

NEW POLYMER ALLOYS BASED ON *IN SITU*-POLYMERIZABLE POLYAMIDE 6 APPLICABLE TO HIGH CYCLE RESIN TRANSFER MOLDING (1)

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1 Introduction

Continuous fiber-reinforced composites have begun to be investigated as the replacement of metals for the purpose of light weighting especially in automotive industry because they have as high Young's modulus as metals do while they are much lighter than metals. Resin transfer molding (RTM) process is useful for manufacturing continuous fiber-reinforced composites with various kinds of shape like parts of car. In the automotive field, however, very high productivity is substantially needed. From this viewpoint, RTM is not always suitable for the manufacture for automotive use because of the slow curability of conventional matrix resins such as epoxy resin. So we have been proposing the *in situ*-polymerizable polyamide 6 for the matrix because this resin has both a low viscosity and very fast curability, and it could be applicable to a high cycle resin transfer molding process [1].

By the way, the *in situ*-polymerizable polyamide 6 consists of ϵ -caprolactam as the monomer, a strong base as the catalyst and an isocyanate compound as the activator. This monomer mixture is very low viscosity at the initial state, and when temperature is elevated up to 140-160 °C, it can be rapidly

converted into polyamide 6 by anionic ring-opening polymerization as shown in Fig. 1. This resin has also good mechanical properties such as high Young's modulus and high strength because of its higher crystallinity than the conventional polyamide 6 for injection molding, which unfortunately results

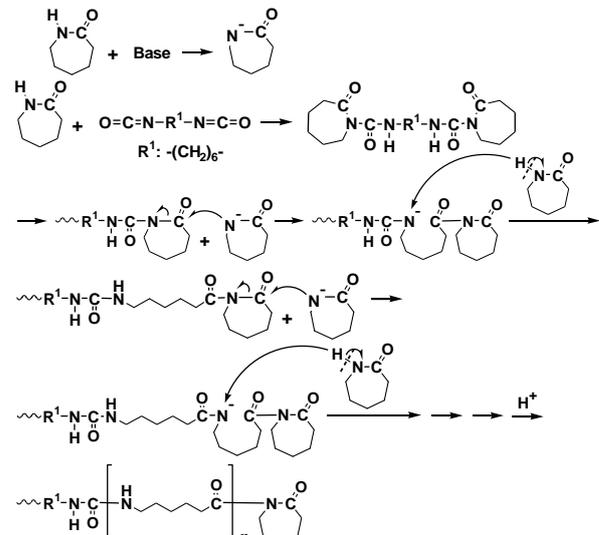


Fig. 1 Anionic polymerization mechanism of *in situ*-polymerizable polyamide 6.

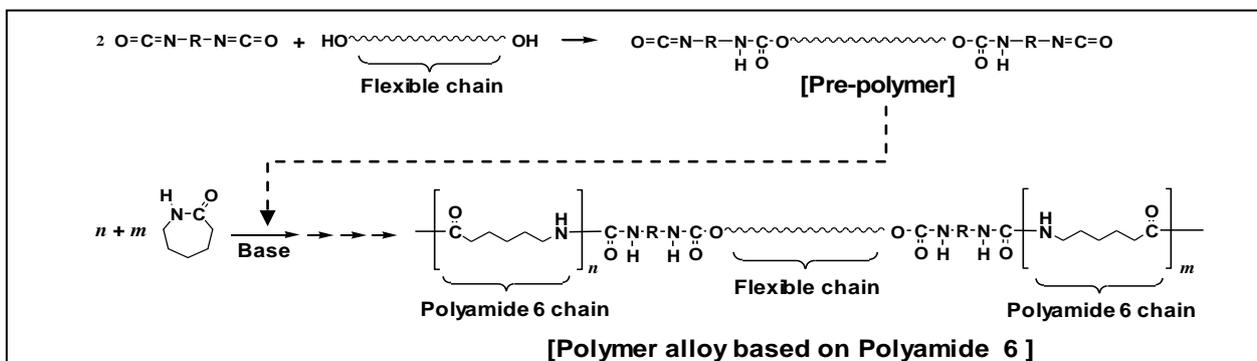


Fig. 2 Synthesizing process of the newly developed polymer alloy based on *in situ*-polymerizable polyamide 6.

in the decrease in its toughness.

In this study, in order to improve the toughness of *in situ*-polymerizable polyamide 6, we tried to form polymer alloy without reducing the excellent workability of the monomer mixture by using isocyanate prepolymers having flexible chain oligomers in the middle instead of mere isocyanate compounds as the activator. In this system, polymer alloy that had flexible chain in the middle of polyamide 6 was automatically constructed during the *in situ*-polymerization (Fig. 2). We evaluated the properties of both the polymer alloy and the glass fiber-reinforced composite using such polymer alloy as the matrix resin.

2 Experimental

2.1 Preparation of Polymer Alloy

Various kinds of flexible chain oligomers with hydroxyl groups at both ends shown in Fig. 3 were end-capped with 2 molar ratio of hexamethylene diisocyanate (HMDI) to obtain urethane prepolymers still having isocyanate groups at both ends. In this study, 5 kinds of telechelic diols, which have various hydrophilicities, were used because we tried to discuss about the influence of compatibility between the flexible chain oligomer and the basically hydrophilic polyamide 6 segment on the toughening effect and the crystallinity of the matrix of polyamide 6. The monomer mixture which consists of ϵ -caprolactam, sodium lactamate and the each obtained pre-polymer, was poured into the metal moulds at 160 °C to polymerize. Then, the corresponding polymer alloy was obtained and its crystallinity, Izod impact strength were measured.

2.2 Measurement of Crystallinity.

The crystallinities (ϕ_{c1}) of the obtained polymer alloys based on polyamide 6 just after polymerization were estimated by using the following equation.

$$\phi_{c1} = (\Delta H_m / \Delta H_f) \times 1/(1-w_f) \times 100 (\%) \quad (1)$$

,where ΔH_m is the endothermic heat corresponding to the fusion of crystalline domains of polyamide 6 segments, which was detected in the process of heating scan at 20 °C/min by DSC(differential scanning calorimeter) for the test specimen just after the polymerization, ΔH_f is the heat of fusion of

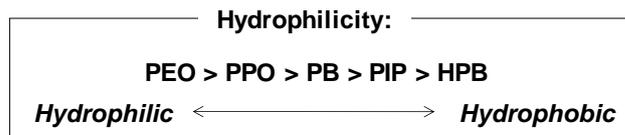
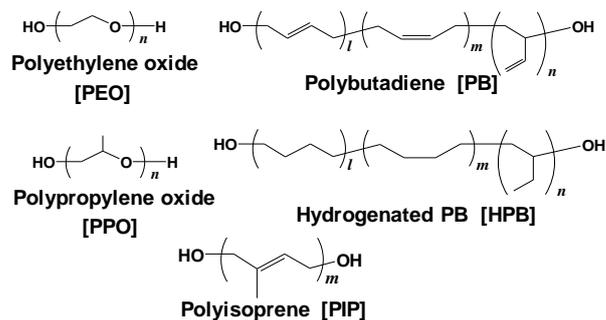


Fig. 3 Telechelic diols used in this study as modifiers with a flexible chain and the order of decreasing hydrophilicity of them.

polyamide 6 homopolymer reported in another literature [2], which is defined as 188 J/g in this study, and w_f is the weight fraction of flexible chain oligomer added as a modifier.

The cooling scan was also conducted to investigate the influence of the modification by alloy formation on the crystallizing rate of polyamide 6 segment. Test specimens were cooled at -20 °C/min, which is so fast that only high crystallizable crystals can be crystallized in this cooling process. The crystallinities (ϕ_{c2}) of the crystals which could be crystallized in such fast cooling process from molten state at 250 °C was estimated by the following equation.

$$\phi_{c2} = (\Delta H_c / \Delta H_f) \times 1/(1-w_f) \times 100 (\%) \quad (2)$$

,where ΔH_c is the exothermic heat corresponding to the crystallization of polyamide 6 segments during the cooling scan from their molten state in the DSC furnace.

2.3 Izod Impact Test for the Obtained Polymer Alloys Based on Polyamide 6.

The Izod impact test was conducted for the obtained polyamide 6-based alloys in accordance with ASTM D-256.

2.4 Preparation of GF RTP.

Table 1 IZOD impact strength of polymer alloys based on *in situ*-polymerizable polyamide 6 modified with various flexible oligomers or HMDI-prepolymers derived from them.

Flexible chain oligomer	Blank	Polypropylene oxide(PPO)		Isocyanate-terminated PPO		Hydrogenated polybutadiene (HPB)		Isocyanate-terminated HPB		Polyisoprene (PIP)	Isocyanate-terminated PIP
		PP-2000	PP-3000	PP-2000-HMDI	PP-3000-HMDI	GI-1000	GI-2000	GI-1000-HMDI	GI-2000-HMDI	Poly ip	Poly ip-HMDI
		Mw*	3100	5600	9400	10020	4100	4900	7600	9200	8850
Solubility in ϵ-CL @ 120°C**	-	S	S	S	S	I	I	S	I	S	S
Appearance of polymer alloy	No bleed	Bleed Wet	Bleed Wet	No bleed	No bleed	Bleed Wet	Bleed Wet	No bleed	No bleed	No bleed	No bleed
IZOD impact strength (J/m)	60.0	108.3	132.7	124.8	31.8	76.7	45.9	73.1	75.8	86.5	91.1

* Mw: Weigh average molecular weight measured by GPC calibrated by standard polystyrene

** Solubility: S=Soluble, I=Insoluble

The glass fiber-reinforced thermoplastics (GFRTTP) using the corresponding polymer alloy as the matrix were prepared by infusion process.

2.5 Impact Compression Test for the GFRTTP.

The impact compression test for the obtained GFRTTP was conducted to confirm the effect on the improvement of composites' toughness by the modification of the matrix via alloy formation. A small piece of test specimen (w=5 mm, l=20 mm, t=2 mm) of the GFRTTP was vertically fixed into the sample holder which was equipped on the load cell and a steel striker (12 kg) hit it to break in the compression mode at the speed of 1.4 m/s. The displacement of the striker just after the striker reached the test specimen and the load were simultaneously monitored during the breaking.

3 Results and Discussion

3.1 Polymer Alloy Based on Polyamide 6

In many cases of this study, both the formation of polymer alloy by using various isocyanate-terminated flexible pre-polymers and the mere addition of flexible chain oligomers to the ϵ -caprolactam mixture improved the Izod impact strength of the polyamide 6. However, the exudation or bleed of the flexible chain oligomer from the obtained polyamide 6 occurred in the case of the mere addition of not only an insoluble telechelic diol

in ϵ -caprolactam such as HPB but also a soluble telechelic diol such as PIP or even PPO (Table 1).

On the contrary to this, when an urethane pre-polymer derived from a telechelic diol and HMDI was added to the ϵ -caprolactam mixture to form a polymer alloy, however insoluble in ϵ -caprolactam the telechelic diol was, no exudation or bleed was observed after polymerization (e.g. GI-2000-HMDI in Table 1).

Table 2 showed the results of the measurement of crystallinity for the polyamide 6-based polymer alloys. The crystallinity measured by the heating scan just after the polymerization indicates the crystallinity the polyamide 6 could reach during the *in situ*-polymerization. The unmodified polyamide 6, represented by 'Blank', had 49% of crystallinity just after polymerization. When a flexible chain oligomer highly compatible with ϵ -caprolactam such as PPO was used for forming an alloy, the crystallinity of polyamide 6 segment decreased significantly, resulting in unfavorably lowering the thermal stability of the polyamide 6. On the other hand, when a flexible chain oligomer highly incompatible with ϵ -caprolactam such as HPB with a long hydrophobic chain was used, the crystallinity did not decrease at all.

The same tendency was also observed in the cooling process from molten state. In this study, the crystallinity measured by the cooling scan is considered to reflect the crystallizing rate of

polyamide 6 segments because the cooling rate was very high as described above. In the fast cooling process from molten state, the crystallization of polyamide 6 segments were somehow depressed, so the crystallinity of even homopolymer of polyamide 6 could reach only up to 30%. The polyamide 6-based alloy with a flexible chain oligomer compatible with polyamide 6 chain such as PPO could reach a lower level of crystallinity than the unmodified polyamide-6 could. Even though a flexible chain oligomer incompatible with polyamide 6 chain was used as the modifier, in the case that the length of oligomer was not so long, the crystallinity was lowered a little bit. On the other hand, in the case that the flexible chain oligomer was incompatible and enough long, even after the chain was completely embedded in the middle of polyamide 6 chain with chemical bonds, the crystallinity did not decrease at all. So, it is concluded that the toughness of polyamide 6 could be improved without decreasing in crystallinity by the alloy formation with a urethane pre-polymer derived from a long hydrophobic telechelic diol.

Table 2 Crystallinities of polyamide 6 segments in the various types of polymer alloys based on polyamide 6.

Polymer sample	Blank PA6	PA6-alloy using PP2000	PA6-alloy using GI-1000	PA6-alloy using GI-2000
Flexible segment type	-	Long PPO	Short HPB	Long HPB
Crystallinity just after polymerization	49%	36%	43%	50%
Crystallinity that can reach in the -20°C /min cooling process	30%	26%	29%	31%

3.2 Glass fiber-reinforced composites

Fig. 4 shows the result of the impact compression test for the GFRTTP using the polymer alloy based on isocyanate-terminated polyisoprene and in situ-polymerizable polyamide 6 as the matrix. The load-displacement curve became smoother by forming alloy while the original curve was very zigzag. That means the formation of micro clacks or delamination on the interfacial surface between the reinforcing glass fiber and the matrix resin during the destruction was suppressed. This test also revealed that the absorption of impact energy was improved

by approximately 40 % compared with the GFRTTP using the blank polyamide 6, resulting from that the level of load increased.

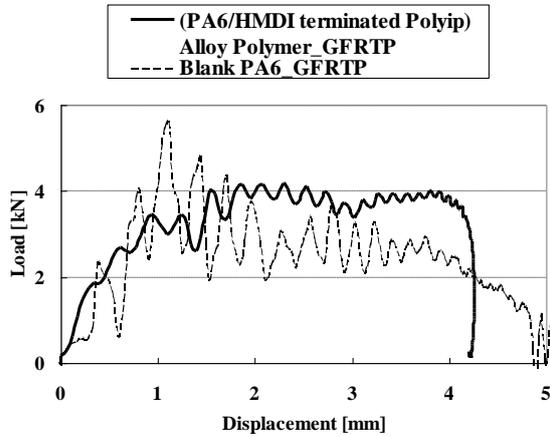


Fig. 4 Impact compression test for the GFRTTPs using the polymer alloy or blank polyamide 6 as the matrices.

4 Conclusions

1. We have investigated the use of the ‘*in situ*-polymerizable polyamide 6’ as the matrix of thermoplastic composite (FRTP).
2. We successfully developed the new polymer alloy technology to improve the toughness of PA6 without lowering its crystallinity as well as without impairing its advantage of *in situ*-polymerizability.
3. The polymer alloy based on the combination of PA6 with insoluble flexible telechelic diols end-capped with diisocyanate improved the impact strength of the fiber-reinforced composite thereof.

References

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