Enhanced and Horizontal Recycling of FRP Using Subcritical Water

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Abstract
In enhanced and horizontal recycling of FRP, Fiber Reinforced Plastics, which are very difficult to be recycled, styrene-fumaric acid copolymer (SFC) separation and modification processes using 1-octanol were examined. Almost 100% of the SFC was extracted to 1-octanol. After extraction, SFC:water content with SFC was 1:0.25. The SFC extracted was modified with 1-octanol using H_2SO_4 as a catalyst at 175 C for 17 hours. The modification rate was almost 100%. The modified SFC was mixed with a commercial low profile additive (LPA), high value-added shrinkage controlling additive for FRP forming, to produce FRP sample board and tested. At 50% of the modified SFC mixing ratio, the modified SFC showed equivalent performance to the commercial LPA. It proposes “enhanced recycling” of FRP thermo-setting resin. The scale-up of this process was also examined. Pilot plants of subcritical water hydrolysis and inorganic materials separation processes were built and tested. Pilot test results showed performances which were more than 90% of that of reaction pipe test. Bench plants of the SFC separation and modification processes were also built and tested. The bench test showed performances which were more than 85% of that of beaker test.

1. Introduction
Fiber Reinforced Plastics, FRP, is a composite material of thermo-setting polyester resin, inorganic filler such as calcium carbonate, and glass fiber. Thermosetting resins cannot be re-formed after final cure. The inorganic materials of FRP cause a difficulty of incineration. Thus, FRP is very difficult to be recycled. In spite of that shortage of dump yards has been growing into serious problem, 400, 000 tons of FRP has been landfilled in Japan. It is also wasteful use of oil resources. In addition, in terms of prevention of global worming, a great amount of CO_2 is needed to produce a raw material of thermo-setting resin form crude oil. In order to accomplish the sustainable society, the material recycling method including the resin is highly requested to reduce the amount of dumping wastes, to utilize exhaustible oil resources effectively, and to prevent global worming.
Several approaches such as cement kiln method[1)], ester exchange reaction methods using glycol[2)] or benzyl alcohol[3)] were tried to recycle FRP. However, there is no method to achieve recycling of FRP including the thermo-setting resin.
We reported the chemical recycling of FRP using subcritical water.[4)] Subcritical water has an advantage over other chemical recycling approaches due to its ion product and dielectric constant.[5)] It can break ester bond of the thermosetting resin much more effectively.[6)] Fig.1 shows a concept of chemical recycling of the thermosetting polyester resin using subcritical water. The thermosetting resin was cross-linked polymer of styrene as a cross-linking agent and unsaturated polyester (UP). The UP is condensation polymer consisting glycol and organic acid generally. They are condensed to make ester bonds with dehydration. After hot press curing of the UP resin, the lattice structure with styrene bridge is constructed. The ester bonds of the thermosetting resin are hydrolyzed ideally using subcritical water on the reaction condition at 230C, 2.8MPa, for 2 hours with NaOH. After the reaction, the thermosetting resin was dissolved. Raw resin materials of UP such as glycol and styrene-sodium fumarate copolymer are existed in the reaction liquid. Glycol is recovered and mixed with new raw resin materials to produce recycled UP resin. After acidification, styrene-fumaric acid copolymer (SFC) is separated out in the reaction liquid. The SFC has a similar molecular structure to a low profile additive (LPA). It is a very high value-added additive to control shrinkage during hot press forming of FRP. Its market price is from 5 to 10 times more expensive than that of styrene monomer whish is raw material of the SFC. The SFC is separated from the reaction liquid and modified to generate shrinkage control effect. It can be used in FRP as recycled LPA.[7)]
It proposes *“Enhanced Recycling”* of the thermosetting resin.

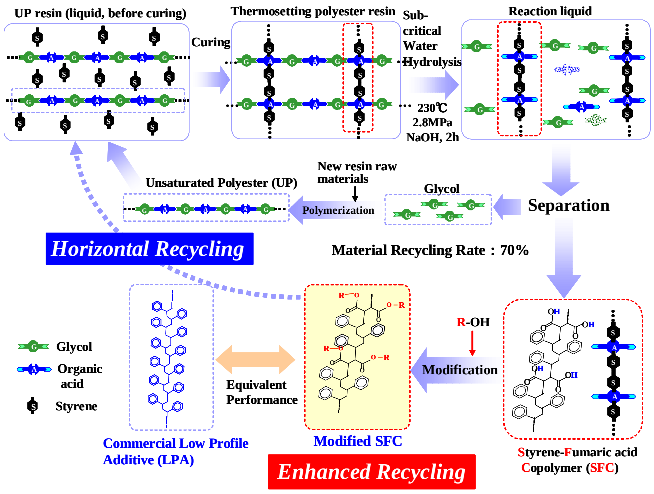

Fig.1 A concept of chemical recycling of the thermosetting polyester resin using subcritical water

Fig.2 shows a process flow of *"Enhanced and Horizontal Recycling of FRP Using Subcritical Water"*. After subcritical water hydrolysis of FRP, inorganic materials such as glass fiber and inorganic filler can be separated from the reaction slurry. Glycol and the SFC are separated from the reaction liquid. Glycol is recycled to UP resin after mixing with new raw resin materials. The SFC is modified to be enhanced to become recycled LPA. Recovered inorganic materials can be used as recycled inorganic filler. Recycled UP resin, LPA, inorganic filler are mixed with new raw materials to produced SMC (Sheet Molding Compound) sheet. It is hot press cured to produce recycled FRP. It proposes *"Horizontal Recycling"* of FRP including thermosetting resin.

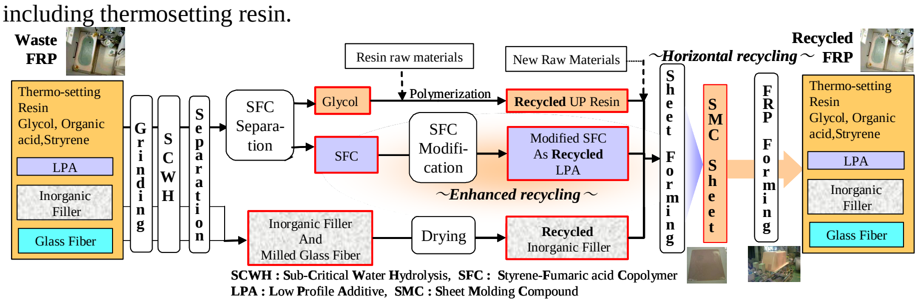

Fig.2 A process flow of *"Enhanced and Horizontal Recycling of FRP Using Subcritical Water"*

Several subjects are examined in this approach. The SFC is very difficult to be separated from the reaction liquid due to its high very hydrophilicity. Water content in the SFC after separation using conventional filter press method was 90%. The SFC:Water was 1:9. Water content should be minimized for the next step, modification process. In enhanced recycling of the SFC, compatibility with styrene is required to generate shrinkage control effect Therefore, the SFC has to be modified to be hydrophobic. In order to solve those subjects, SFC separation and modification processes using 1-octanol were examined. The modified SFC was mixed with a commercial LPA to produce FRP sample board and tested.

To scale up this FRP recycling process, bench tests of subcritical water hydrolysis and inorganic materials separation were conducted.[4,8] A pilot plant of subcritical water hydrolysis was built for further scale up. It can treat 400kg of FRP per operation, 10 times more than that of the bench plant. It has a reaction vessel with effective volume of 2.4 m^3. The maximum temperature and pressure is 260C, 5.5MPa. Pilot test was conducted with inorganic materials separation pilot plant. Bench plants of the SFC separation and modification processes using 1-octanol were also built and tested.

2. Experiment

In SFC separation experiment, reaction liquid after inorganic materials separation from reaction slurry was used. The reaction slurry was obtained from FRP subcritical water hydrolysis on the reaction condition at 230C, 2.8MPa, for 2 hours. FRP: 0.8 mo/L NaOH solution was 1:4. Firstly, H_2SO_4 was added to the reaction liquid to separate out the SFC. Then, 1-octanol was added and stirred at 90C for 1 hour to extract the SFC from the reaction liquid to 1-octanol. After extraction, it is cooled and left for 1 hour to separate 1-octanol extracting the SFC and aqueous solution. They were separated by liquid-liquid extraction.

In SFC modification, H_2SO_4 was added to 1-octanol extracting the SFC as a modification catalyst. The modification reaction was conducted at 175C for 17 hours. SFC:1-octanol: H_2SO_4 was 1:7.5:0.08. After modification reaction, water was added to remove impurities such as H_2SO_4. After purification, 1-octanol containing the modified SFC and aqueous solution containing H_2SO_4 was separated as same as SFC separation process.

The modified SFC was mixed with a commercial LPA to produce FRP sample board. Shrinking ratio was measured. Hot water durability test (JIS-K-6911) was also conducted. Appearance and color change of the FRP sample board after dipping in 90C hot water for 120 hours were evaluated and compared with a FRP sample board using the commercial LPA.

Pilot tests of grinding ~ subcritical water hydrolysis ~ inorganic materials separation processes were conducted using FRP bathtub manufacturing waste. (700mm×700mm) It is grinded to the level of less than 10 mm mesh under. They were supplied with NaOH solution to subcritical water hydrolysis pilot plant. Subcritical water hydrolysis was conducted on the reaction condition at 230C, 2.8MPa, for 2 hours. The reaction slurry was discharged from the reaction vessel and supplied to filter press type inorganic materials separation pilot plant. Inorganic materials such as inorganic filler and grinded glass fiber were separated from the reaction slurry. The reaction liquid filtered was used in bench tests of SFC separation and modification processes.

3. Results and Discussions

In modification of the SFC, it was found that esterification using 1-octanol was effective.[9)] We focused that 1-octanol has higher solubility for the SFC than water. Fig.3 shows the experiment result of the SFC separation and modification processes using 1-octanol. H_2SO_4 was added to the reaction liquid containing styrene-sodium fumarate copolymer to separate out the SFC. They became clouded as shown in Fig.3. 1-octanol was added to the white water. They were stirred at 90C for 1 hour to extract the SFC to 1-octano. After extraction, it was cooled and left at 25C for 1 hour. 1-octanol extracting the SFC and aqueous solution were separated as shown in Fig.3. They were separated by liquid-liquid extraction. Almost 100% of the SFC in the white water was extracted to 1-octanol. The SFC:water was 1:0.25. Water content with the SFC was drastically reduced against the conventional method.

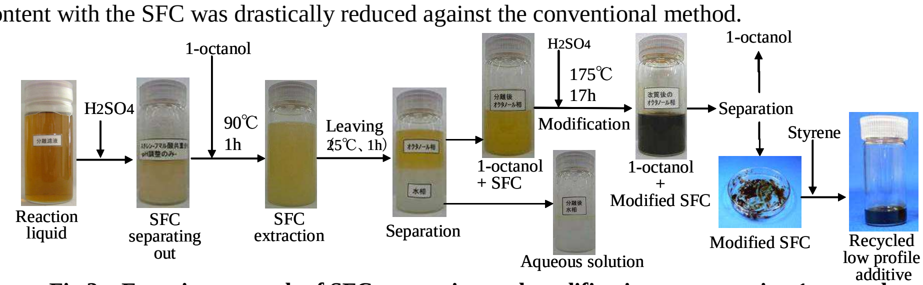

Fig.3 Experiment result of SFC separation and modification process using 1-octanol

Fig. 4 shows a reaction formula of esterification reaction of the SFC using 1-octanol. H_2SO_4 as a catalyst was added to 1-octanol extracting the SFC and esterification reaction was conducted on the reaction condition at 175C for 17 hours. The modified SFC was obtained as shown in Fig.3. Its color was black. Almost 100% of the SFC in 1-octanol was modified. After modification reaction, water was added to the reaction liquid. They were stirred at 80C for 1 hour to remove impurities such as H_2SO_4. 90% of H_2SO_4 was removed. After purification, 1-octanol and aqueous solution were separated as the SFC separation process. The black modified SFC was separated from 1-octanol as shown in Fig.3. Styrene was added to the modified SFC to verify the styrene compatibility. It was a recycled LPA.

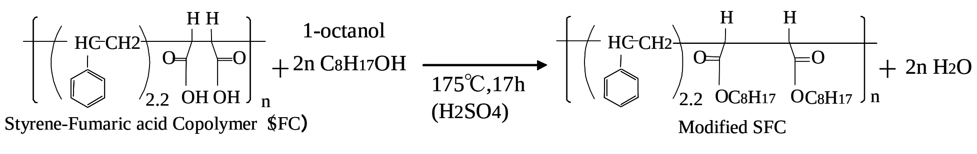

Fig.4 SFC estrification reaction formula using 1-octanol

The modified SFC was mixed with a commercial LPA to produce FRP sample boards and tested. Table 1 shows evaluation results. The modified SFC showed almost equivalent shrinkage control effect and hot water durability to the commercial LPA. It suggested that the modified SFC was enhanced to become from 5 to 10 times more expensive material. It verified the possibility of *"enhanced recycling."*

Table 1. Evaluation result of the modified SFC

		Modified SFC／Commercial LPA				Blank (No LPA)
		0／100 (Reference)	**10**／90	**30**／70	**50**／50	
Shrinkage ratio (%)		0.21	0.20	0.20	0.21	0.32
Hot water durability	Appearance	—	○	○	○	—
	⊿E	—	○	○	○	—

SFC:Styrene-fumaric acid copolymer, LPA:Low profile additive,
⊿E:Color change, ○ :Equivalent to commercial LPA

Fig.5 shows a subcritical water hydrolysis pilot plant. FRP manufacturing waste was grinded to less than 10 mm under mesh level by the grinding pilot plant. The grinded FRP samples were fed to a grinded FRP tank at the third floor. Fig. 6 shows a reaction vessel of the subcritical water hydrolysis. The grinded FRP samples were supplied with NaOH solution to the reaction vessel. The subcritical water hydrolysis was conduced on the reaction condition at 230C, 2.8MPa, for 2 hours.

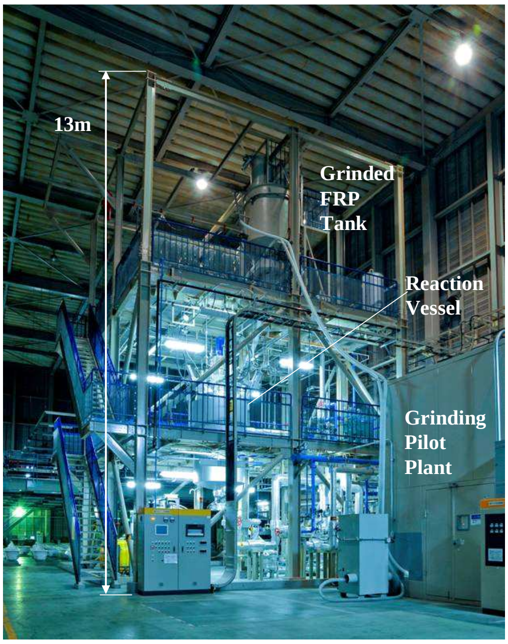

Fig.5 A pilot plant of subcritical water hydrolysis pilot plant. **Fig. 6 Reaction vessel.**

Pilot test results of subcritical water hydrolysis process are shown in Table 2 with test results of reaction pipe, reaction pod, and bench plant for comparison. Conversion, SFC generation rate, and glycol generation rate of the pilot test was 81%, 83%, and 62% respectively. In spite of 100,000 times scale-up, pilot test demonstrated successfully with more than 90% performance of that of reaction pipe test.

Fig.7 shows an inorganic materials separation pilot plant. Reaction slurry from the subcritical water hydrolysis pilot plant was supplied to the pilot plant. Inorganic materials were filtered and separated from the reaction slurry. Recovery rate of inorganic materials was 95% as same as bench test result.

Fig. 8 shows a pilot test result of grinding ~ subcritical water hydrolysis ~ inorganic materials separation. Gypseous inorganic materials filtered was scraped by hand as shown in Fig.8.

Fig.9 shows a SFC separation process bench plant. Reaction liquid separated from reaction slurry by the inorganic materials separation pilot plant was supplied to a reaction liquid tank. It was supplied to extraction vessel and heated at 90C for 1 hour after addition of H_2SO_4 and 1-octanol to extract the SFC. After extraction, they were supplied to separation vessel and cooled and left at 25C for 1 hour to separate 1-octanol extracting the SFC and aqueous solution.

Table 2 Pilot test result of subcritical water hydrolysis

	Effective volume	Capacity per operation	Conversion	SFC generation rate	Glycol generation rate
Reaction pipe	20cc	4g	87%	92%	69%
Reaction pod	3L	0.6kg	84%	93%	65%
Bench plant	200L	40kg	85%	94%	57%
Pilot plant	2.4m^3	400kg	81%	83%	62%

SFC :Styrene-fumaric acid copolymer

Fig.7 Inorganic materials separation pilot plant

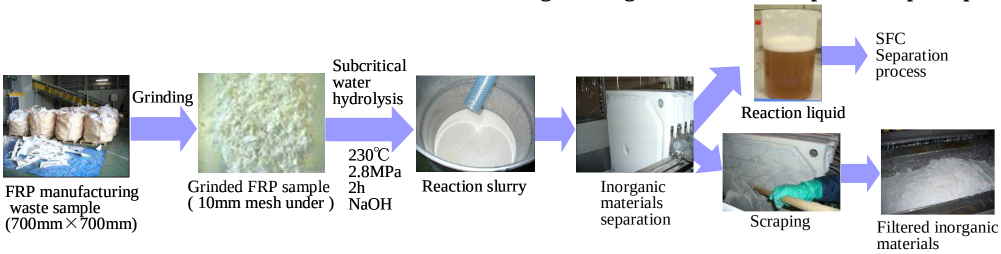

Fig.8 Pilot test result of grinding ~ subcritical water hydrolysis ~ inorganic materials separation

Fig.10 shows a SFC modification bench plant. 1-octanol extracting the SFC separated by SFC separation bench plant was supplied to a modification reaction vessel with H_2SO_4. The SFC was esterified with 1-octanol on the reaction condition at 175C for 17 hours and stored in a modification reaction liquid tank. The modification reaction liquid containing the modified SFC was supplied to a purification vessel with water and heated at 80C for 1 hour to remove impurities such as H_2SO_4. After purification, the modification reaction liquid was separated as same as SFC separation process.

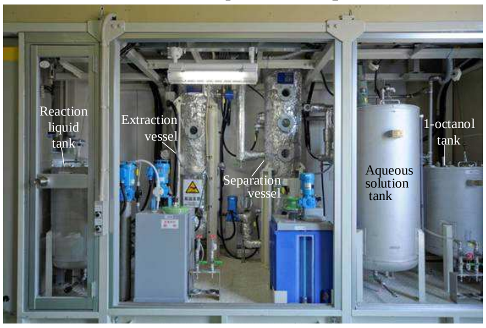

Fig.9 SFC separation process bench plant

Table 3 Bench test result of SFC separation and modification processes

	Volume	Scale-up magnification	Beaker scale test result	Bench scale test result
SFC separation process	150L	×300	100%*	97%*
SFC modification process	7L	× 10	100%**	85%**
Purification process	60L	× 60	90%***	85%***

* SFC extraction rate, ** Conversion, *** Purification rate

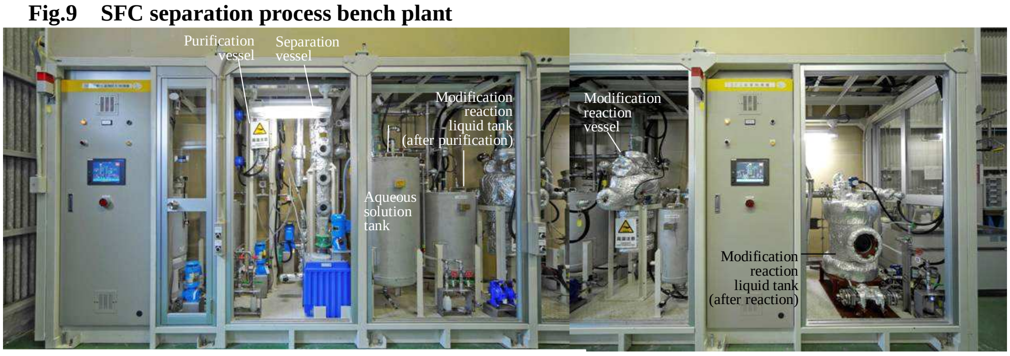

Fig.10 SFC modification process bench plant

Bench test results of SFC separation and modification processes are shown in Table 3 with beaker test results for comparison. In SFC separation process, SFC extraction rate of beaker test and bench test were 100% and 95%, respectively. In SFC modification process, conversion of beaker test and bench test were

100% and 85%, respectively. In purification process, purification rate of beaker test and bench test were 90% and 85%. respectively. Bench tests of each processes also demonstrated successfully with more than 85% performance of that of beaker test.

4. Conclusion and future prospect

In enhanced and horizontal recycling of FRP using subcritical water, SFC separation and modification processes using 1-octanol was examined. Almost 100% of the SFC was extracted from reaction liquid to 1-octanol with extremely less water than conventional method. The SFC extracted in 1-octanol was esterified with H_2SO_4 on the reaction condition at 175C for 17 hours. Modified SFC was obtained with almost 100% conversion. The modified SFC mixed with a commercial LPA was evaluated. It showed almost equivalent shrinkage control effect and hot water durability to the commercial LPA. It verified the possibility of from 5 to 10 times *"enhanced recycling"* comparing with market price of its raw materials, styrene.

Pilot plants of subcritical water hydrolysis and inorganic materials separation processes were built and tested. The subcritical water hydrolysis pilot plant has a capacity of 400kg FRP per operation. It demonstrated successfully with more than 90% performance of that of reaction pipe test. Inorganic materials separation pilot plant also demonstrated successfully with same recovery rate of inorganic materials as bench plant. Bench plants of SFC separation and modification processes were also built and tested. It also demonstrated successfully with more than 85% performance of that of beaker test for each processes.

We are planning to start to recycle 200 tons of FRP manufacturing waste annually in 2012 after the following research and development. Pilot plant of the SFC separation and modification processes and an inorganic materials drying process will be completed to be built until the beginning of 2010. We are now doing quality evaluation of recyclate obtained from this recycling process to verify *"enhanced and horizontal recycling of FRP."* We are also trying to apply this technology for various kinds of other FRP products, such as tanks, boats, automobile parts, and so on. In addition, exploring new application of the SFC for other high value-added materials has been started.

Acknowledgement

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REFERENCES

[1] Y.Shoji, "Current Status for Wasted FRP Recycling Business", Lecture summaries of 50th FRP CON-EX 2004, 51(2005)

[2] S.Kubota et.al, The 1st International Symposium on Feedstock Recycling of Plastics, pp.247 (1999) Sendai

[3] K.Maekawa et.al, "FRP Recycling Technology Invalving Depolymerization of Unsaturated Polyester Under Ordinary Pressure ", Lecture summaries of 50th FRP CON-EX 2004, 37(2005)

[4] T. Nakagawa et al, ""FRP Recycling Technology Using Sub-critical Water Hydrolysis", Abstracts of 8^{th} International Symposium on Supercritical Fluids, 136 (2006)

[5] J.W.Tester et.al, Asc Symp.Ser., 518, and 35 (1993)

[6] T.Nakagawa et.al, "FRP Recycling Technology Using Subcritical Water Hydrolysis", Network Polymer, Vol.27, No.2, pp.28 (2006)

[7] T.Yoshimura et.al, "Upgrade Recycling Technology of FRP Sub-critical Water Hydrolysate to Low Profile Additive", Network Polymer, Vol.28, No.3,.27 (2007)

[8] T.Nakagawa et.al, "FRP Recycling Technology Using Subcritical Water Hydrolysis", Proceeding of the Network Polymer Symposium Japan 2005, 129 (2005)

[9] T.Nakagawa rt al. "Chemical Recycling of FRP Using Subcritical Water (3)", Proceeding of the SCEJ 73^{rd} Annual Meeting.,493 (2008)