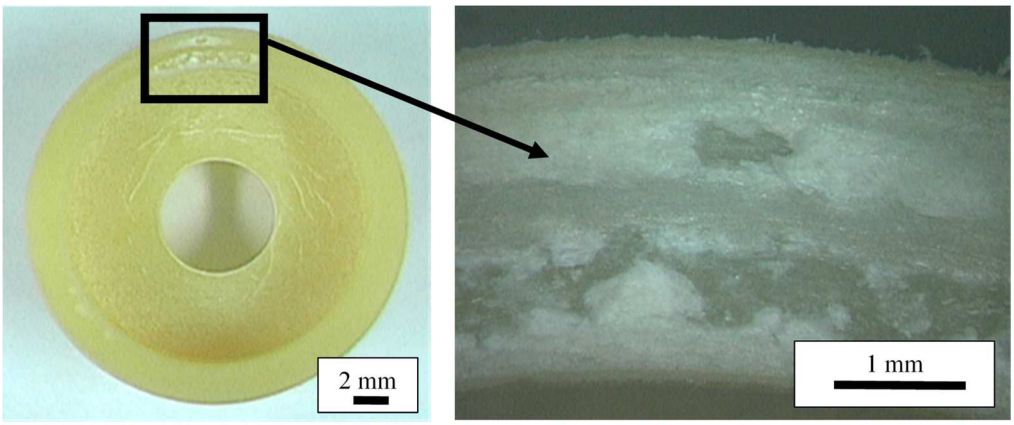

Fig. 14 Optical microscope image of the sliding surface of the material with added carbodiimide (sample No. 8)

Fig.15 Optical microscope image of wear debris in grease

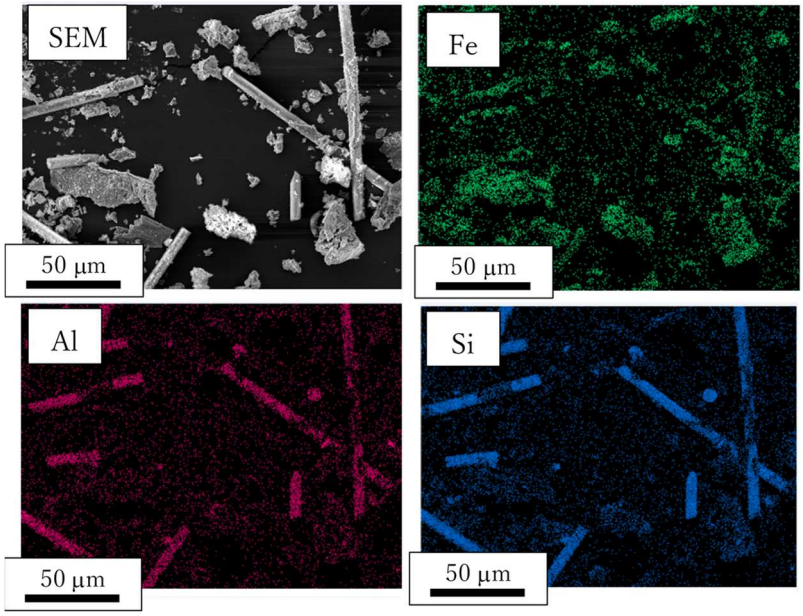

Fig.16 SEM-EDX analysis of wear debris in grease

3.4 Wear resistance of AF-reinforced PA66

For the AF-reinforced material, a composite material was prepared in which AF was extruded with high molecular weight raw PA66 (sample No. 12, viscosity number of the raw resin = 230 ml/g). The wear resistance of this material was then investigated in comparison to the material with carbodiimide added. Fig. 17 shows the height loss after the sliding test and the molecular weight of specimens of the AF-reinforced PA66 composite material. The results show that the wear was decreased largely by the addition of carbodiimide compounds and the increase in molecular weight. Extruding AF with high molecular weight PA66, the molecular weight of the molded specimen was much lower than that of the material with carbodiimide added, and was approximately equal to that of the material extruded with normal molecular weight PA66. Thus, the effect of decomposition

during extrusion was much more significant. We suppose that this is because AF are soft organic fibers, which are difficult to be damaged through the shear force of extrusion, compared to GF and CF. Therefore, the viscosity of the melted resin, temperature, and torque during extrusion were increased, and the effect of decomposition during extrusion became much more severe. By contrast, for the carbodiimide-added material, 0.9 wt.% carbodiimide could remain unreacted in the pellets, the same as in the GF-reinforced composite material. Thus, AF was extruded with low molecular weight PA66, i.e., under conditions of low resin viscosity, and reacted further during the injection molding process. Therefore, a high molecular weight of molded samples and high wear resistance were obtained.

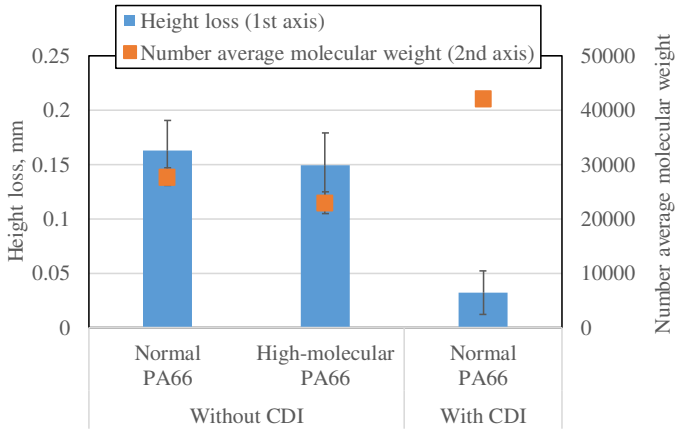

Fig. 17 Height loss after sliding tests and the number average molecular weight for each sample

Fig. 18 shows optical microscope images of the sliding surfaces after sliding tests, and Fig.19 shows SEM images of the sliding surface after sliding tests. For the material with no carbodiimide added (sample No. 11), exposure of fibers was observed on all sliding surfaces, and peeling of the sliding surface was also observed. In contrast, for the material with added carbodiimide (sample No. 13), the resin peeling was partially limited, and the exposure of fibers was controlled. This difference of wear mode is attributed to the difference of the strength of the molecular chain entanglement, and the initiation and propagation of the crack were reduced in the carbodiimide added high molecular weight resin. In addition, considering their chemical structures, carbodiimide is assumed to be reactive not only with polyamide, but also with AF, which are fully aromatic polyamide fibers. Therefore, adding carbodiimide compounds likely contributes to improving the adhesion strength between the PA66 resin and AF in addition to its effect of increasing the molecular weight. Thus, in high contact pressure sliding conditions, the dropping off of fibers was likely reduced by the high molecular weight related to the addition of carbodiimide compounds. In addition, high wear resistance was obtained.

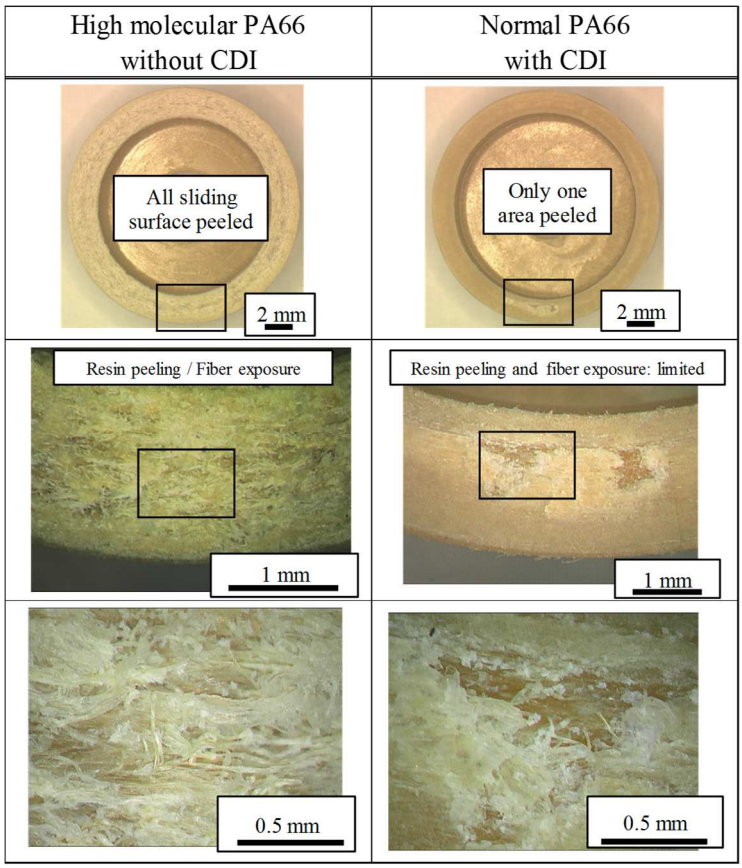

Fig. 18 Microscope observation of the sliding surface of AF-reinforced PA66 materials

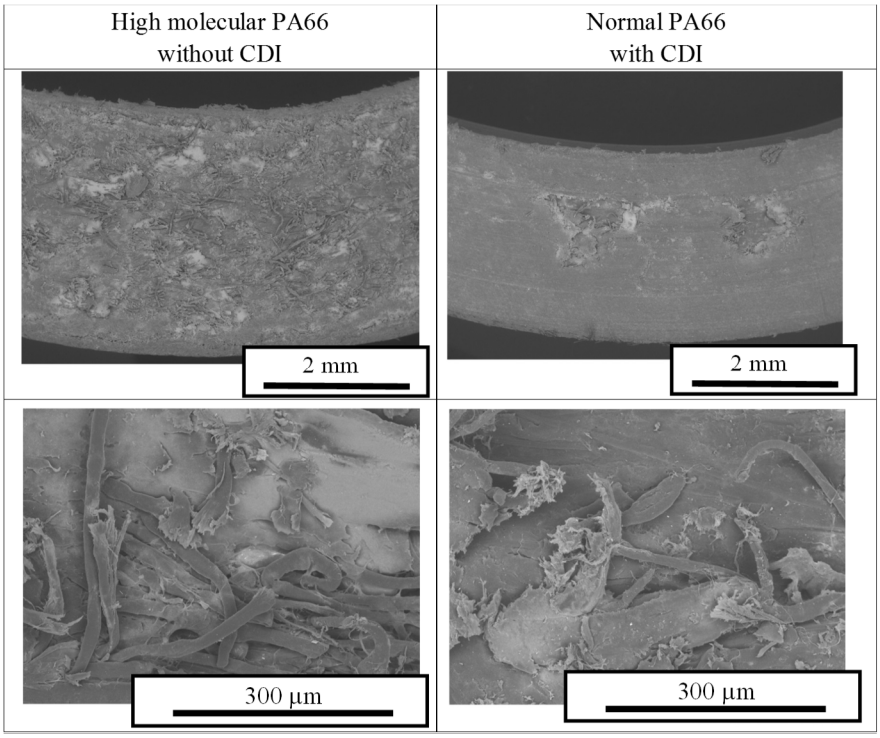

Fig. 19 SEM observation of the sliding surface of AF-reinforced PA66 materials

3.5 Toughness of PA66-GF-carbodiimide with added olefin polymer

The effects of adding olefin polymer to the PA66-GF-carbodiimide material on the mechanical properties were investigated to reflect a case in which a much higher impact strength and toughness may be required. Fig. 20 shows the Charpy impact strength, which acts as a barometer of the impact resistance properties of a material. Furthermore, Fig. 21 shows the tensile breakage energy, which indicates the toughness of a material. When the MAH-modified olefin polymer was added, an improvement in the Charpy impact strength was observed. However, the tensile breakage energy decreased (see samples No. 1 and No. 13). This was because the tensile strength and tensile elongation at breaking decreased with the addition of the soft olefin polymer. In addition, when carbodiimide was added without adding the olefin polymer, the tensile breakage energy was increased, as described in Section 3.2. However, improvement in the Charpy impact strength was not observed (see samples No. 1 and No. 2). On the other hand, when adding both the MAH-modified olefin polymer and aliphatic poly-carbodiimide compounds, a synergistic improvement effect on the tensile breakage energy, which was not predicted by the results of the addition of each individually, was obtained in addition to the improvement in the Charpy impact strength (see samples No. 1, No. 2, No. 13, and No. 14). Furthermore, this synergistic effect was observed only when MAH-modified olefin polymer was added. When GMA-modified olefin polymer (sample No. 15) was added, these effects became less pronounced. Furthermore, no improvement in the tensile breakage energy or Charpy impact strength were observed when the unmodified olefin polymer was added (sample No. 17).

In addition, the distribution of the olefin polymer in the molded samples was investigated to consider the reactive properties of each component in the material with no added carbodiimide; the results are shown in Fig. 22. When unmodified poly-olefin polymer was added (No. 16), the olefin polymer existed as 5–10 μm coarse-sized grains. In contrast, when the MAH-modified olefin polymer was added (No. 13), the olefin polymer existed as sub-micron-sized grains. These results demonstrate that the MAH-modified functional group had a high affinity for PA66, and the olefin polymer was in contact with a much larger surface area of PA66. Hence, the olefin polymer can exist in finely dispersed conditions and exert a strong effect on improving the impact resistance properties. Meanwhile, the unmodified olefin polymer was in contact with a smaller surface area of PA66 because the unmodified polymer did not contain a functional group with strong affinity. Consequently, the distribution size became coarse, and a weak effect on improving the impact resistance was obtained.

The reactivity of the MAH-modified olefin polymer and carbodiimide compounds were verified using FT-IR analyses. Fig. 23 shows the change in the FT-IR detected peak before and after heating the material to 260 °C, at which the olefin polymer was swelled by toluene and the powder of the carbodiimide compounds was penetrated. The results show that the strengths of the -COOH (carboxyl) peak at 1710 cm^{-1} and the -CO-O-CO- (carboxylic acid anhydride) peak at 1790 cm^{-1}, which re related to the structure of the MAH-modified olefin polymer, decreased with heating, as did the strength of the -NCN- (carbodiimide) peak at 2120 cm^{-1}. The -NH-CO-NH- (urea) peak at 1640 cm^{-1} and -NCO (isocyanate) peak at 2260 cm^{-1} were newly detected. This was

because the carboxyl functional group in the MAH reacted with the carbodiimide group and new chemical bond structures were obtained.

Hence, the PA66, carbodiimide, and MAH-modified olefin polymer reacted with each other, and the bonding at each interface was supposed to be strengthened. Consequently, it appears that synergistic effects for improving the toughness can be obtained, beyond those obtained by the addition of each ingredient individually.

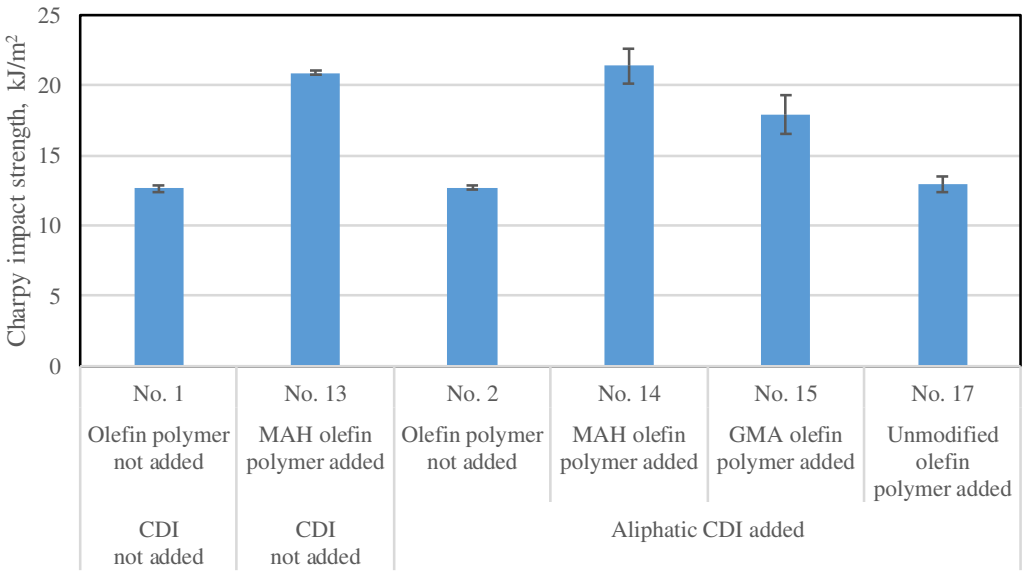

Fig. 20 Charpy impact strength for various materials

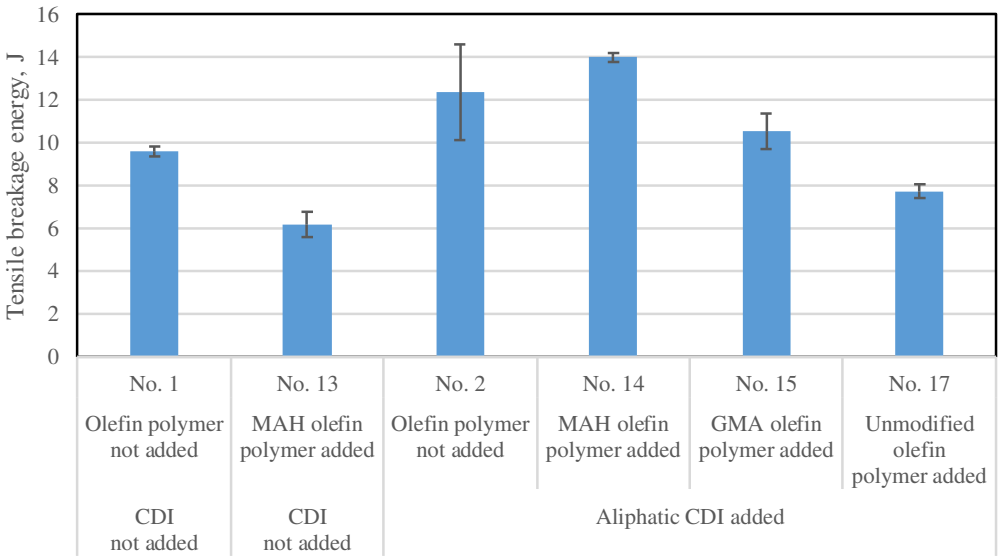

Fig. 21 Tensile breakage energy for various materials

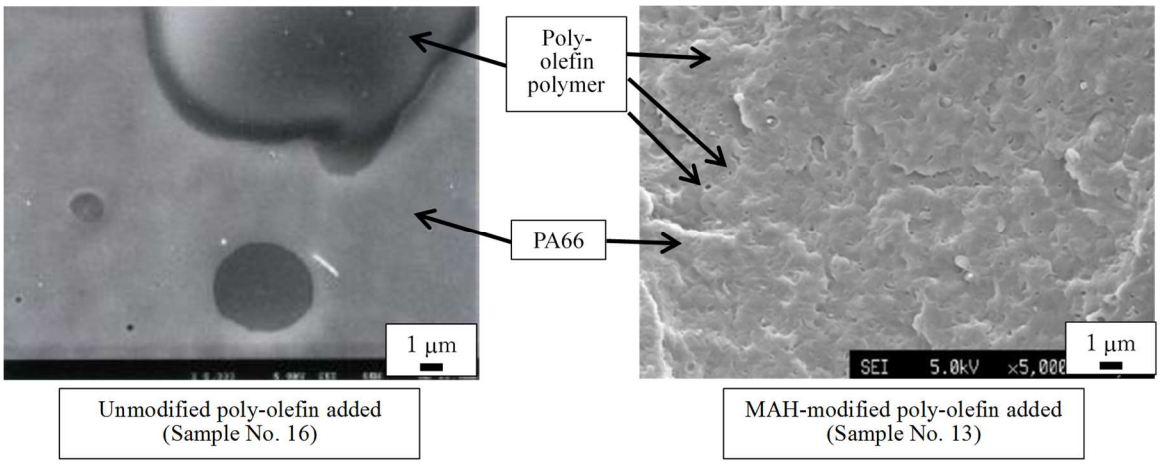

Fig.22 SEM images of the poly-olefin distribution

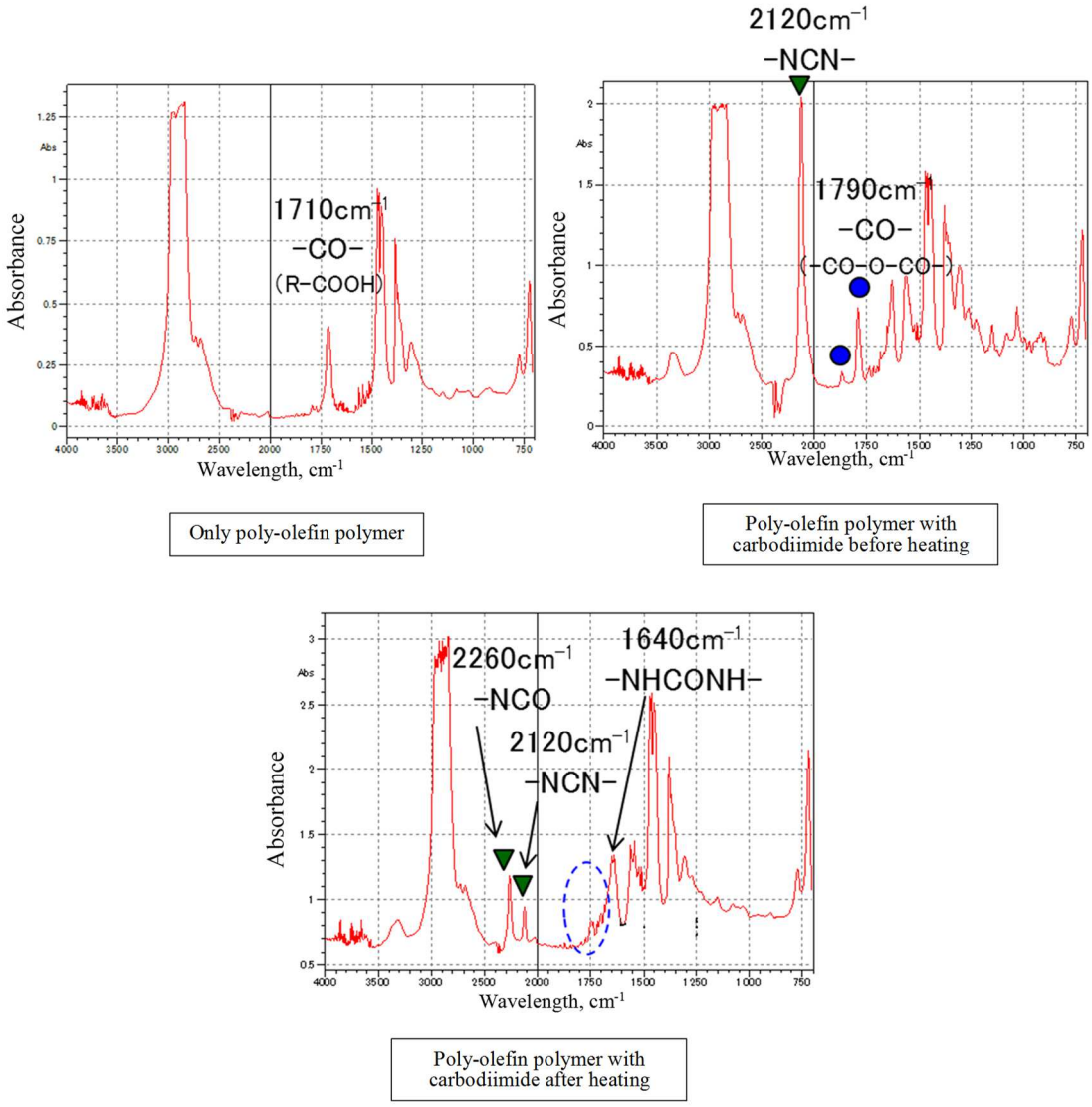

Fig. 23 FT-IR spectra obtained before and after heating

4. Conclusions

The reaction mechanism for a fiber-reinforced polyamide 66 with added carbodiimide during extrusion was clarified, and the mechanical properties and tribological behavior were investigated. The following points should be highlighted:

- Addition of carbodiimide compounds to GF-reinforced PA66 can increase the molecular weight of the PA66 and improve the toughness. Using aromatic carbodiimide can contribute to controlling the reaction velocity, allowing the carbodiimide to remain partially unreacted in the extruded pellets. In addition, a much higher toughness was obtained with side-feeding of the carbodiimide compounds in the twin screw extruder, and there the toughness generally increased with increasing unreacted carbodiimide in the pellets.
- The wear resistance of GF- or AF-reinforced PA66 materials under high contact pressure and grease-lubricated conditions can be improved significantly by the addition of carbodiimide compounds and the increase in molecular weight.
- Synergistic effects on the improvement in toughness were confirmed by adding both carbodiimide and a MAH-modified olefin polymer. The reason for this synergistic effects is suggested to be the reactions between PA66, carbodiimide, and the olefin polymer, which strengthened the interfacial strength of each component.

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Declaration of Interest

Declarations of interest: non

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

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