

Study on Recycling Thermosetting Polyester Resin into
High Performance Additives Using Subcritical Water

Takaharu Nakagawa

Study on Recycling Thermosetting Polyester Resin into
High Performance Additives Using Subcritical Water

Takaharu Nakagawa

Table of Contents

1. Introduction	p.1
1.1. Background	
1.2. Previous study and aim of this study	
1.3. Concept of this study and actual work	
2. Subcritical hydrolysis of thermosetting polyester resin	p.12
2.1. Fundamental verification	
2.1.1. Introduction	
2.1.2. Materials and methods	
2.1.3. Results and discussion	
2.1.4. Conclusions	
2.2. Functional mechanism of alkali catalyst and optimization of reaction conditions and catalysts	p.22
2.2.1. Introduction	
2.2.2. Materials and methods	
2.2.3. Results and discussion	
2.2.4. Conclusions	
2.3. Evaluation of subcritical hydrolysis process for various FRPs	p.39
2.3.1. Introduction	
2.3.2. Materials and methods	
2.3.3. Results and discussion	
2.3.4. Conclusions	
2.4. Overall conclusions (Subcritical hydrolysis of thermosetting polyester resin)	p.47

3. Application of styrene-fumaric acid copolymer (SFC)	p.49
3.1 Introduction	
3.2. Low profile additive (LPA)	p.51
3.2.1. Introduction	
3.2.2. Materials and methods	
3.2.3. Results and discussion	
3.2.4. Conclusions	
3.3. Aqueous agent	p.65
3.3.1. Introduction	
3.3.2. Materials and methods	
3.3.3. Results and discussion	
3.3.4. Conclusions	
3.4. Compatibilizing agent for polymer alloy	p.77
3.4.1. Introduction	
3.4.2. Materials and methods	
3.4.3. Results and discussion	
3.4.4. Conclusions	
3.5. Overall conclusions	p.110
(Application of styrene-fumaric acid copolymer (SFC))	
4. Overall conclusions	p.112
(Study on Recycling Thermosetting Polyester Resin into High Performance Additives Using Subcritical Water)	
Acknowledgements	p.116
References	p.117
Research achievements	p.122

1. Introduction

1.1. Background

Thermosetting polyester resins are generally used in fiber reinforced plastics (FRP). Unsaturated polyester (UP) resin, glass fiber, and inorganic filler such as CaCO_3 are cured by hot press machine to produce FRP. UP resin became thermosetting polyester resin. FRP is widely applied to bathtubs in Japan and also various products such as boats, various tanks, corrugated panels, automobile parts, motors, and so on in worldwide as shown in Fig.1-1.

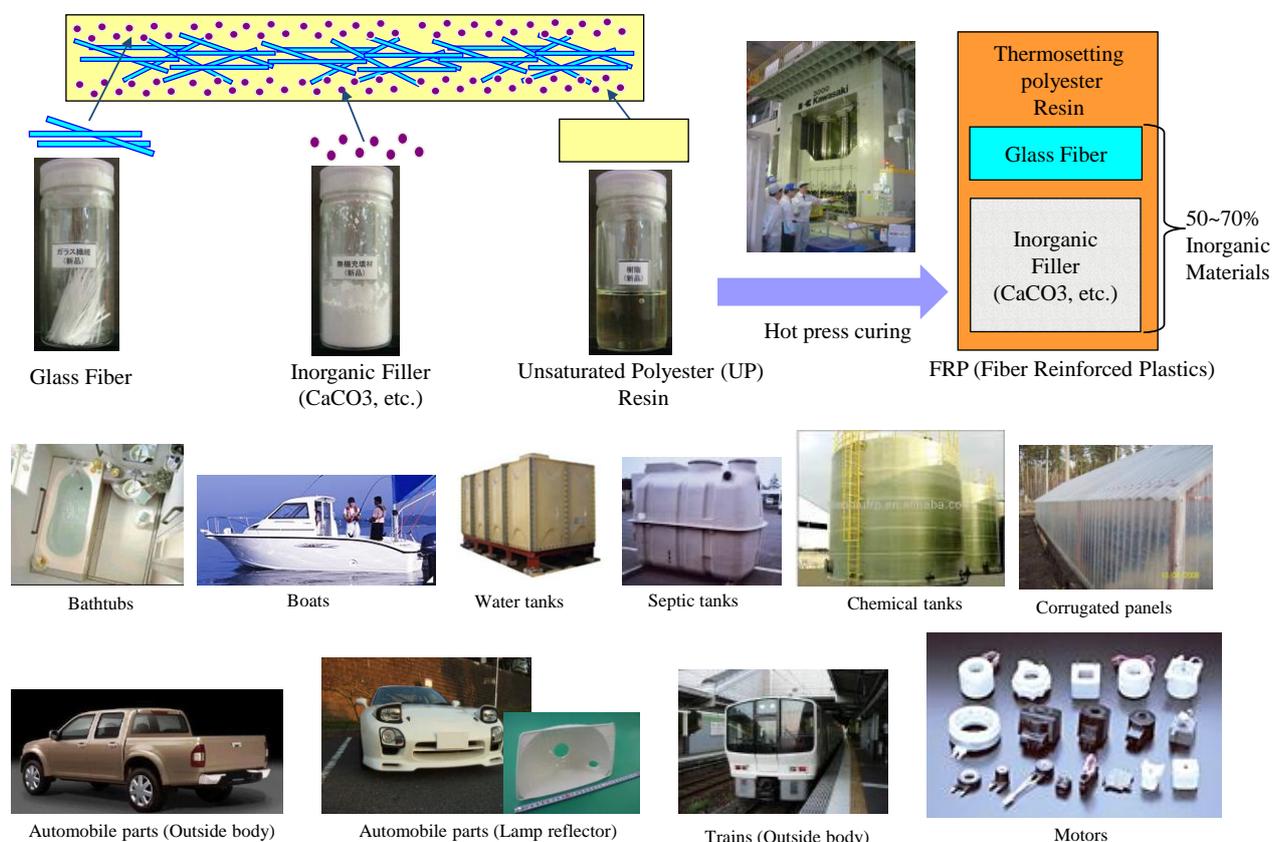


Fig.1-1 FRP composition and various applied products

Figure 1-2 shows a process from resin raw materials of unsaturated polyester (UP) to form thermosetting polyester resin. Thermosetting polyester resin is obtained by crosslinking unsaturated polyester (UP) polymer with styrene. The UP consists of glycol and carboxylic acid such as fumaric acid and ortho- or isophthalic acid. Maleic anhydride is used as the UP raw material, which isomerizes to fumaric acid during polyesterification [1]. Styrene is added to the UP to produce UP resin which is very

viscous liquid. The UP resin is mixed with glass fiber and inorganic filler such as CaCO_3 and then hot press cured. During curing process, styrene reacts with the fumaric acid of the UP to create a styrene chain and three-dimensional resin matrix is developed shown in **Fig.1-2**.

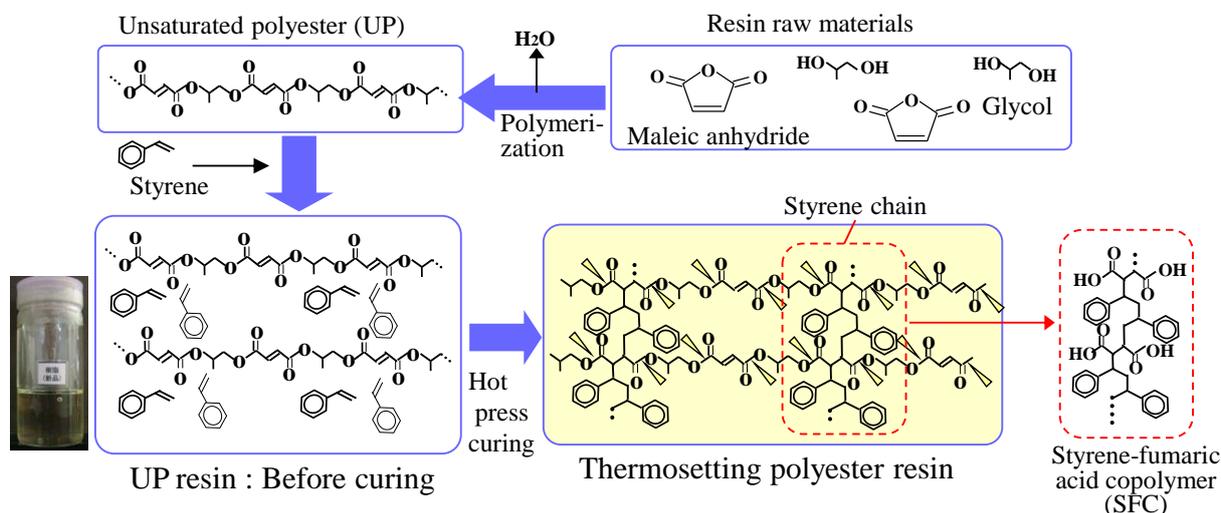


Fig. 1-2 Process of producing thermosetting polyester resin

Thermosetting resins cannot be re-molded like thermoplastic resins. PET is same polyester resin with no styrene bridge. When it is heated, alignment of each PET polymer can be slipped. Therefore it can be re-molded. On the other hand, in the case of thermosetting polyester resin, each alignment is fixed by styrene chain. Therefore, it cannot be re-molded. In addition, high content of inorganic material in FRP creates difficulties in incineration. Therefore, most FRPs have been landfilled. Environmental legislation such as the EU-directives also requires true material recycling of FRP. However, no chemical recycling technology of thermosetting polyester resins into raw materials for resins or other organic compounds has been commercialized.

Chemical recycling of thermosetting polyester resins is worth considering not only for a view point of horizontal recycling into resin raw material, but also for enhancing recycling into functional polymer. Styrene chain has a molecular structure of functional polymer. If all ester bonds trapping the styrene chain are hydrolyzed, styrene-fumaric acid copolymer (SFC) should be obtained as described in **Fig.1-2**. The molecular structure of SFC is similar to that of styrene maleic anhydride copolymer (SMA). SMA is a functional polymer and is applied to high performance additives such as dispersing agent, detergent builder, surface sizing agent for paper, emulsion polymerization, overprint varnish, inks, textile/leather treatment, carpet cleaners, polymer modification,

adhesives, and so on [2, 3]. Moreover, the styrene-maleic acid copolymer could become more expensive due to a lack of benzene according to the demand-supply gap of benzene, the raw material of styrene, which cannot be produced from shale gas [4]. Dicarboxylic acids of the SFC are assumed to have higher reactivity than anhydrides of the SMA. However, copolymer of dicarboxylic acid and styrene does not exist in the market due to difficulty of polymerization reaction. Therefore, the SFC is considered to have a unique molecular structure and a possibility of generating new function. It is expected that the new function of the SFC creates innovative new materials or products.

The SFC now existing in thermosetting polyester resin waste landfilled is a precious functional polymer resources described above. It contains styrene which is prospected to become more expensive in future due to the gap of demand and supply. Chemical recycling of thermosetting polyester resin to obtain the SFC and applying it to high performance additives should be significant outcome.

1.2. Previous studies and aim of this study

There are various strategies for recycling FRP. In the grinding method, mechanically ground FRP is applied as inorganic filler in concrete, cement components, plastic, etc. [5-7]. In the thermolysis method, glass fiber and/or inorganic filler are recovered after pyrolysis or combustion [8-11]. In these approaches, thermosetting resin is not recovered as precursor for new resins.

Various chemical recycling approaches of FRP such as solvolysis have also been studied. Diethyleneglycol monomethylether (DGMM) and benzyl alcohol (BZA) [12], glycol [13-15], amino alcohols, and polyamines [16, 17] were investigated. Supercritical methanol was also applied to recover dimethyl phthalate (DMP) [18-22].

Water has also been applied as an agent for chemical recycling of FRP. Superheated steam [23] and subcritical water [24, 25] have been used to recover glass fibers. Oliveux et al. used subcritical water to recover propylene glycol and phthalic acid [26, 27]. Suyama et al. also used subcritical water to recover hydroxyl compounds having a long alkyl chain and alkyl amines [28, 29]. The author reported that subcritical hydrolysis of thermosetting polyester resin at 360°C, 18.7 MPa. Only glycols and fumaric acids were recovered [30]. In the reaction product liquid, 60% of initial glycol and 23% of initial fumaric acid were observed. However, their total weight was only 20% of the initial thermosetting polyester resin. Moreover, there were many impurities. It was impossible to separate them. Therefore, they were unable to recycle to resin raw materials although existing in the reaction product liquid. [30]

In some of the above chemical recycling approaches, material recycling of the resin

was demonstrated. However, all of them are horizontal recycling methods. Horizontal recycling method recovers raw materials from the resin waste and recycle them to the new resin as raw materials. One example is recycling from PET bottle to PET bottle. In horizontal recycling of thermosetting polyester resins, resin raw materials such as glycol or phthalic acid or polystyrene derivative were recovered and re-crosslink them with new resin raw materials. There has been no method to recover SFC as a functional polymer from the thermosetting polyester resin waste and apply it to high performance additives. This approach has a potential to clarify the unknown molecular structure of the thermosetting polyester resin. It is expected to improve the property.

The main aims of this study are as follows.

- i) The first aim is to establish the technology which can efficiently recycle thermosetting polyester resin to recover resin raw materials and the SFC as functional polymer with high yield and high quality. In this process, it is also planned to clarify the unknown molecular structure of the thermosetting polyester resin.
- ii) The second aim is to verify the possibility for the SFC applying to high performance additives. It should be not only for substituting existing commercial additives but also for creating new additives. In addition, it is also planned to investigate the mechanism of function to create a new concept of high performance additives and to explore the possibility for new innovative materials or products utilizing them.

1.3 Concept of this study and actual works conducted

1.3.1 Concept of this study

Concept of recycling thermosetting polyester resins using subcritical water is described in **Fig.1-3**.

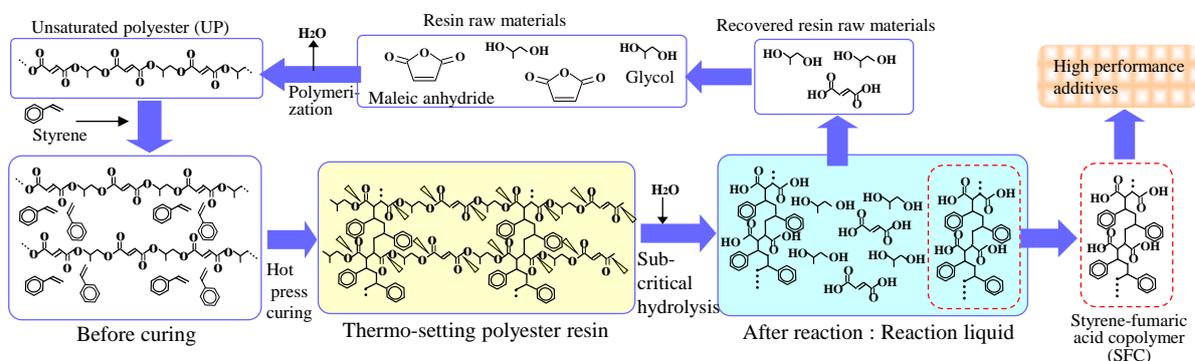


Fig. 1-3 Concept of recycling thermosetting polyester resins using subcritical water

In order to recover the SFC, all ester bonds connecting to the SFC should be broken. However, it is almost impossible for water on the condition of temperature less than 100°C. Then, we focused subcritical water. **Figure 1-4** shows phase diagram of water. Critical point of water is at a temperature of 374°C and at a pressure of 22.1 MPa. Water in the area of temperature above 374°C and pressure above 22.1 MPa as shown in **Fig. 1-4** is called “supercritical water.” The supercritical water has extremely high oxidation reactivity. It enables to decompose most of organic materials completely and no organic materials can be recovered. Therefore, it is not suitable for recycling organic materials. Supercritical water treatment plant requires extremely high pressure resistance and corrosion resistance. High corrosive-resistance alloy metal such as Hastelloy is needed inside the vessel. Hence, application of supercritical water oxidation is limited for the hazardous materials which other methods cannot decompose such as poly chlorinated biphenyl (PCB).

“Subcritical water” is high temperature and high pressure liquid water. The temperature of subcritical water should be less than the critical temperature of 374°C. The lowest temperature boundary is not defined clearly. The pressure should be equal to or above the saturated vapor pressure at given temperature as shown in **Fig. 1-4**.

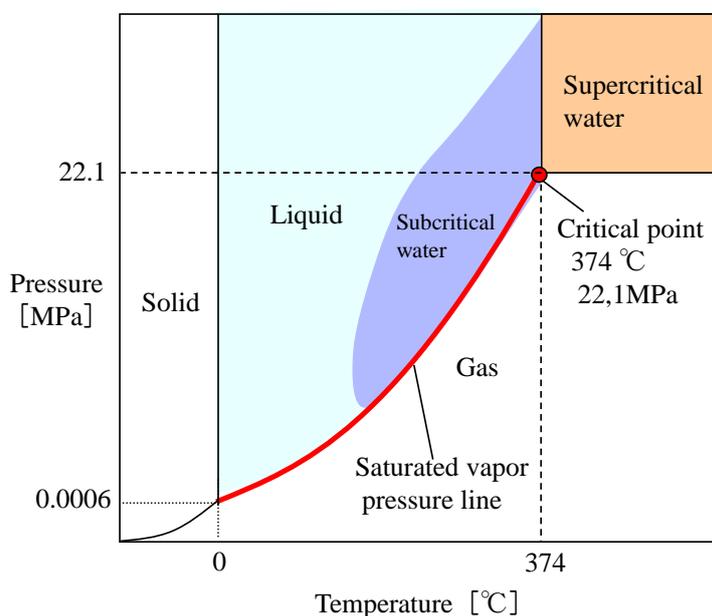


Fig. 1-4 Phase diagram of water

Figure 1-5 shows ion product and dielectric constant of water at temperature of a range from 0°C to 800°C. Subcritical water is well known to have significant hydrolysis reactivity [31]. Ion product (K_w) of subcritical water at the temperature above 200°C is

approximately a range from 100 to 1,000 times greater than that of normal water. Greater ion product should have an advantage for hydrolysis reaction. Dielectric constant (ϵ) of water decreases with increasing temperature. Dielectric constant of subcritical water at the temperature above 200°C is equivalent to that of organic solvent. It indicates the subcritical water should have sufficient affinity with organic materials such as resin. Therefore, it has an advantage over other chemical recycling approaches in terms of breaking ester bonds much more effectively. On the other hand, ion product drastically decreases at the critical temperature. It is approximately 1/10,000 and decreases further with increasing temperature. Therefore, it is considered that hydrolysis cannot be dominant in supercritical water.

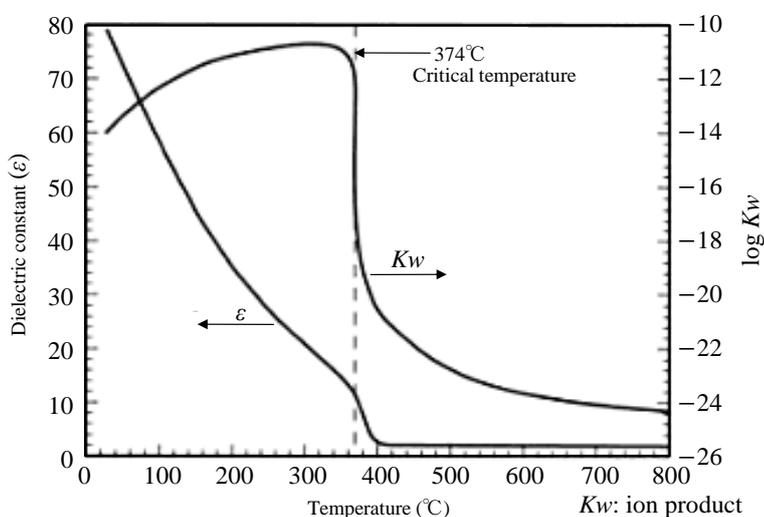


Fig. 1-5 Ion product and dielectric constant of water

Significant hydrolysis reactivity of subcritical water was applied to break ester bonds of thermosetting polyester resin to recover resin raw materials such as glycol and fumaric acid and styrene chain as the SFC. Resin raw materials are horizontal recycling to UP with new resin raw materials. SFC is recovered as functional polymer then is enhanced recycled into high performance additives.

1.3.2 Subcritical hydrolysis

In the study of subcritical hydrolysis of thermosetting polyester resin, firstly, the fundamental verification of the reaction optimization hypothesis was conducted. The thermosetting polyester resin sample based on the resin composition for FRP bathtub was used in the experiments. After the fundamental verification, functional mechanism of alkali was investigated. Then, the practical optimization of reaction conditions and alkali catalysts were conducted using our manufacturing waste of FRP bathtub as shown

in **Fig. 1-6**. They are defective products after hot press curing and treated by industry waste disposer. Based on the experimental data, the reaction mechanism and the molecular structure of the thermosetting polyester resin were investigated.



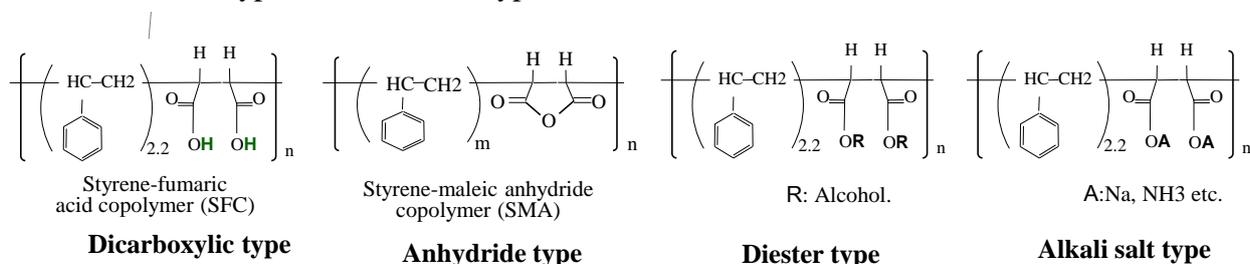
Fig. 1-6 FRP bathtub manufacturing waste.

In addition, the verification of the possibility of this method applying to other FRPs than our bathtubs, such as bathtubs of other manufacturers, boats, tanks, automobile parts, and so on was conducted. The reactivity and yield of the SFC for various FRPs were evaluated. The molecular structure of SFC obtained from different FRP was also analyzed directly by GPC and NMR. It represents the molecular structure information of the styrene chain of various FRPs.

The molecular structure of the thermosetting polyester resin including the styrene chain was unknown since the styrene chain could not be directly extracted. The distance between the styrene chain and the ratio of styrene chain and polyester chain are consider very valuable and useful information to design the thermosetting polyester resin. To clarify the molecular structure should be of great significance in the industry of the thermosetting polyester resin and its applied products since it is expected to contribute to improve the mechanical property.

1.3.3 Application of styrene-fumaric acid copolymer (SFC)

In the study of application of SFC obtained, it was verified the possibility of the SFC applying to various high performance additives. SFC has diester type, alkali salt solution type, and dicarboxylic type. **Scheme 1-1** shows molecular formula of SFC, SMA, diester type, and alkali salt type.



Scheme 1-1 Molecular formula of SFC, SMA, Diester type, Alkali salt type

Candidates of application were selected for each type. SFC samples of each type were evaluated with commercial additives to be compared.

Firstly, in the application of diester type, low profile additive (LPA) for FRP forming was selected. The LPA is a key additive to determine product quality such as surface appearance of FRP with controlling shrinkage during curing process. The effectiveness of the LPA is shown in **Fig.1-7**. Without LPA, the FRP shrank with corrugation and crack after curing process. The LPA produces voids during curing process to compensate volume shrinkage to prevent corrugation and crack generation as shown in **Fig.1-7**. In commercial LPA, polystyrene is used mainly. Styrene skeleton of SFC was expected to create shrinkage control performance.

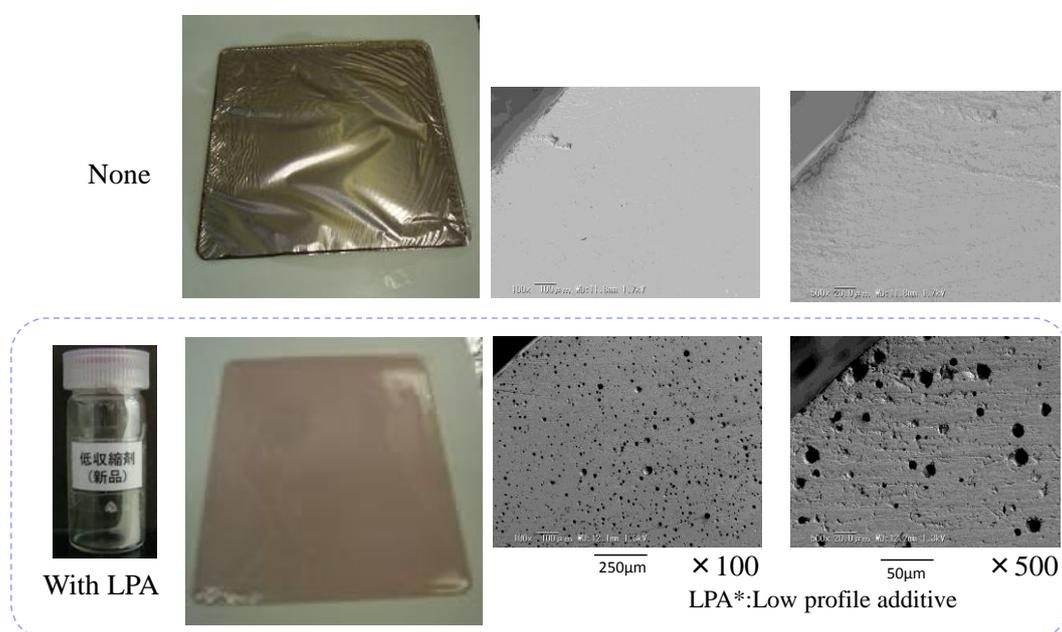


Fig. 1-7 Low profile additive (LPA) for FRP forming

Secondly, in the application of alkali salt solution type for aqueous agent was examined. There are various aqueous agent applications. Among them, dispersing agent, detergent builder, and surface sizing agent for papers were selected. They should have hydrophobic region and hydrophilic region. Alkali salt of SFC has styrene skeleton as hydrophobic region and alkali salt of dicarboxylic acid as hydrophilic region. They were expected to contribute to create performance as aqueous agent.

Dispersing agent contributes to promote the dispersion of powder uniformly with preventing agglomeration. **Figure 1-8** shows an example of dispersing agent effect for carbon black in coating material. Without dispersing agent, many agglomerations were observed. The dispersing agent contributes to prevent the agglomeration [32].

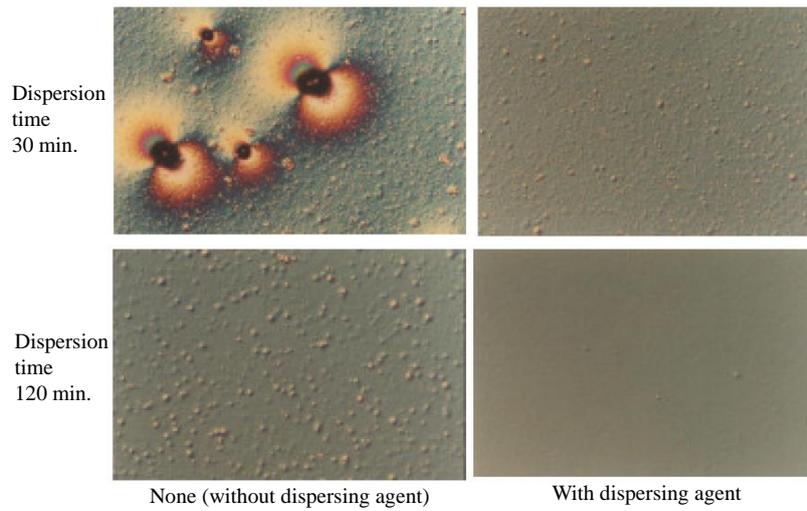


Fig. 1-8 Example of dispersing agent for carbon black [32]

Detergent builder is auxiliary agent for detergent to prevent cleaning performance due to calcium ion, Ca^{2+} and pH change. The detergent builder is required Ca^{2+} trapping ability and alkali buffering capacity mainly.

Surface sizing agent is used to prevent bleeding of ink on the paper surface. **Figure 1-9** shows an example of effect for surface sizing agent [33]. The surface sizing agent contributes to prevent the bleeding to make the border clear.

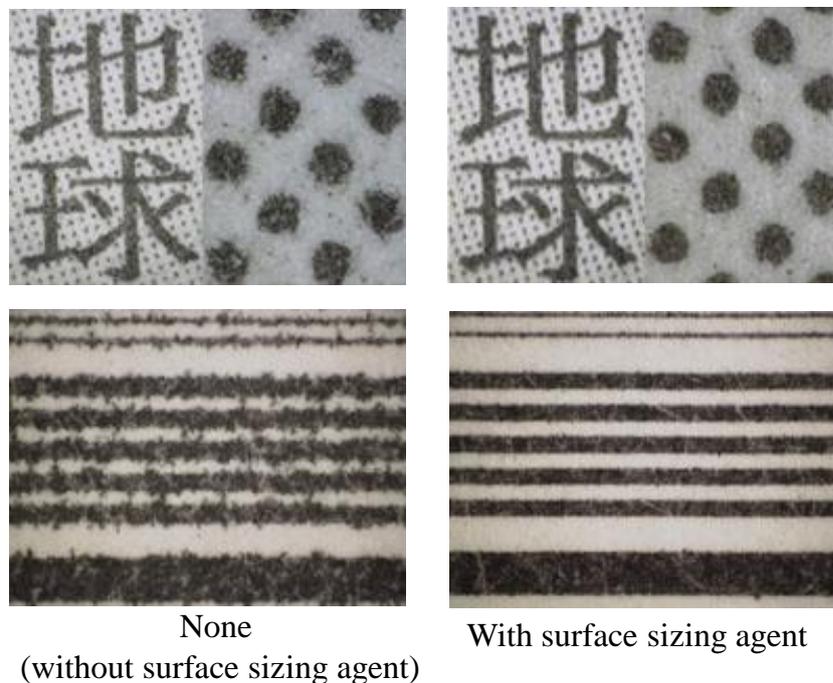


Fig. 1-9 Example of surface sizing agent [33]

Third application of SFC is dicarboxylic type, SFC itself. Compatibilizing agent was selected as a candidate for application of SFC. Polymer alloy has been attracted attention to improve the resin property since improvements of the original resins should be considered to have limitations. Polymer alloy is expected to break through the limitations to create innovative polymer and its applied products. In polymer alloy of two immiscible polymers, compatibilizing agent should be essential and it is the most important key technology [34-37]. **Figure 1-10** shows an example of compatibilizing agent for polymer alloy of immiscible polymer A and B [37]. In general, block polymer or graft polymer is used as compatibilizing agent. It has two regions which are compatible with polymer A and B. Their each region grasp polymer A or B to show anchoring effect to increase compatibility for both polymers.

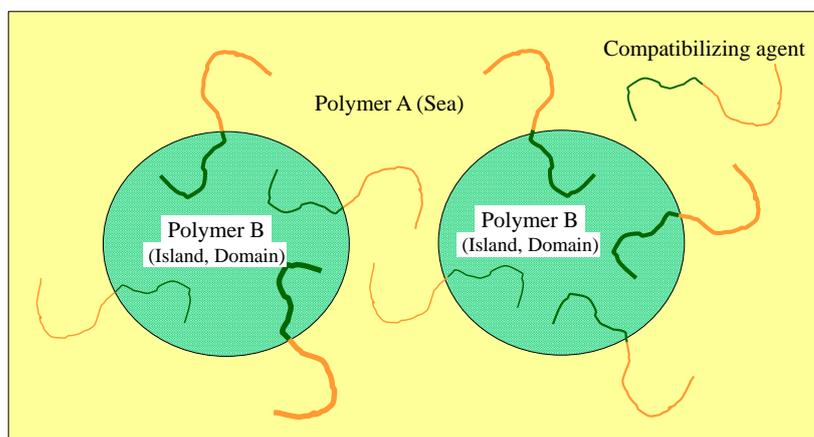


Fig. 1-10 Example of compatibilizing agent for polymer alloy[37]

In polymer alloy, reactive processing for immiscible polymers is expected to create new innovative materials [36-38]. Reactive processing requires reactive compatibilizing agent which reacts with one polymer during kneading process. SFC has styrene skeleton and carboxylic acid which are hydrolyzed from polyester chain of thermosetting polyester resin. Carboxylic acid can easily react with OH group of polymers. Therefore it was assumed that SFC had a potential to be applied to reactive compatibilizing agent for polymer alloy of polystyrene type resin and polyester type resin. They are incompatible each other.

It was reported that polymer alloy of polyethylene naphthalate (PEN) and syndiotactic polystyrene (SPS) could improve voltage resistance and processability of PEN stretched thin film used in film capacitor [40, 41]. SPS is high performance engineering plastic and has higher thermal stability [39].

Polyethylene terephthalate (PET) stretched thin film is also used in film capacitor. PET film capacitor is much more popular than PEN film capacitor and is widely used in various electronic products such as lighting fixtures, home appliances, and so on. Disadvantage of PET for film capacitor is thermal stability and voltage resistance. PET/SPS polymer alloy is expected to improve them as PEN/SPS polymer alloy film. SFC was verified the possibility applying to compatibilizing agent for polymer alloy of PET and SPS.

PET/SPS polymer alloy film has a potential to reduce capacitor size drastically and to realize same size of aluminum (Al) electrolytic capacitor. Al electrolytic capacitor is used in most of electronic products such as LED lighting fixture and power conditioner of PV system (**Fig.1-11**). Disadvantage of Al electrolytic capacitor is that its life is the shortest in all parts of electronic products. Therefore, life of most of electronic products is defined as life of Al electrolytic capacitor. If PET/SPS polymer alloy film can realize same size as Al electrolytic capacitor, it should provide much longer life to most of electronic products. It is expected the revolutionary impact for electronic products in world wide.

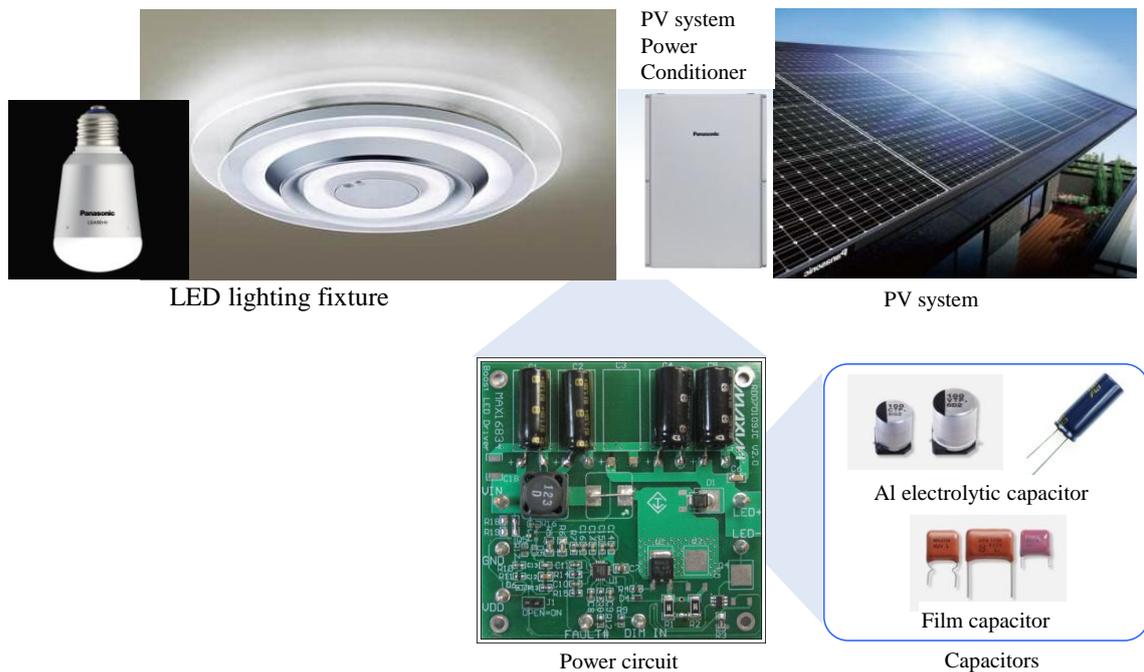


Fig. 1-11 Example of capacitor used in electronics products

2. Subcritical hydrolysis of thermosetting polyester resin

2.1 Fundamental verification

2.1.1. Introduction

At the beginning of this research, the goal was set to achieve the reaction time should be less than 20 minutes since the plant of subcritical water hydrolysis with high temperature and high pressure was very expensive. To achieve the reaction time of 20 min., temperature above 300°C was needed. The reaction condition at temperature above 300°C, glycol and fumaric acid was dissolved in the reaction product liquid but the SFC was not considered to be recovered. Total weight of glycols and fumaric acid dissolved was less than 20% of initial weight of thermosetting polyester resin. In these reaction conditions, CaCO₃ was the best catalyst [30]. The experiment using super critical water on the reaction condition at a temperature of 380°C, at a pressure of 25.3MPa, and a reaction time of 20min. was also conducted. The results was as same as that of subcritical water above 300°C.

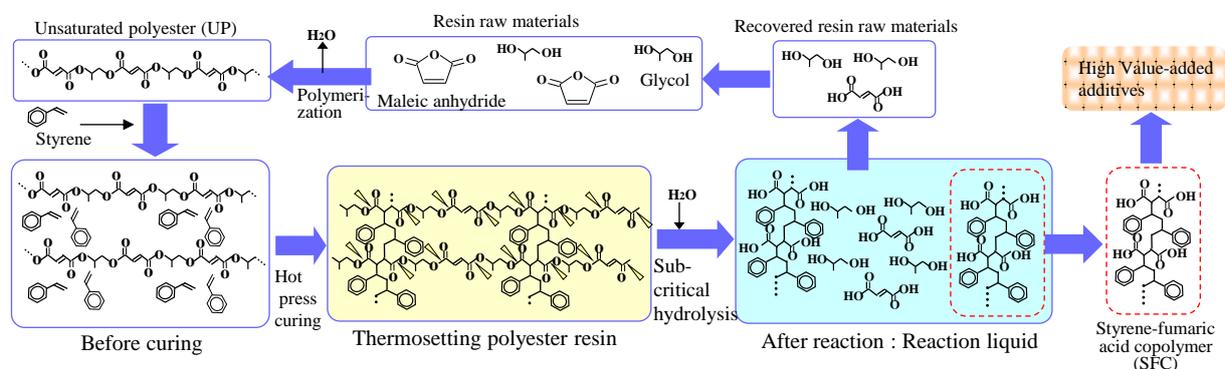


Fig. 2-1-1 Concept of recycling thermosetting polyester resins using subcritical water

Figure 2-1-1 shows concept of recycling thermosetting polyester resins using subcritical water. Fundamental verification of this concept was conducted. In optimization of reaction condition and catalyst, pyrolysis should be suppressed.

2.1.2. Materials and methods

Thermosetting polyester resin sample was prepared according to the composition given in **Table 2-1-1**. UP was prepared by polymerization with glycols and maleic anhydride. Propylene glycol, dipropylene glycol, and neopentyl glycol were used as

glycol. UP resin is viscous liquid consisting of styrene and the UP. The UP resin and calcium carbonate (CaCO_3) were mixed and cured at 100°C for 2 hours to produce thermosetting polyester resin sample. The obtained material was then heated to release unreacted styrene monomers after curing.

Table 2-1-1 Composition of thermosetting polyester resin sample

Material			Content	
Thermosetting polyester resin sample	UP* Resin	UP* sample	Glycols	12 wt%
			Maleic anhydride	12 wt%
			Styrene	26 wt%
	Calcium carbonate (CaCO_3)			50 wt%
Total			100 wt%	

UP*:Unsaturated Polyester

Figure 2-1-2 shows experiment process flow of subcritical hydrolysis. Pure water or alkali catalyst solution was added to the thermosetting polyester resin samples 5 times the weight. Sample and pure water or alkali catalyst solution was placed into a 20 mL batch tubular reactor. They were heated and kept in predetermined time in salt bath. The pressure was the saturated vapor pressure of water at a given temperature.

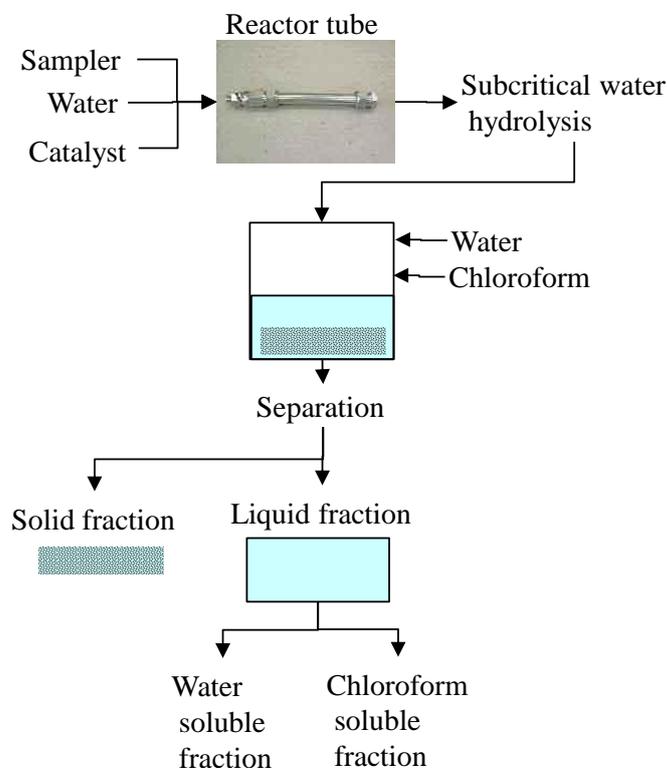


Fig.2-1-2 Subcritical hydrolysis experiment process flow

After the reaction, the reaction slurry was removed from the reactor. It was filtered by filter paper to separate the solid fraction containing unreacted resin and CaCO₃ and the liquid fraction then measured the weight. Water was added to wash the solid residue to recover water soluble solution containing water soluble ingredients. Then, chloroform was added to wash the solid residue to recover chloroform soluble solution containing chloroform soluble ingredients.

Concentration of glycols and organic acids in the liquid fraction was obtained by gas chromatography (GC, Yanaco:G3800) and ion chromatography (IC, Dionex:DX-500), respectively. To precipitate the SFC, hydrochloric acid was added to the liquid fraction to pH 4. The SFC was filtered and then measured the weight after drying.

Resin conversion rate and production rate were calculated according to equations (2-1-1) - (2-1-3):

$$W_{r \text{ resid.}} = W_{\text{solid.}} - W_{\text{CaCO}_3} \quad (2-1-1)$$

where $W_{r \text{ resid.}}$; the weight of UP resin residue, $W_{\text{solid.}}$; the total weight of solid fraction, and W_{CaCO_3} ; the initial weight of CaCO₃.

$$\text{Resin conversion rate (\%)} = (1 - W_{r \text{ resid.}} / W_{r \text{ init.}}) \times 100 \quad (2-1-2)$$

where $W_{r \text{ init.}}$; the initial weight of UP resin.

$$\text{Production rate (\%)} = (W_{p \text{ detect.}} / W_{p \text{ init.}}) \times 100 \quad (2-1-3)$$

where $W_{p \text{ detect.}}$; the detected weight of product and $W_{p \text{ init.}}$; the initial weight of product.

Weight-average molecular weights (M_w) in terms of polystyrene was analyzed by Gel Permeation Chromatography (GPC, Tosoh Corporation: HLC8120 GPC) . Molecular structure of SFC was analyzed by ¹³C Nuclear Magnetic Resonance (NMR, JEOL Ltd.: AL-400S, 400 MHz) and Fourier Transform Infrared Spectroscopy (FT-IR, Thermo Nicolet Inc.: Magna 550), and Gas Chromatograph Mass Spectrometer (GC-MS, PerkinElmer Inc.: TurboMass and TurboMatrix ATD) .

2.1.3. Results and discussion

Subcritical hydrolysis of thermosetting polyester resin sample was conducted on the reaction condition at a temperature of 360°C, a pressure of 18.7MPa, and a reaction time of 20 min. The reaction product liquid after the reaction was black as shown in **Fig.2-1-3**. Before the reaction, UP resin and water was almost transparent. The change of color indicates the generation of various byproducts. Conversion was 100%. Therefore, white powder shown in **Fig.2-1-3** was CaCO₃. Production rate of glycol and fumaric acid were 46.6% and 21.2%, respectively. Their total weight indicated

only 16% of the initial weight of the thermosetting polyester resin sample. In the reaction product liquid, 65% of organic ingredient was chloroform soluble ingredients and rest of 35% was water soluble ingredients.

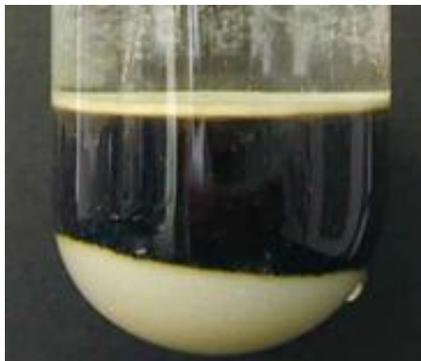


Fig.2-1-3 Reaction product liquid (360°C, 18.7MPa, 20min, CaCO₃)

Figure 2-1-4 shows GC-MS chart of chloroform soluble ingredients. Many byproducts derived from styrene chain were observed. It is known that in vaporizing polystyrene in a temperature range from 310°C to 350°C, dimer and trimer generates and it is reversible reaction [42]. Therefore, it is obvious that pyrolysis of styrene chain occurred.

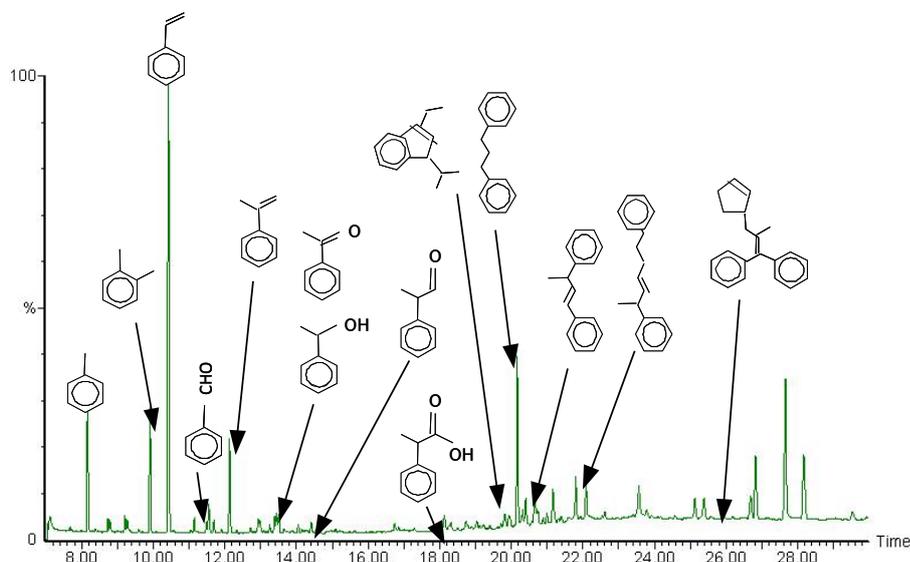


Fig.2-1-4 GC-MS chart of chloroform soluble ingredients (360°C,20min.,CaCO₃)

Figure 2-1-5 shows GC-MS chart of water soluble ingredients. Many byproducts, such as fumaric acid ethyl ester were detected in the aqueous solution. They were considered to be generated in the deterioration of glycol or fumaric acid. Their molecular structures were similar to resin raw materials. Therefore, it was considered impossible to be separated.

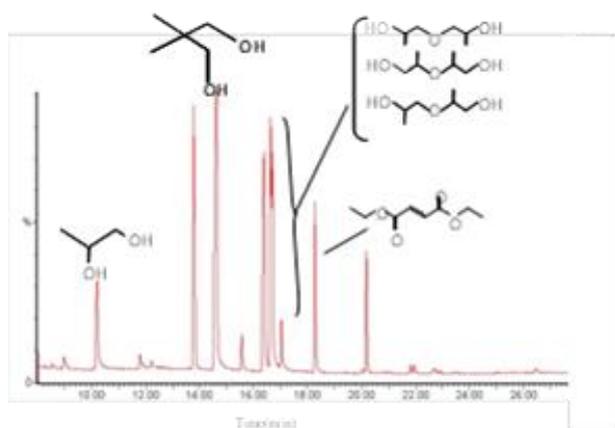


Fig.2-1-5 GC-MS Chart of water soluble fragment(360°C, 20min., CaCO₃)

Adschiri reported that glycol degradation by terephthalic acid (TPA) produced in supercritical hydrolysis of PET [43]. In supercritical water at a temperature of 400°C and a pressure of 40MPa, for 30 min., ethylene glycol (EG) decomposed 93.5% accompanying with TPA although EG decomposed only 4.8% without TPA.

Secondary reaction of decomposing glycol by fumaric acid was verified. **Figure 2-1-6** shows the experimental result. In subcritical water at temperature of 350°C and a pressure of 16.5MPa, propylene glycol (PG), dipropylene glycol (DPG), and fumaric acid (FA) were exposed. In the case of PG only and DPG only, more than 90% of glycols were remained after 30 min. However, in the case of PG and DPG accompanying with FA, PG and DPG drastically decreased and only 4% and 2% of them were remained, respectively. It was obvious that fumaric acid decomposed glycol on this reaction condition.

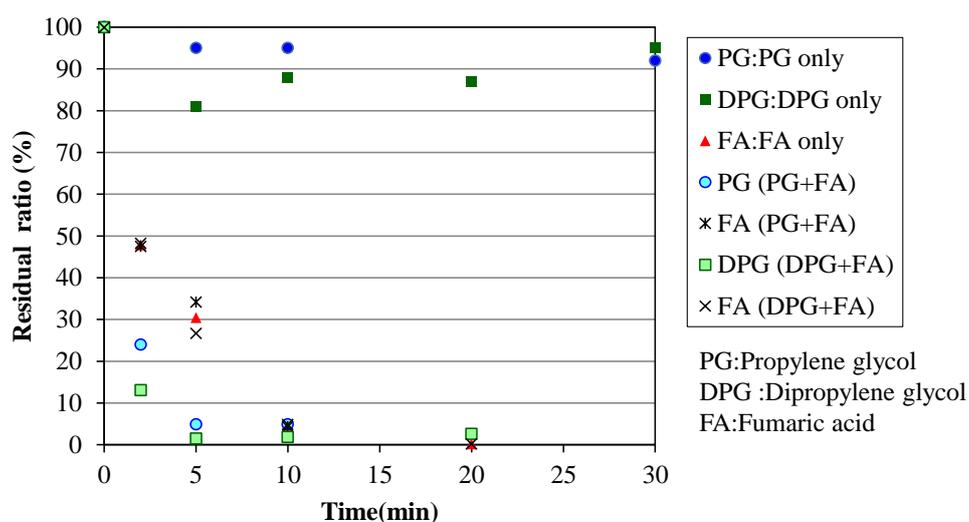


Fig.2-1-6 Decomposition of glycols in subcritical water.(350°C, 16.5MPa)

On this reaction condition, pyrolysis of styrene chain and secondary reaction

caused by fumaric acid were dominant although the conversion reached 100% for 20 min. Even 46.6% of glycol and 21.2% of fumaric acid were dissolved in the reaction product liquid, they were only 16% of the initial thermosetting resin sample. In addition, there were too many impurities. They were obviously impossible to be separated. Therefore, all of them cannot be recycled to resin raw materials practically even existing in the reaction product liquid.

Then, we conducted literature survey of previous study again and found the papers which reported that the pyrolysis of styrene chain occurred above 230°C in glycolysis of thermosetting polyester resin [13, 15]. Weight-average molecular weights (M_w) of reactants tended to decrease with increasing reaction temperature.

Based on the information, the hypothesis of reaction optimization that reaction condition of temperature under 230°C with longer time was proposed. It was suggested that it enabled to suppress the pyrolysis and then to realize the ideal reaction which the hydrolysis reaction was dominant. The saturated vapor pressure at 230°C is 2.8 MPa. The weak point of this idea was that plant cost might be increased due to longer reaction time. However, we also obtained the information that high pressure vessel of 2.8 MPa was approximately only 50% more expensive than normal pressure vessel. In addition, the share of the vessel cost was assumed only 10% of the total plant cost. There were some processes of FRP solvolysis at normal pressure demonstrated. It was considered to be close to commercialization even its reaction time was 12 hours. Therefore, approximately 4 hours reaction time should be considered practical range in terms of plant cost.

Then, the fundamental verification of the hypothesis to realize the ideal reaction to suppress pyrolysis of styrene chain on the reaction condition at a temperature of 230°C, at pressure of 2.8MPa was conducted. If it is effective, the SFC should be obtained.

Figure 2-1-7 shows the reaction product liquid at 230°C, 2.8MPa, for 4 hours. It was drastically changed to transparent as shown in **Fig.2-1-7**.

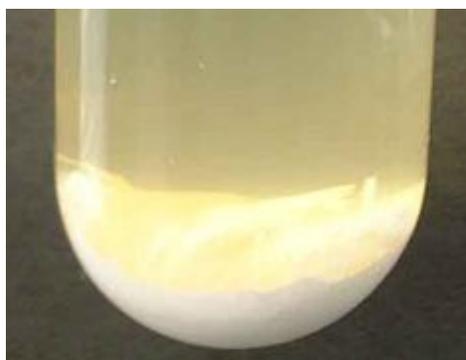


Fig.2-1-7 Reaction product liquid (230°C, 2.8MPa, 20min, CaCO_3)

Chloroform soluble ingredients which were 65% of the organic matter at 360°C were disappeared completely. No styrene derived ingredients were generated. Soluble ingredients indicated 100%. It suggested that pyrolysis of styrene chain was almost perfectly suppressed. Conversion, production rate of glycol and fumaric acid were 30.8%, 32.2%, and 1.2%, respectively.

Figure 2-1-8 shows GC-MS Chart of water soluble ingredients. Many byproducts observed at 360°C were also disappeared. Only raw glycols were observed. Based the fact that no styrene derived ingredients and no byproducts were observed and only raw glycols were observed, it was definitely to suppress the pyrolysis of styrene chain and secondary reaction. It was concluded that the hypothesis was successfully verified. Glycols should be able to be recycled to UP since no impurities were existed.

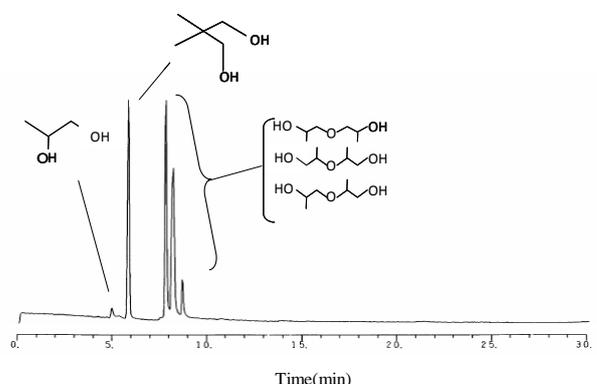


Fig.2-1-8 GC-MS Chart of water soluble fragment (230°C, 2.6MPa, 4h, CaCO₃)

However, conversion was only 30.8%, the experiment with other catalysts was on the same reaction condition was conducted to increase conversion. **Table 2-1-2** shows the experimental results of conversion and production rate of glycol and fumaric acid.

Table 2-1-2 Evaluation of various catalysts (230°C, 4 h)

Catalyst	Conversion	Glycol production rate	Fumaric acid production rate
None	15.9%	33.7%	9.0%
CaCO ₃	30.8%	32.2%	1.2%
K ₃ PO ₄	41.5%	58.6%	3.6%
KOH	96.9%	70.7%	21.8%

Potassium hydrate (KOH) showed 96.9% as conversion, 70.7% and 21.8% as glycol production rate and fumaric acid production rate, respectively. It was concluded that KOH was the best catalyst. Only uncross-linked fumaric acid was produced. That was considered the reason why the fumaric acid production rate was lower than glycol. It

suggested that the ideal reaction was almost realized. Then, the SFC existing in the reaction product liquid was verified. When hydrochloric acid (HCl) was added to the reaction product liquid, white precipitate was observed. It was filtered and dried and then white powder was obtained as shown in **Fig.2-1-9**.

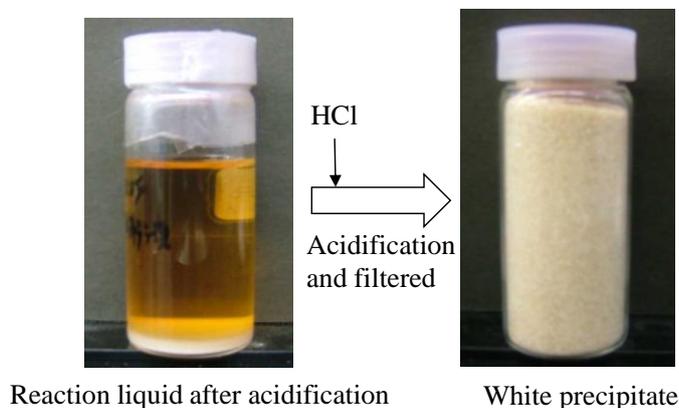


Fig.2-1-9 Precipitation experiment result (230°C, 4h, KOH)

The white powder was analyzed by GPC. Weight averaged molecular weight (Mw) in terms of polystyrene was 30,000. If it is the SFC which has dicarboxylic acid, anhydride should be generated by heating. Then, the white powder was heated at 180°C and then analyzed by FR-IR. **Figure 2-1-10** shows FT-IR spectrum of the white powder heated. Peaks which indicate anhydride were observed. It indicated that the white powder had dicarboxylic acid.

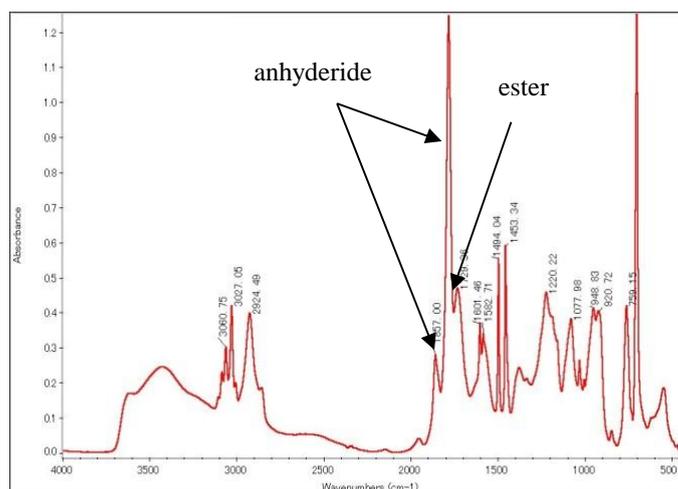


Fig.2-1-10 FT-IR spectrum of the precipitate

Next, 2 dimensional NMR analysis was conducted. **Figure 2-1-11** shows 2 dimensional NMR spectrum of the white powder. The peak indicates relationship between hydrogen atom of hydrocarbon of styrene and hydrogen atom of hydrocarbon of fumaric acid was observed. It was identified that the white powder was the SFC.

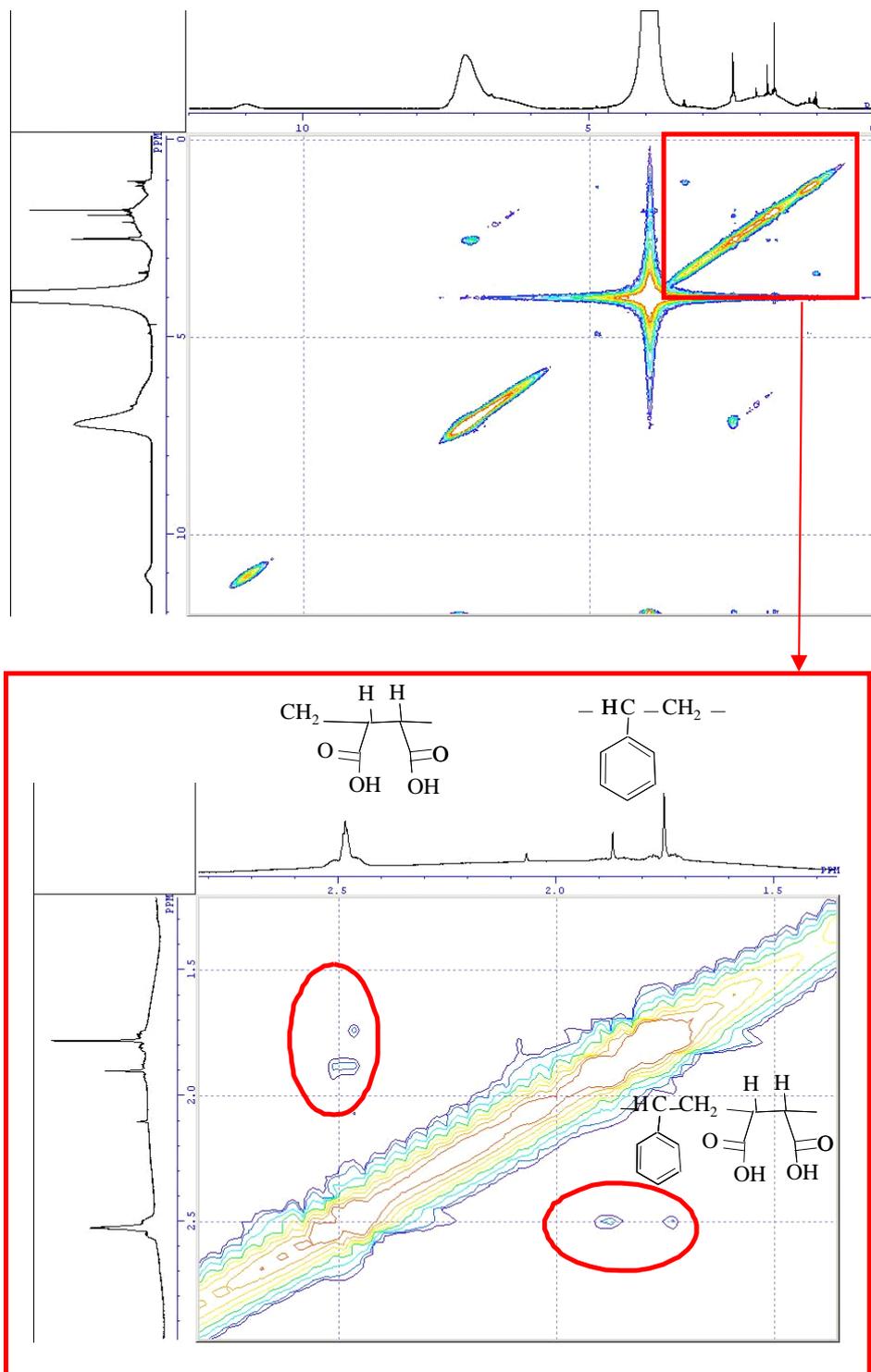


Fig.2-1-11 Two dimensional NMR spectrum of the white powder (230°C, 4h, KOH)

To evaluate the S/F molar ratio of the white powder, SFC, heated powder which has anhydride was analyzed by NMR. **Figure 2-1-12** shows ^{13}C -NMR spectrum. Ratio of peak area of styrene and fumaric acid was 2.2. S/F molar ratio was identified 2.2.

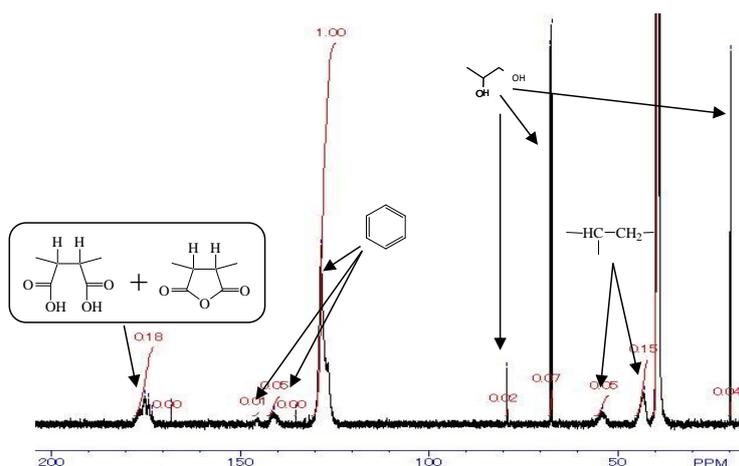
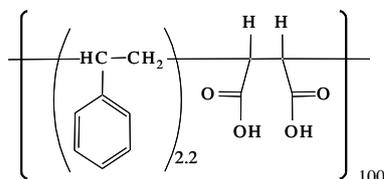


Fig.2-1-12 ^{13}C - NMR spectrum of the solid (230°C, 4h, KOH)

Base on the GPC analysis and ^{13}C - NMR, molecular formula of the SFC was described in **Scheme 2-1-1**.



Scheme 2-1-1 Styrene-fumaric acid copolymer (SFC)

The weight of SFC extracted from the reaction liquid was measured. It was 75% of the initial thermosetting resin weight. Thus, it was shown that up to 96wt% amount of the initial resin was existed in the reaction liquid as reusable matters. It was obvious that hydrolysis was ideally dominant in this reaction condition. After the separation process of glycol from the reaction liquid, 72% of the glycol in the reaction liquid was recovered. Recovered glycol was used to produce the UP resin with new resin raw materials.

2.1.4. Conclusions

Subcritical water hydrolysis of FRP was conducted. Reaction condition at 230°C, for 4 hours, with KOH, thermosetting resin was perfectly dissolved and 70.7wt% and 21.8wt% of initial glycol and fumaric acid, respectively, were detected in the reaction liquid. SFC was extracted in the reaction liquid with 75wt% of the initial thermosetting resin. It was shown that up to 96wt% amount of the initial resin was existed in the reaction liquid as reusable matters.

The SFC had Mw of 30,000 and S/F molar ratio of 2.2 with almost no degradation of carboxylic group. It indicates that the SFC has a high quality as functional polymer. It is considered the first achievement to extract the styrene chain as functional polymer and to clarify its molecular structure in the thermosetting polyester resin.

2.2. Functional mechanism of alkali catalyst and optimization of reaction conditions and catalysts

2.2.1. Introduction

In 2.1, subcritical hydrolysis at 230°C, 2,8MPa, 4 hours with KOH realized the ideal reaction which hydrolysis was dominant and pyrolysis was minimized. Most of thermosetting polyester resin was verified to be dissolved in the reaction product liquid as SFC and resin raw materials. SFC has a high quality as functional polymer. In such an ideal reaction, KOH seemed to play important role. Then, functional mechanism of KOH affecting the reactivity represented by conversion and production rate was investigated. Experiment of subcritical hydrolysis with KOH was conducted using samples of thermosetting polyester resin and UP.

For commercialization, substitution of expensive KOH to less expensive NaOH is preferred and optimization of reaction condition was investigated. Experiment of subcritical hydrolysis using real FRP bathtub manufacturing waste was conducted to find the effect of alkali concentration, reaction temperature, and reaction time on the reactivity.

2.2.2. Materials and methods

2.2.2.1 Functional mechanism of alkali

Same thermosetting polyester resin sample described in **Table 2-1-1** was used as thermosetting polyester resin sample. The UP sample was prepared to heat the UP resin before curing to vaporize styrene. Pure water or KOH aqueous solution (0.2-1.0 mL/L) was added to the thermosetting polyester resin samples and to the UP samples 4 times and 17.7 times the weight, respectively.

Experimental procedures, analyses, calculations were same as described in 2.1.2 The reaction was carried out at 230 °C, 2.8MPa for 4 hours.

2.2.2.2 Optimization of reaction conditions and catalyst

Samples were taken from real manufacturing waste of FRP bathtub. **Table 2-2-1** shows its composition. Other organic materials include commercial low profile additive (LPA) and other additives. The composition of the UP resin was the same as the UP resin described in **Table 2-1-1**. The commercial LPA is of polystyrene type and has a weight-average molecular weight ranging from 150,000 to 250,000. It was diluted with styrene at a ratio of 30 wt%. The weight ratio of FRP ground sample: KOH or NaOH solution was 1:4. The samples were ground and placed in the reactor described and treated as described in the section 2.1.

Table 2-2-1 Composition of FRP sample

FRP raw material	Content (wt%)
UP* resin	25.6 wt%
Other organic materials	5.1 wt%
CaCO ₃	51.3 wt%
Glass fiber	18.0 wt%

UP* : Unsaturated polyester

The residue weight of UP resin ($W_{r \text{ resid.}}$) was calculated according to equation (2-2-1):

$$W_{r \text{ resid.}} = W_{\text{solid.}} - (W_{\text{CaCO}_3} + W_{\text{gf}} + W_{\text{other om}}) \quad (2-2-1)$$

where $W_{\text{solid.}}$; the total weight of solid fraction, W_{CaCO_3} ; the initial weight of CaCO₃, W_{gf} ; the initial weight of glass fiber $W_{\text{other om}}$; the initial weight of other organic materials.

The resin conversion rate and the glycols and SFC production rates were calculated according to equations (2-1-2) and (2-1-3).

2.2.3. Results and discussion

2.2.3.1 Functional mechanism of alkali

In subcritical hydrolysis of thermosetting polyester resin, KOH seems to play an important role to promote the reaction and to achieve high yield of SFC and glycols. The effect of KOH concentration on the reaction was investigated under the conditions of 230 °C, 2.8 MPa, and 4 hours. Ionic product and dielectric constant (DC) of water at 230 °C is about 10^{-11} and 33, respectively. Dielectric constant of subcritical water on this condition is equivalent to that of methanol.

Figure 2-2-1 shows the resin conversion rate and the production rates of glycol, organic acids, and SFC. The resin conversion rate and production rates increased with increasing KOH concentration. There was a drastic change between 0.2 mol/L and 0.5 mol/L. The production rates of glycol at 0 mol/L and 0.2 mol/L were 47 % and 42 %, respectively, although no SFC was produced. The production rate of glycols should be related to the number of ester bonds broken. Glycols might be decomposed by oxidation by the carboxylic acid produced during hydrolysis. Glycols degradation by carboxylic acids in supercritical hydrolysis of PET [43] and subcritical hydrolysis of thermosetting polyester resin [25] were reported.

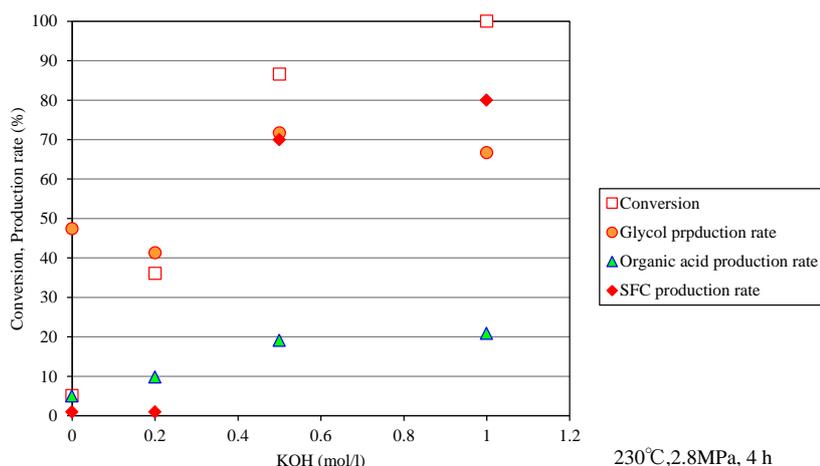


Fig. 2-2-1 Subcritical water hydrolysis of thermosetting polyester resin samples

High ionic product and low dielectric constant of subcritical water caused breaking ester bonds to produce glycols efficiently. However, it seemed to be insufficient to break all ester bonds between glycol and fumaric acid which was cross-linked with styrene to release the SFC. The hypothesis of the reaction at KOH (0mol/L) is described in Fig.2-2-2. In this condition, approximately half of ester bonds were seemed to be hydrolyzed but it was insufficient for releasing SFC. Most of styrene chain was still connected to the next styrene chain. Even if only a few ester bonds connecting each other remain, the SFC cannot be free.

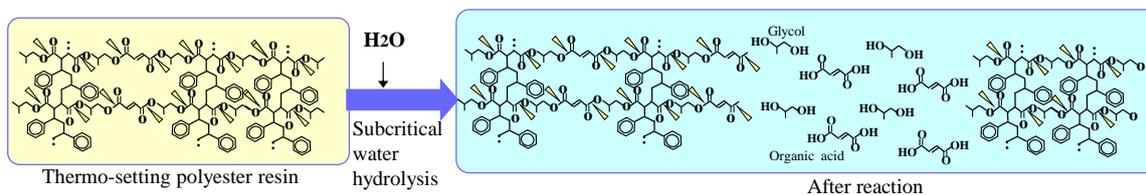


Fig. 2-2-2 Hypothesis of reaction (KOH=0 mol/L, 230°C,4h)

Oliveux reported that the thermosetting polyester resin composite sample was still solid in subcritical hydrolysis at 275 °C during 3 hours [27]. Fumaric acids were used as cross-linked with styrene and terephthalic acids were mainly used in polyester chain in thermosetting polyester resin composite sample. Oliveux proposed the hypothesis that there were two different ester bonds in the thermosetting polyester resin sample. One was defined as “non-hydrolysable ester bonds” between glycol and fumaric acid which was cross-linked with styrene. Another one was defined as “hydrolysable ester bonds” between glycol and phthalic acid. “Non-hydrolysable ester bonds” could not be broken by subcritical water even at 275 °C during 3 hours. That’s the reason why the

thermosetting polyester resin sample still remained as solid. A certain amount of glycol was observed because “hydrolysable ester bonds” were hydrolyzed to release glycol.

Figure 2-2-3 shows the hypothesis of “non-hydrolysable ester bonds” and “hydrolysable ester bonds”, which Oliveux proposed [27]. Upper figure indicates before the reaction and under figure indicate after the reaction. **Figure 2-2-3** indicates 4 pattern of polyester chain indicating from (i) to (iv) based on the number of phthalic acid from 0 to 3. In the thermosetting polyester resin composite sample which Oliveux used, terephthalic acid mainly used in polyester chain between fumaric acid cross-linked with styrene. “Non-hydrolysable ester bond” and “hydrolysable ester bond” defined by Oliveux were indicated in **Fig. 2-2-3**. In polyester chain (i), glycol cannot be released since both ester bonds of glycol are “non-hydrolysable ester bond.” In polyester chain (ii), glycol also cannot be released since it has one “non-hydrolysable ester bond.” Phthalic acid between two glycols can be released if both “hydrolysable ester bond” is hydrolyzed. In polyester chain (iii), a center glycol can be released firstly if both “hydrolysable ester bond” of the glycol is hydrolyzed. Two phthalic acids might be released. In polyester chain (iv), two glycols and three phthalic acids might be released.

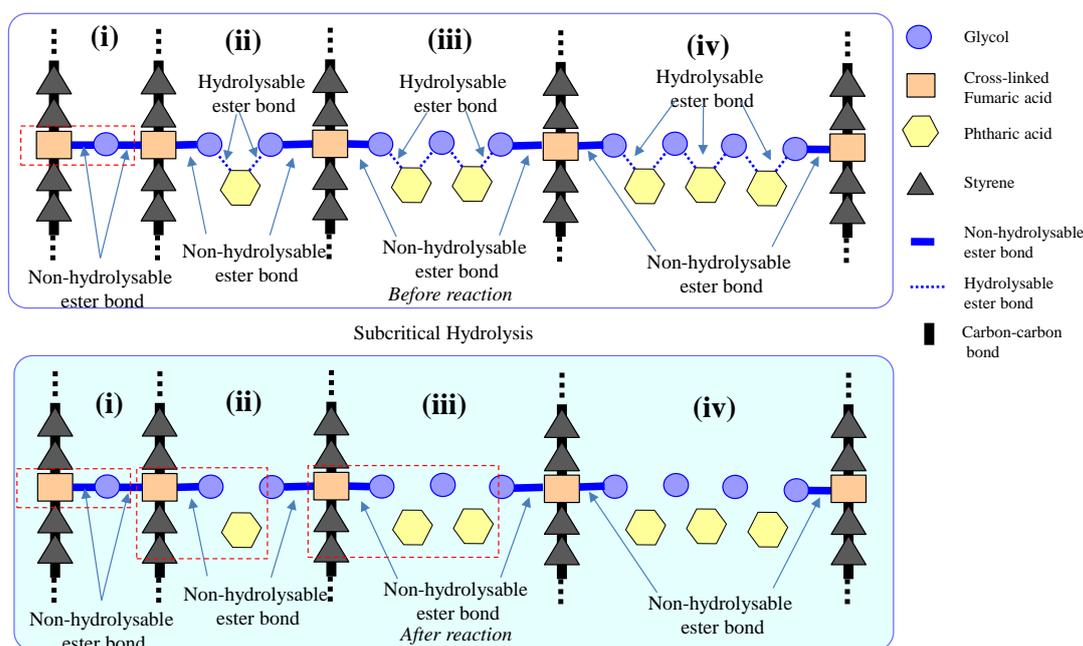


Fig. 2-2-3 Hypothesis of hydrolysable ester bond and non-hydrolysable ester bond

In this study, the difference was to use only fumaric acid and not to use terephthalic acid. However, it was verified that this hypothesis could be applied to the thermosetting polyester resin sample of this study. In **the section 2.1**, S/F molar ratio was identified by NMR analysis as **the section 2.2**. **Table 2-1-1** shows composition of styrene and fumaric acid in UP resin was 52% and 24%, respectively. Based on these information,

fumaric acid which is cross-linked with styrene (cross-linked FA) and fumaric acid which is not cross-linked with styrene (free FA) should be 73wt% and 27% of total fumaric acid, respectively. Ratio of cross-linked FA / free FA (cl-FA /free-FA) should be 2.7.

In order to consider the share of each polyester chain based on the above information, ratio of cross-linked FA / free FA (cl-FA /free-FA) in each polyester chain was described in **Fig.2-2-4**. If all ester bonds are hydrolyzed, in polyester chain (i)' there is 1 cl-FA and no free-FA, thus cl-FA /free-FA is ∞ . In polyester chain (ii)', there are 1 cl-FA and 1 free-FA, thus cl-FA /free-FA is 1. In polyester chains (iii)' and (iv)', cl-FA /free-FA is 0.5 and 0.33, respectively. In total of the thermosetting polyester resin, cl-FA /free-FA was calculated as 2.7. Therefore, polyester chains (i)' and (ii)' should be dominant. Polyester chain (iii)' and (iv)' should be very rare case.

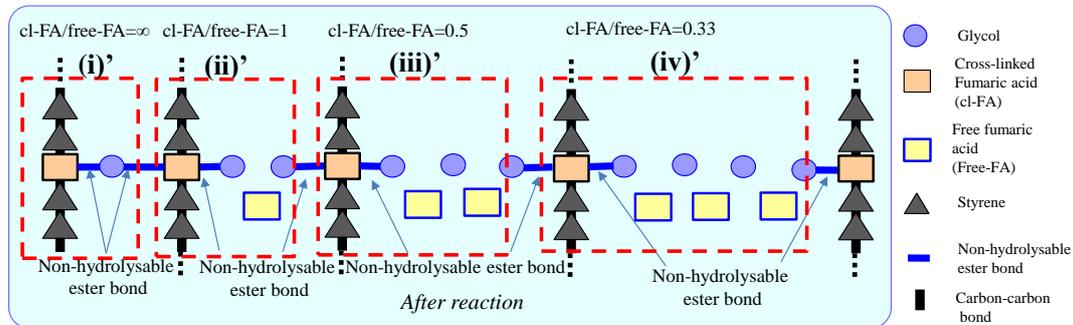


Fig. 2-2-4 Ratio of cross-linked fumaric acid and free fumaric acid

Calculation of share of polyester chains (i)' and (ii)' was described as follows.

$$\text{cl-FA total} = 1 \times X + 1 \times Y = X + Y \quad (a)$$

$$\text{free-FA total} = 0 \times X + 1 \times Y = Y \quad (b)$$

where, X: share of polyester chain (i)', Y: share of polyester chain (ii)'

$$\text{Share of polyester chain (ii)'}: Y = 1 - X \quad (c)$$

$$\text{cl-FA /free-FA calculated} = 2.7 = (a)/(b) = (X+Y)/Y$$

$$2.7 = (X + (1 - X)) / (1 - X) \quad \text{Result; } X = 0.63 \quad Y = 0.37$$

It indicated that polyester chain (i)' and (ii)' were 63% and 37% in the thermosetting polyester resin sample, respectively. It suggests that it should be very rigid structure. It is much more rigid than believed generally.

The stoichiometrically calculation result indicated polyester chains (i) and (ii) were dominant. However, based on the hypothesis which Oliveux proposed [27], glycol was not produced from both polyester chains. Glycol was produced at a production rate at least 40% or more. Therefore, it was concluded that definition of “non-hydrolysable ester bond” between glycol and fumaric acid cross-linked with styrene was not

applicable for the thermosetting polyester resin sample in this study. However, concept of the hydrolysability difference for each ester bond seemed to be reasonable.

Figure 2-2-5 shows a hypothesis of reaction condition at $\text{KOH}=0\text{mol/L}$. Based on the above information, the hypothesis is proposed that there are two different ester bonds called “hardly hydrolysable ester bond” and “easily-hydrolysable ester bond.” As mentioned before, all ester bonds were hydrolyzed at 230°C , 4 hours, with KOH . Therefore, the term, “non-hydrolysable”, is not proper. However, the experimental results indicated the difference of hydrolysable resistance in each ester bonds.

“Hardly-hydrolysable ester bond” was defined as ester bonds of glycol connected to two cross-linked fumaric acid with styrene (cl-FA). “Easily-hydrolysable ester bond” was defined as other ester bonds than “hardly hydrolysable ester bond.” In the case of $\text{KOH}=0\text{mol/L}$, it was assumed that “hardly-hydrolysable ester bonds” were not broken although some of “easily-hydrolysable ester bonds” were broken to produce 47% of glycol. Styrene chain was assumed to be still connected to the next styrene chain by some of “the hardly-hydrolysable ester bonds.” That is the reason why SFC was not produced. In addition, the hardly-hydrolysable ester bond of propylene glycol may be considered most hardly to be hydrolyzed due to the molecular size of PG.

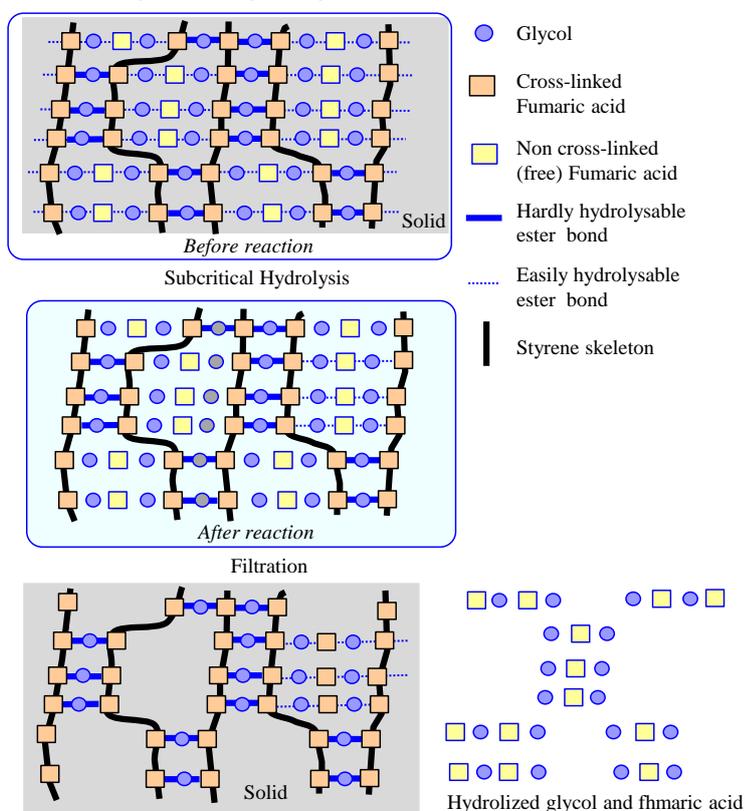


Fig. 2-2-5 Hypothesis of hardly hydrolysable ester bond and easily-hydrolysable ester bond ($\text{KOH}=0\text{ mol/L}$, 230°C , 4h)

For other concentration of KOH in Fig.2-2-1, SFC was produced drastically from 0.5 mol/L with production rate of 70%. At 1.0 mol/L, production rate of SFC, glycol, and fumaric acid were 80%, 67%, and 21%, respectively. In this case, most of ester bonds were hydrolyzed and SFC was produced as potassium salt (SFC-K) as described in Fig.2-2-6.

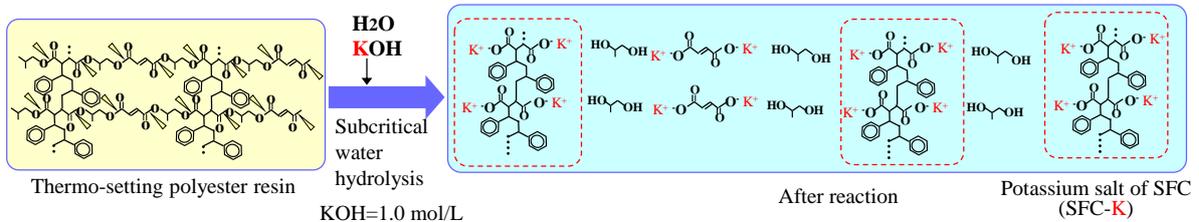


Fig. 2-2-6 Hypothesis of reaction (KOH=1.0 mol/L, 230°C,4h)

Most of ester bonds including “hardly-hydrolysable ester bonds” were seemed to be hydrolyzed to release much SFC described in Fig.2-2-7.

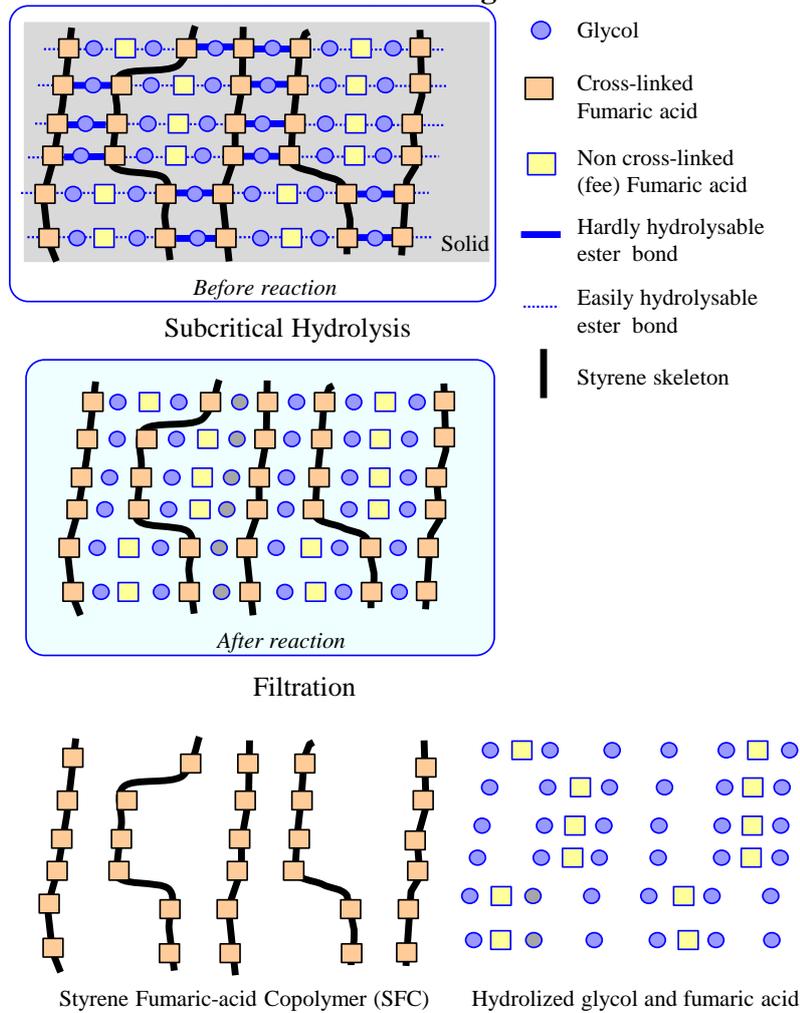


Fig. 2-2-7 Hypothesis of hardly hydrolysable ester bond and easily-hydrolysable ester bond (KOH=1.0 mol/L, 230°C, 4h)

In order to evaluate the effectiveness of KOH addition for breaking ester bonds of polyester chain, subcritical hydrolysis of uncured UP sample before curing was conducted under the same reaction conditions, which therefore did not contain styrene. Therefore all ester bonds are considered as “easily-hydrolysable ester bonds.” This UP sample does not have styrene chains. **Figure 2-2-8** shows the resin conversion rate and production rates of glycol and organic acids for subcritical water hydrolysis of the UP sample. The resin conversion rate was 100 % for all cases, even without KOH. However, the production rate of glycol was only 59 % and the production rate of carboxylic acid was 85 %. Organic acids included fumaric acid and other carboxylic acids such as malic acid which was degraded from fumaric acid. It was assumed that a secondary reaction decomposed the glycols. Therefore, it was reasonable to conclude that most of ester bonds were broken even without KOH. It suggested that KOH was not essential for breaking ester bonds in polyester chain of the thermosetting polyester resin, “easily-hydrolysable ester bonds,” under these reaction conditions. KOH was assumed to be necessary to break “easily-hydrolysable ester bonds.”

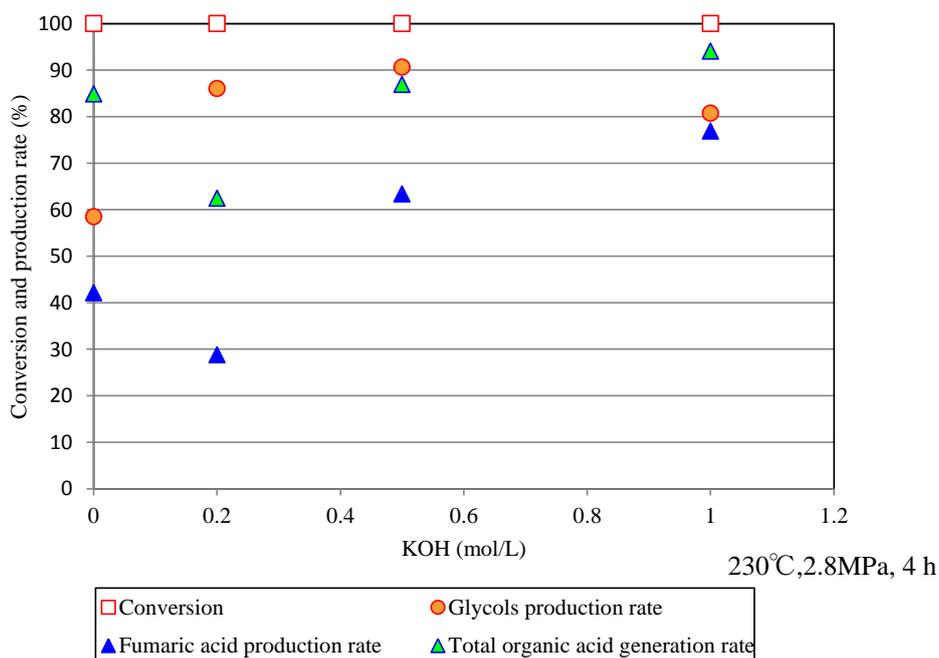


Fig. 2-2-8 Subcritical water hydrolysis of UP * samples

KOH might contribute to provide the solubility with the SFC released to promote the reaction. However, the SFC solubility in subcritical water is unknown. It might have a sufficient solubility based on high ionic product and low dielectric constant (DC). DC at 230°C of water is about 33, similar to that of methanol (DC=32.6). The SFC

dissolves slightly in methanol. Dimethyl sulfoxide (DMSO, DC=48.9) and acetone (DC=20.7) had higher solubility than methanol. On the other hand, it couldn't be dissolved in chloroform (DC=4.8). The SFC solubility seemed to be difficult to be estimated by only DC. The solubility of the SFC in subcritical water should be verified to discuss about the diffusion limitation.

KOH seemed to play another role in realizing the ideal reaction. The organic acids and SFC during the reaction were assumed to act as acid catalysts in a secondary decomposition reaction. The carboxyl group of the SFC was also broken, causing loss of quality of the functional polymer. However, KOH could neutralize the organic acid and the SFC to suppress their catalytic activity and self-decomposition. Thus, KOH contributed to the recovery of undamaged SFC.

In addition, the thermosetting polyester resins are generally used with inorganic materials such as glass fibers and inorganic filler. After the reaction, the SFC (not soluble in pure water at room temperature) was in the solid residue, coating the glass fibers and the filler, and was therefore difficult to recover. On the other hand, the potassium salt of the SFC was dissolved due to its water solubility. The reaction liquid containing the potassium salt of the SFC was easily separated from the solid component.

It is important to know the molar ratio of KOH according to carboxyl group of the SFC. In the case of a KOH solution at 0.5 mol/L of KOH solution, the ratio was approximately 4.8, whereas it was approximately 1.9 in the case at KOH concentration of 0.2 mol/L KOH. A molar ratio of more than 1.9 is suggested as the minimum requirement to completely dissolve SFC in water.

As described above, KOH was concluded to contribute to the reaction acceleration and the maximization of SFC yield as following points.

- i) To accelerate to break "hardly-hydrolysable ester bonds."
- ii) To prevent secondary reaction to keep higher quality level of SFC as functional polymer.
- iii) To make the separation process efficiently by providing water solubility with SFC to be dissolved in the reaction product liquid.
- iv) To provide solubility with SFC in subcritical water.

However, point iv) should be verified since solubility of SFC in subcritical water at 230°C are unknown.

2.2.3.2 Optimization of reaction conditions and catalysts

The efficiency of KOH was shown in **the section 2.2.3.1**. However, in view of commercialization, NaOH was investigated since it is less expensive than KOH.

Optimization of reaction condition is also needed. Real manufacturing waste sample of FRP bathtub was used in the experiment instead of the thermosetting polyester resin sample. Experimental samples are shown in **Fig.2-2-9**.

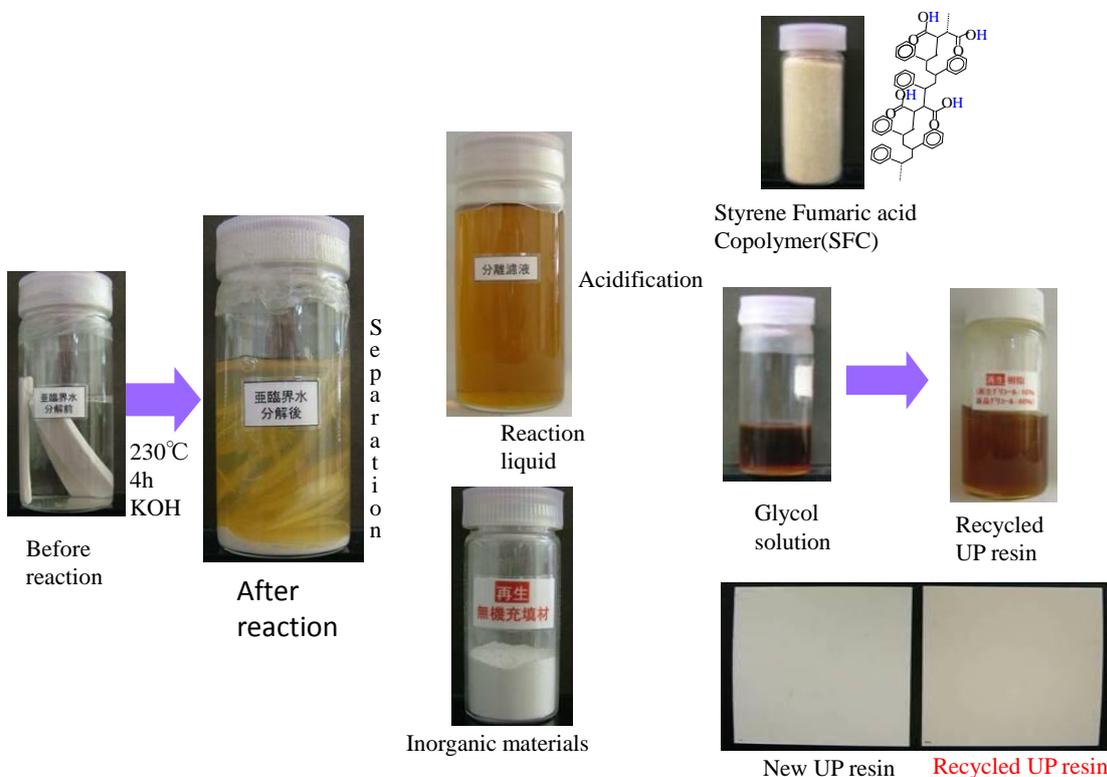


Fig. 2-2-9 Experimental sample using FRP bathtub manufacturing waste

Small board sample of real manufacturing waste of FRP bathtub was hydrolyzed. Thermosetting polyester resin was completely dissolved and glass fiber and CaCO₃ were exposed. They were filtered to separate solid fraction and reaction product liquid. SFC was precipitated by acidification and was separated by filter. The glycol was recovered by vaporizing of the filtrate, glycol solution. Recovered glycol was mixed with new resin raw materials at concentration of 10% to produce the recycled UP resin. FRP board used by the recycled UP resin was produced and tested. It showed the equivalent strength to a FRP board used new commercial UP resin. Appearance was also within the allowance level. Therefore, recovered glycol was verified to be horizontal recycled to FRP.

The optimization of reaction conditions such as temperature, pressure, reaction time, and concentration of KOH and NaOH was conducted. The resin conversion rate and production rates of glycol and the SFC were then measured.

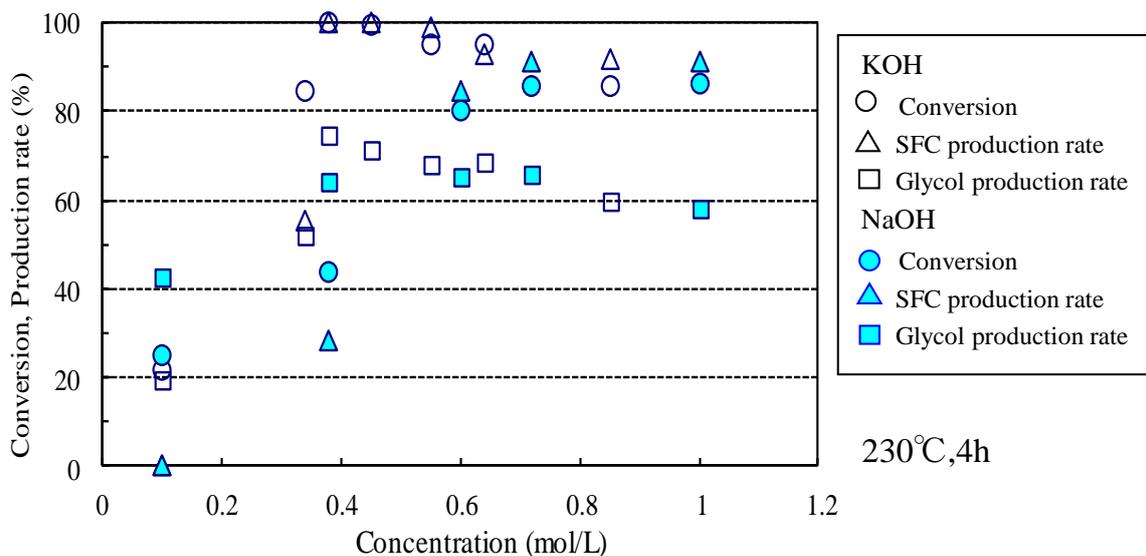


Fig. 2-2-10 Effect of concentration of KOH or NaOH (230°C, hours)

Figure 2-2-10 shows the effect of concentration of the KOH and NaOH concentrations on the resin conversion rate and the production rates of glycols and SFC. Reaction conditions were 230 °C and 2.8 MPa for 4 hours. In the case of KOH, conversion and SFC production rate reached almost 100% at 0.38 mol/L. At a concentration of more than 0.38 mol/L, they tended to decrease. In the case of NaOH, conversion and production rate of SFC and glycol were increased with increasing concentration and reached maximum value at 0.72 mol/L. Conversion and SFC production rate were lower than KOH at all concentration, especially, SFC production rate. SFC production rate at 0.38 mol/L was only 28.5%. However, glycol production rate at 0.1 mol/L showed 42.8% which was higher than KOH and 64.4% at 0.38 mol/L although SFC production rate was only 28.5%. It suggests that hydrolysis reactivity for “easily-hydrolysable ester bonds” of NaOH was almost equivalent to KOH. However, the hydrolysis reactivity for “hardly-hydrolysable ester bonds” of NaOH seemed to be inferior to KOH.

Alkali concentration should be minimized not only for considering the initial raw material cost but also for waste water treatment cost. Under these reaction conditions, the best concentrations for KOH and NaOH were 0.38 mol/L and 0.72 mol/L, respectively. The difference of suggested concentration for both alkalis was assumed to be based on the difference of basicity. In addition, the suggested concentration of NaOH was considered the upper limit based on the waste water treatment cost.

Figure 2-2-11 shows the effect of the temperature for a reaction time of 4 hours in

solutions of KOH and NaOH at 0.38 mol/L and 0.72 mol/L respectively. The highest value of resin conversion rate and production rates of SFC and glycols were obtained at 230 °C for both KOH and NaOH. The glycols production rates in presence of either KOH or NaOH were similar from 200 °C to 230 °C. Over 230 °C, they tended to decrease due to secondary reactions. The conversion rate and the SFC production rate also tended to decrease for NaOH. Styrene chain destruction might be occurred. Kubota reported that destruction of styrene chain of thermosetting polyester resin was observed at 230°C in glycolysis and Mw of the decomposition products tended to decrease with increasing temperature and time of decomposition [9, 11].

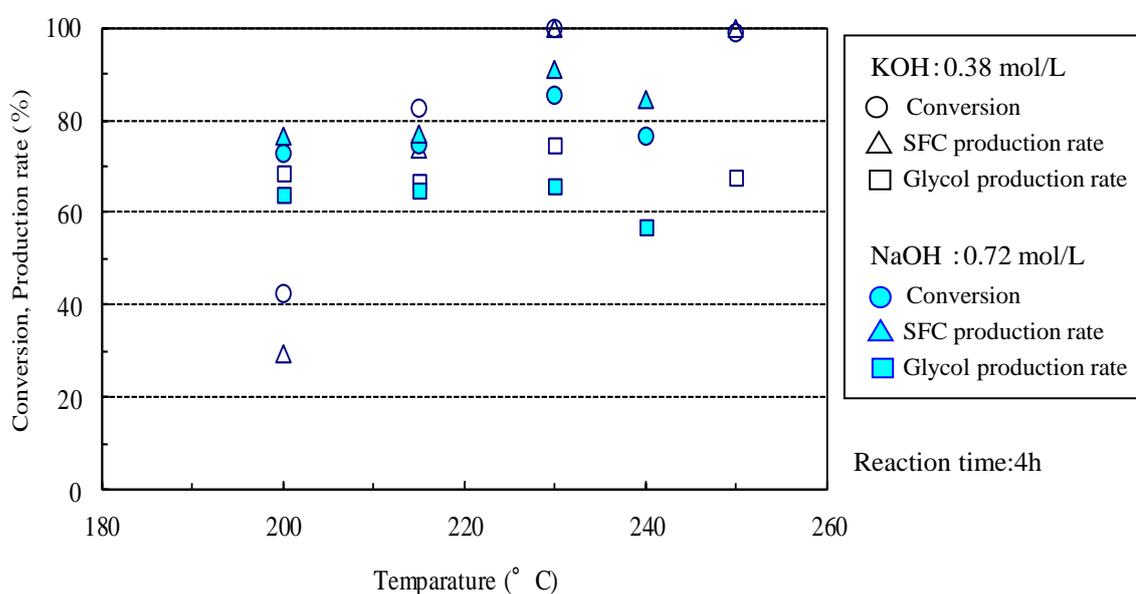


Fig. 2-2-11 Effect of temperature (Reaction time; 4 hours)

On the reaction condition at a temperature of 230°C which pyrolysis of styrene chain starts to occur, SFC production rate of NaOH (0.72 mol/L) was lower than that of KOH(0.38 mol/L) at all concentrations described in **Fig.2-2-10**. It suggested that hydrolysis reactivity of NaOH(0.72 mol/L) for “hardly-hydrolysable ester bonds” was inferior to KOH(0.38 mol/L). However, it was worth to remark that conversion and SFC production rate of NaOH(0.72 mol/L) were much higher than that of KOH(0.38 mol/L) at 200°C. Moreover, SFC production rate was higher than glycol production rate. It suggests that “hardly hydrolysable ester bond” was broken as same as “easily-hydrolysable ester bond.” On the other hand, conversion and SFC production rate of KOH(0.38 mol/L) at 200°C were much lower than glycol production rate. It suggests that hydrolysis reactivity of “Hardly hydrolysable ester bond” was much lower than that of “Easily-hydrolysable ester bond” at 200°C for KOH.

Figure 2-2-12 shows the effect of reaction time. The reaction temperature and pressure were 230 °C and 2.8 MPa. Solutions of KOH and NaOH were used at concentrations of 0.38 mol/L and 0.72 mol/L respectively. In the case of KOH (0.38 mol/L), the resin conversion rate and the production rates of glycols and SFC increased with the reaction time. The SFC production rate reached 100 % after 2 hours. In the case of NaOH (0.72 mol/L), the resin conversion rate, the SFC production rate, and the glycol production rate reached about 70 % , 80 % and 50 %, respectively after 0.5 hours. After 1 hour, they increased to 82 % and 90 %, respectively. The SFC production rate almost reached its highest value. The NaOH (0.72 mol/L) was more efficient than the KOH (0.38 mol/L) in terms of resin conversion rate and production of SFC. The secondary reaction that degrades the glycols did not seem to occur. It was assumed that increasing the temperature induce the destruction of the styrene chain resulting the decrease of the SFC yield [13, 15, 43].

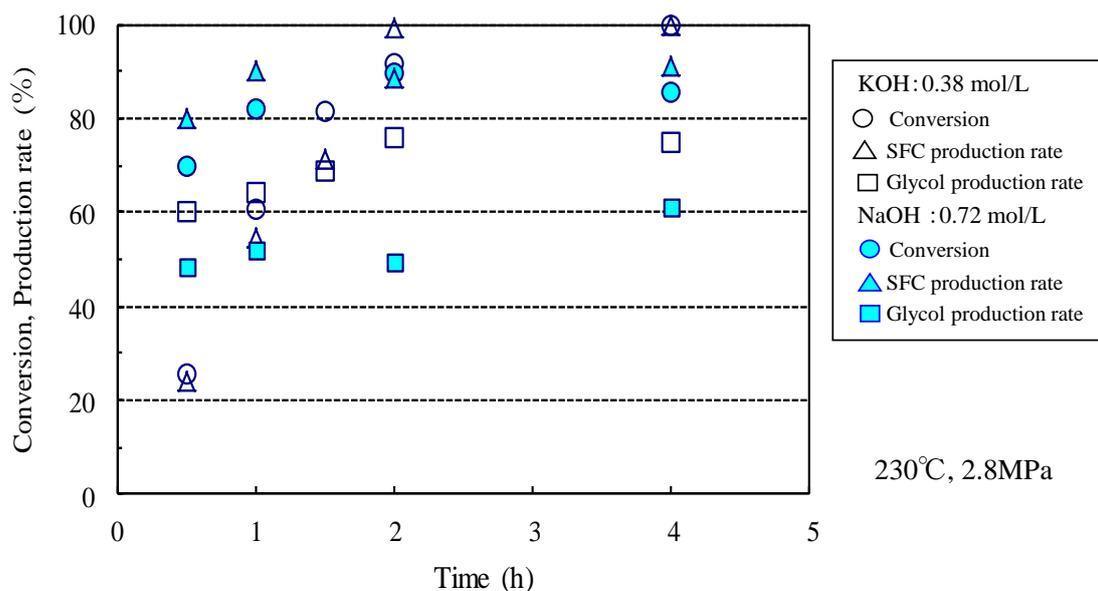


Fig. 2-2-12 Effect of reaction time (230°C)

In this experimental results, the production behavior of glycols and the SFC was different between NaOH (0.72 mol/L) and KOH (0.38 mol/L) as same as the case at 200 in **Fig. 2-2-11**. In the case of KOH, the glycol production rate was 60 % although the SFC production rate was only 24 % at 0.5 hours. It also suggests the difference of hydrolysis resistance for two types of ester bond. It was assumed that “easily-hydrolysable ester bonds” in polyester chain were broken to produce glycols rapidly but “hardly-hydrolysable ester bonds” were not broken sufficiently at 0.5 hours.

After that, the SFC production rate was increased to 100% at 2 hours. KOH (0.38 mol/L) seemed to be very effective to break “hardly-hydrolysable ester bonds.” On the other hand, in the case of NaOH (0.72 mol/L) at 0.5 hours, the production rates of glycol and the SFC were 49 % and 80 %, respectively. It suggests that hydrolysis activity for “hardly-hydrolysable ester bonds” was higher than “easily-hydrolysable ester bonds.” It is hard to explain that “hardly-hydrolysable ester bonds” was selectively broken. However, it should be remarkable fact to be investigated.

It was concluded that the optimized conditions based on the SFC yield were obtained at either a reaction temperature of 230 °C, a reaction time of 2 hours and a KOH concentration of 0.38 mol/L or 230 °C, 1 hour, and a NaOH concentration of 0.72 mol/L. However, the difference in the SFC production rate between 0.5 hours and 1 hour was only 10 %. It is worth considering the balance of the SFC yield and the plant capacity based on those fundamental experimental data. There might be a possibility to improve the reaction by a mixer or by the continuous operation with high solvent flow. In addition, in terms of SFC yield according to the reaction time, NaOH would be preferable for commercialization. The NaOH (0.72 mol/L) seemed to be more effective than KOH (0.38 mol/L) to break “hardly-hydrolysable ester bonds” to produce SFC on the reaction condition at 200°C for 4 hours and at 230°C for a reaction time less than 1 hour.

The difference of reactivity for hardly-hydrolysable ester bond between KOH and NaOH was examined. On the reaction condition at temperature of 200°C for 4 hours and at temperature at 230°C for 1 hour or less, NaOH (0.72 mol/L) showed the higher reactivity for hardly-hydrolysable ester bond than KOH(0.38 mol/L). According to solubility considering, dielectric constant (DC) at 230°C is 33 and almost equivalent to that of methanol (DC=32.6). Solubility of KOH for methanol is higher than that of NaOH. Therefore, it cannot explain the superiority of NaOH at 230°C for 1 hour or less.

The hypothesis is proposed based on the correlation between the length of polyester chain between two styrene chains and the atomic size of alkali. It is assumed that polyester chain (i) may not be uniformly distributed. The length of polyester chain (ii) is roughly three times larger than that of polyester chain (i). **Figure 2-2-13** shows a hypothesis of curing process from unsaturated polyester (UP) resin to thermosetting polyester resin. Firstly, one styrene is reacted with one fumaric acid in UP. Secondly, the reacted fumaric acid reacts with another styrene and another fumaric acid in another UP to develop styrene chain. In the case that another fumaric acid next to the cross-linked fumaric acid in the first UP becomes reactive, the reacted fumaric acid reasonably tends to react with the closest fumaric acid in the second UP to form the

second styrene chain via styrene monomers. It should be a fumaric acid next to the cross-linked fumaric acid in the second UP. The third fumaric acid from the cross-linked fumaric acid in the second UP should be too far to be reacted to form the second styrene chain. In this case, hardly-hydrolysable ester bonds are developed between the both styrene chains. In this case, hardly-hydrolysable ester bonds are developed between the both styrene chains. This tendency is considered to be succeeded in the third UP continuously. The hardly-hydrolysable ester bonds should be developed continuously in vertical direction. Finally, hardly-hydrolysable ester bonds are assumed to be concentrated vertically described in **Fig. 2-2-13**. The molecular structure around hardly-hydrolysable ester bond seems to be very rigid. The styrene chains and the polyester chains there are assumed to be more strongly immobilized than the structure around easily-hydrolysable ester bonds.

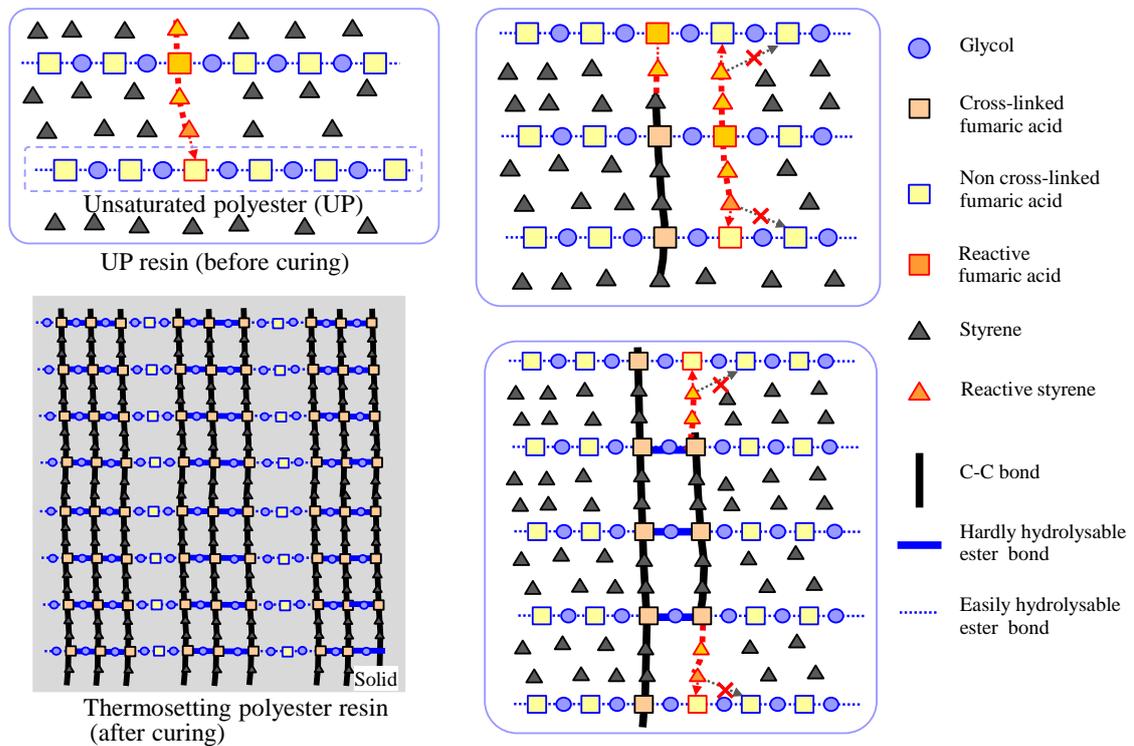


Figure 2-2-13 Hypothesis of curing process from unsaturated polyester (UP) resin

This structure is considered to generate the difficulty of hydrolysis not only for the steric hindrance but also for the limitation of movement of polyester chain. Hydrolysis is reversible reaction, whereas alkaline hydrolysis is irreversible reaction. In hydrolysis of the polyester chain (i) without alkali, even if the ester is reacted with water to be unstable, the ends of both bonds easily reacts to produce ester bond again since the both

ends is too close due to the mobility limitation caused by rigid structure around the ester bonds. Therefore, to break the hardly-hydrolysable ester bond in the narrow polyester chain (i), alkaline ion should be needed to prevent reversible reaction.

Atomic size of sodium is smaller than potassium. Na^+ ion seems to be able to penetrate in the narrow polyester chain (i) faster than K^+ ion to access hardly-hydrolysable ester bond. The situation of gathering polyester chain (i), the diffusion rate difference should be enhanced. On the reaction condition at temperature of 200°C for 4 hours and at temperature at 230°C for 1 hour or less, it is assumed that NaOH (0.72 mol/L) have an advantage due to the diffusion rate. The reaction condition at higher temperature or longer reaction time, yield of the SFC of NaOH (0.72 mol/L) is considered to be saturated and KOH (0.38mol/L) can catch up even its diffusion rate is lower.

2.2.4. Conclusions

In subcritical water hydrolysis of the thermosetting polyester resin of FRP, it was verified that the use of alkali catalysts such as KOH and NaOH played an important role in the subcritical hydrolysis of thermosetting polyesters reinforced with glass fibers, leading to high resin conversion rate and high production rates of glycols, organic acids, and SFC.

The evaluation results suggested that there were two types of esters due to different hydrolysable resistance as the hypothesis proposed by Oliveux [27]. However it was concluded that the definition of “non-hydrolysable ester bond” between glycol and fumaric acid in the hypothesis was not applicable for the thermosetting polyester resin sample used in this study.

The results indicated that roughly 63% of the polyester chain (i) between two styrene chains had only one glycol and roughly 37% of the polyester chain (ii) had only 2 glycols. It must be the first time to be proposed the molecular structure of the polyester chain in the thermosetting polyester resin. Based on these results, new hypothesis and definitions of “hardly-hydrolysable ester bond” and “easily-hydrolysable ester bond” were proposed. “Hardly-hydrolysable ester bond” was defined as ester bonds between glycol and two cross-linked fumaric acids in the polyester chain (i). “Easily-hydrolysable ester bond” was defined as ester bonds other than “hardly-hydrolysable ester bond.” However, this hypothesis should be verified.

More than 1.9 of molar ratio of KOH/carboxylic group of SFC was assumed to be needed to break “hardly-hydrolysable ester bond” to produce SFC. KOH contributions to the reaction acceleration and to the maximization of yield and quality of SFC were

concluded as i) accelerating to break “hardly-hydrolysable ester bonds”, ii) preventing secondary reaction, iii) making the separation process efficiently, and iv) providing solubility in subcritical water. However, iv) should be verified since solubility of SFC in subcritical water at 230°C are unknown.

The optimized conditions of subcritical hydrolysis using manufacturing waste of FRP bathtub based on SFC yield corresponded to either a reaction temperature of 230 °C, reaction time of 2 hours, and KOH concentration of 0.38 mol/L or 230 °C, 1 hour, and NaOH concentration of 0.72 mol/L. Using these conditions, the resin conversion rate and the production rate of SFC reached 92 % and 99.6 % respectively with KOH, and 82 % and 90 % respectively with NaOH.

The remarkable data which suggests the hydrolysis reactivity of NaOH and KOH for two different ester bonds were obtained. The hypothesis to explain the difference of the reactivity for the “hardly-hydrolysable ester bonds” between KOH and NaOH was proposed. It is assumed the difference of diffusion rate due to the difference of atomic size to penetrate the narrow polyester chain (i) to access the “hardly-hydrolysable ester bonds.” However, this hypothesis should also be verified. Their investigation is expected to provide new information of the structure of the thermosetting polyester resin.

2.3 Evaluation of subcritical hydrolysis process for various FRPs

2.3.1. Introduction

In 2.1 and 2.2, thermosetting polyester resin sample based on the same UP resin used in FRP bathtub and real FRP bathtub manufacturing waste sample of our company were used in the experiment. There are various FRPs in many applications with different composition of composites, resin composition of UP, and forming process. There are many UP resin in the market which has different composition of glycols and organic acids. However, all UP resin have fumaric acid for cross-linking with styrene. Therefore, styrene chain should be the SFC for all FRPs. In order to verify the possibility of this subcritical hydrolysis method applying to other FRPs than FRP bathtub of our company, various FRPs samples were tested.

Firstly, composition of each FRP was evaluated to know how much UP resin was contained per unit weight of FRPs. Secondly, subcritical hydrolysis experiment was conducted for each FRP to obtain the reactivity data such as conversion, the yield of SFC and glycol. Thirdly, SFC obtained from each FRP was analyzed to identify the molecular structure. They are considered to have a different Mw and S/F molar ratio. They indicate the molecular structure of styrene chain in thermosetting polyester resin. Such information was not existed since it was not able to analyze directly.

In FRP, there are various forming process. Sheet Molding Compound (SMC) , Bulk Molding Compound (BMC), and Hand lay-up(HL) are major forming process. SMC process has been most popular forming process. About half of FRP is using this process. Five bathtubs including our company and other companies were selected. HL process is preferable to large size FRP. Boat, water tank, septic tank, chemical tank for light and heavy chemical duty, and corrugated panel were selected. BMC process is used in small size FRP. Automobile parts such as lamp reflector, casing of electric breaker and motors were selected.

2.3.2. Materials and methods

In order to evaluate the possibility of applying subcritical hydrolysis to commercial materials, samples from various FRPs produced by different forming processes were tested. In the sheet molding compound (SMC) process, five samples from household bathtubs were tested. Bathtub #1 had the same composition as that of FRP samples used in paragraph 2.2. Samples from parts manufactured by hand lay-up, such as boat hull, tanks and corrugated panels were tested. Finally samples from parts made of bulk molding compound (BMC) and found in motors, breakers, and automobile parts such as

head lamp reflector were tested as well.

The composition of each FRP sample was analyzed by calcination, TG-DTA (SII Nano Technology Inc.:TG/TDA6300), and X-ray fluorescence (Rigaku:Syetem3080E), and FT-IR. FRP samples were evaluated using procedure described in paragraph 2.1 with sodium hydroxide (NaOH). Reaction conditions were 230 °C and 2 hours with 0.8 mol/L of NaOH. The ratio of FRP:NaOH solution was 1:10 for HL FRP samples and 1:4 for other FRP samples in weight. Molecular structure analysis of SFC obtained from each FRP sample was conducted as described in 2.1.

2.3.3. Results and discussion

In FT-IR analysis identified the kind of dicarboxylic acid used in each FRP sample. In bathtub formed by SMC process and automobile parts, breaker, and motor formed by BMC process, fumaric acid was mainly used. In HL process samples, boat, septic tank, and corrugated panel mainly used orthophthalic acid and water tank, and chemical tanks used isophthalic acid.

In TG-DTA analysis, TG-DTA curve become flat around 500°C. In general, total weight loss from initial weight to that point is considered as total weight of organic compound. **Figures 2-3-1** and **2-3-2** show TG-DTA analysis result for bathtub#4 and septic tank, respectively. In **Fig.2-3-1**, another weight loss from around 600°C to around 700°C was observed. It was considered decarbonization of CaCO₃ converting to CaO. Total weight of CaCO₃ was calculated based on the weight loss of carbonation. In **Fig.2-3-2**, another weight loss was not observed. It indicated no CaCO₃ was contained. The weight over 700°C was defined as glass fiber and other inorganic materials.

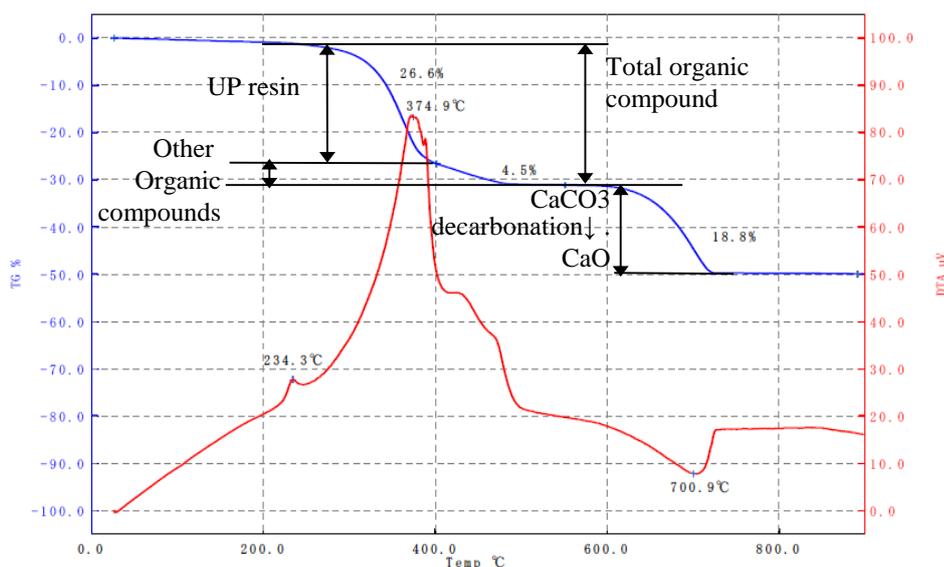


Fig. 2-3-1 TG-DTA of Bathtub #4

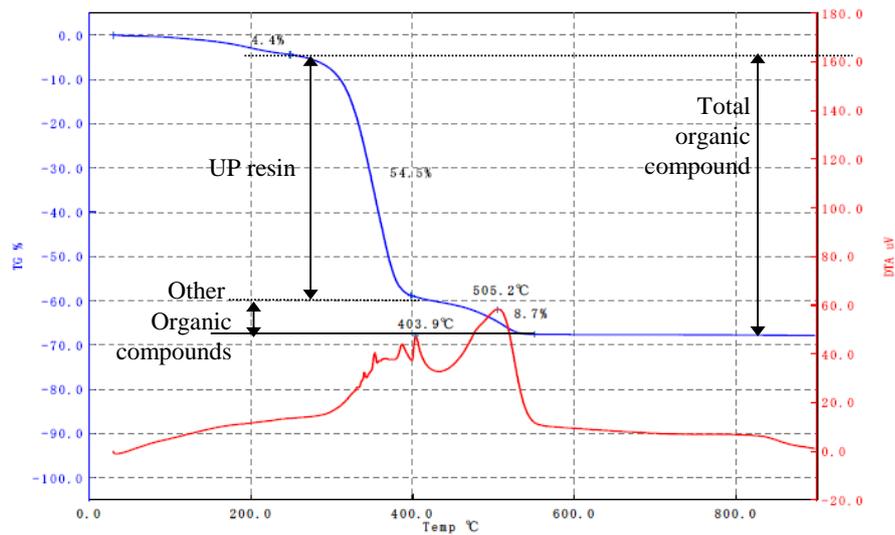


Fig. 2-3-2 TG-DTA of Septic tank

It is difficult to distinguish the UP resin and other organic compound such as LPA and other additives in thermosetting polyester resin by any analysis. TG-DTA curve of all FRP samples, gradient of TG-DTA curve changed around 400°C. Total weight loss from initial weight to that point was assumed the weight loss of UP resin. This assumption was verified by bathtub#1 which composition of organic compound was known. Therefore, it was concluded the weight of UP resin. Rest of total organic compound defined as other organic compound.

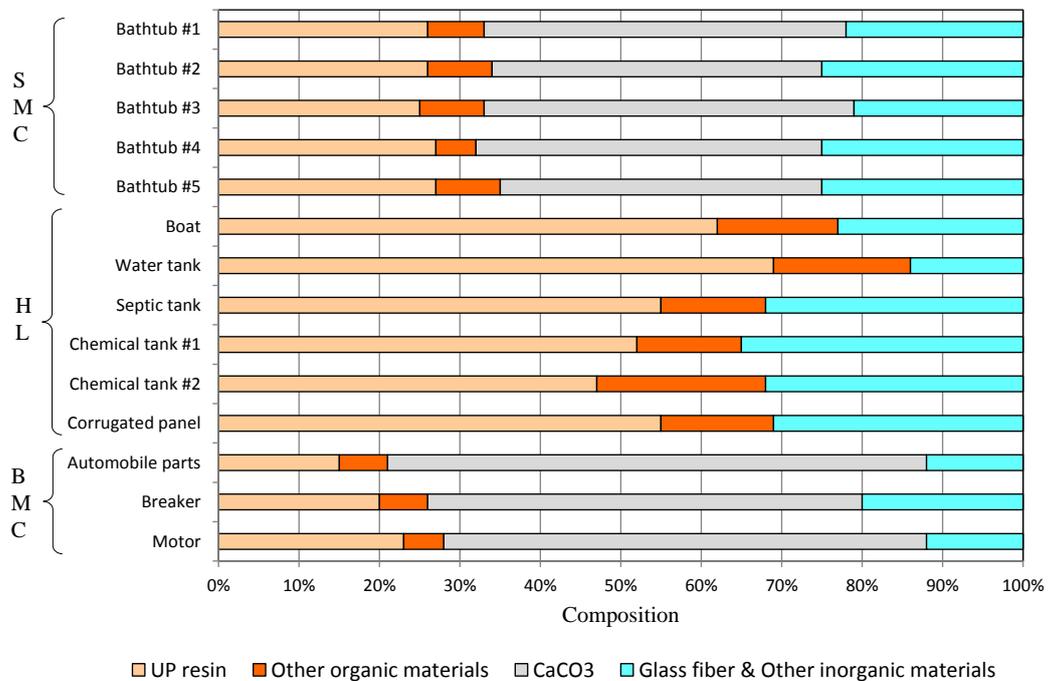


Fig. 2-3-3 Composition of each FRP

Based on the analysis, composition of UP resin, other organic compounds, CaCO₃, and glass fiber and inorganic materials were calculated. **Figure 2-3-3** shows the result of analysis. In HL samples, CaCO₃ was not contained. Ratio of UP resin was higher than other FRPs at a range from 47 to 69%. Especially, boat and water tank showed highest value. The higher SFC yield per unit weight of waste was expected. In BMC samples, ratio of UP resin was smaller and ratio of CaCO₃ was higher than other FRPs.

In order to verify the possibility of this method applying to thermosetting polyester resin of various FRPs, subcritical hydrolysis experiment was conducted and products obtained were analyzed. It is necessary to know the difference of reactivity and obtained products between bathtub #1 and other FRPs to verify the possibility since most of evaluation for various applications used SFC sample obtained from bathtub #1.

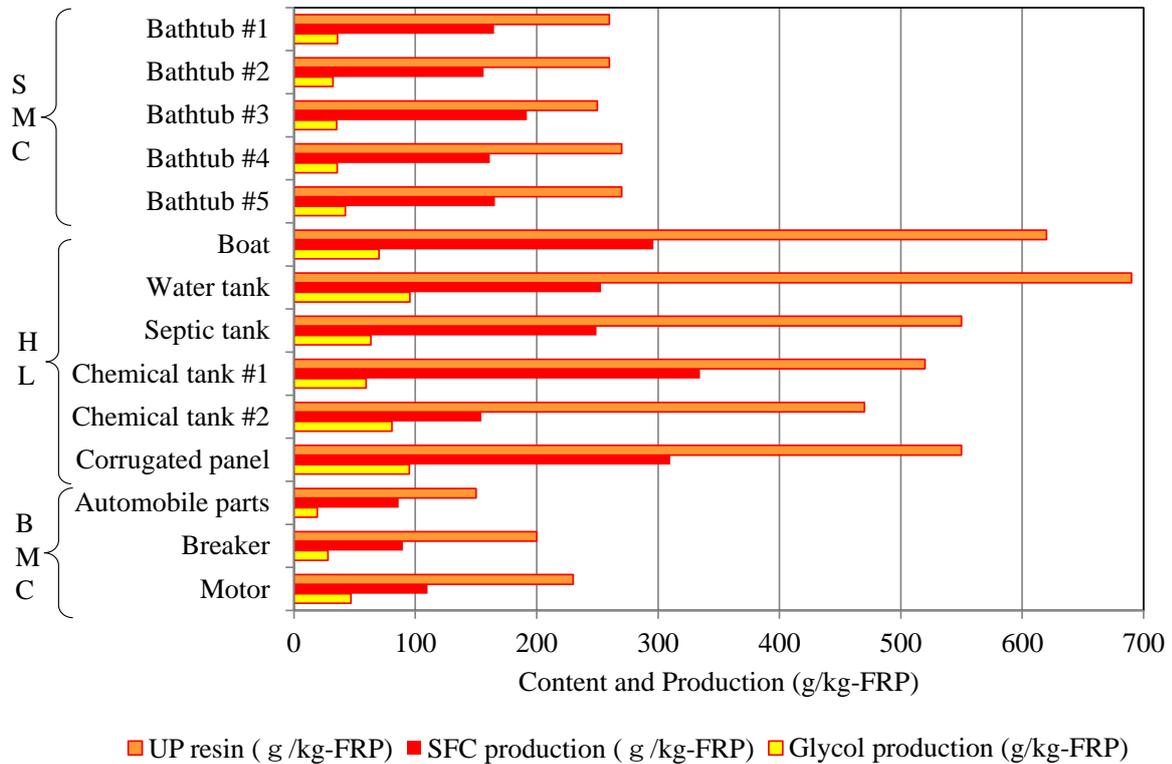


Fig. 2-3-4 Production of SFC and glycol per 1 kg-FRP

Figure 2-3-4 shows the weight of UP resin and the yield of SFC and glycol per unit weight of FRP for various FRPs. In all SMC and HL samples, SFC yields were almost same as or higher than bathtub#1. HL samples showed higher yield of SFC than other FRPs based on higher content of UP resin. In terms of SFC yield, HL process FRPs have an advantage. However, only chemical tank#2 for heavy chemical duty showed

relatively lower SFC yield than other HL samples. BMC samples showed relatively lower SFC yield than that of bathtub #1. However, each SFC has different molecular structure which affects the value of additives. In economical consideration of recycling, income should be based on the yield multiply the value.

Figure 2-3-5 shows yield of SFC and glycol per unit weight of UP resin. A shade diagonal area indicates unreacted resin residue. Rest of total area indicates conversion. All FRPs except chemical tank#2 showed conversions more than 70%. Most of them were more than 80% almost equivalent to bathtub#1 manufactured by our company. Chemical tank#2 for heavy chemical duty was the lowest. It is required higher resistance for chemical duty. Therefore, it is assumed that it should have higher resistance for hydrolysis reactivity. Whereas, chemical tank#1 for light chemical duty, corrugated panel, and motor, showed over 95% conversion. In weight ratio of SFC to initial thermosetting polyester resin, all FRPs except water tank and Chemical tank#2 showed more than 45%. The different between bathtub#1 of 62% and most of them were 20% or less. Therefore, it was concluded that this method was verified effective for most of FRPs. Significant difference of sample using each dicarboxylic acid for the reactivity was not observed.

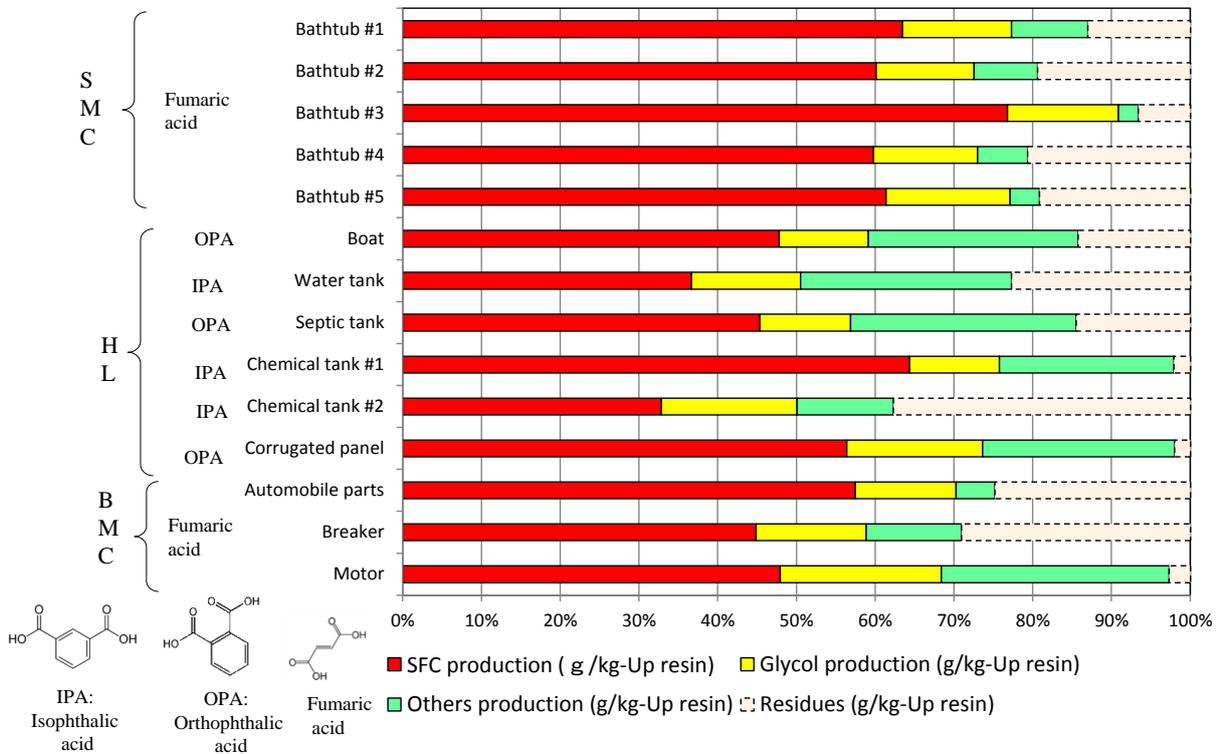


Fig. 2-3-5 Production of SFC and glycol per 1 kg-UP resin

Figure 2-3-6 shows share of SFC and glycol in reactant. Share of SFC showed a range from 48% to 82%. All SMC samples showed relatively higher share of SFC than other FRPs. HL samples showed relatively lower share of SFC except chemical tank#1. In those samples, phthalic acid as saturated carboxylic was used. They can be used only for polyester chain. Therefore, it is assumed that the ratio of polyester chain to styrene chain is higher which causes the relatively low share of SFC.

In the **section 2.2**, the hypothesis of two kinds of ester with different hydrolysable resistance was proposed. It was assumed that “hardly-hydrolysable ester bonds” tend to be remained in unreacted resin residues than “easily-hydrolysable ester bonds.” Therefore, it is reasonable to consider that ratio of styrene chain as SFC in unreacted residue resin was higher than polyester chain. It suggests that SFC share should be increased if conversion reached 100%.

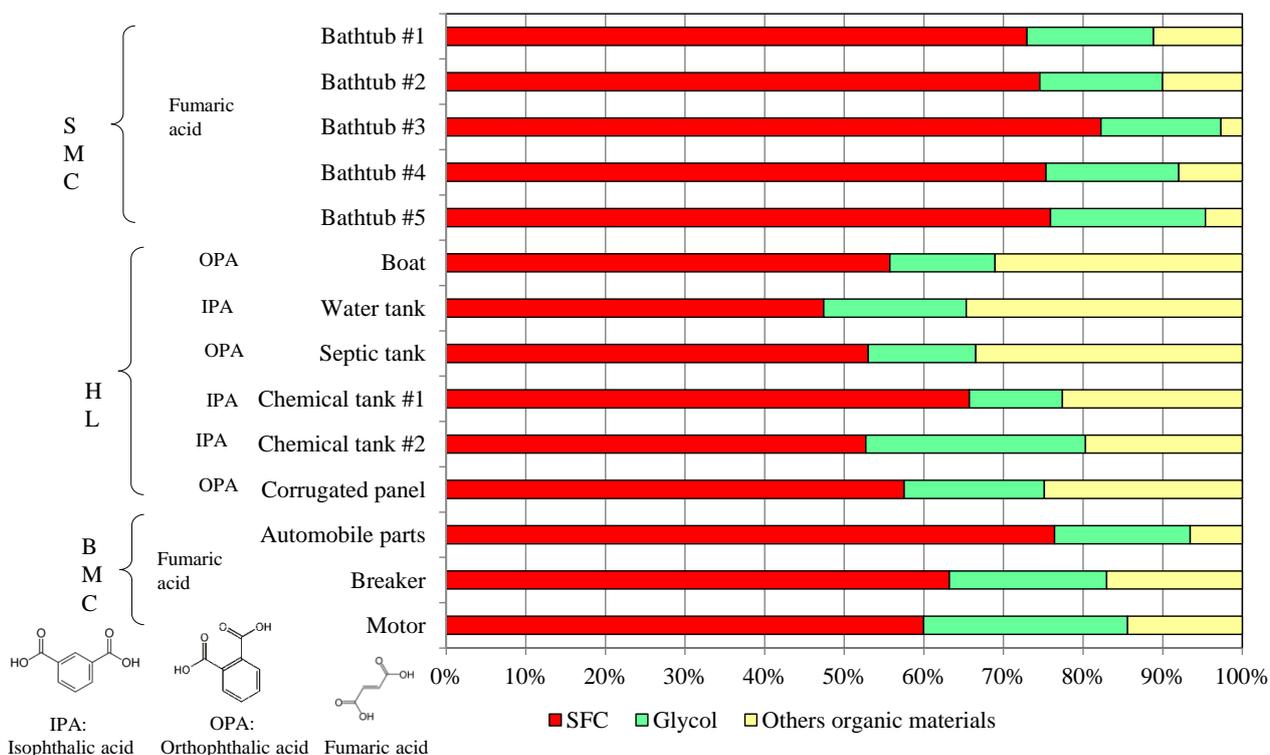


Fig. 2-3-6 Composition of reactants

It is important for the SFC obtained from each FRP to explore the most appropriate application based on the molecular structure. However, molecular structure of inside of the thermosetting polyester resin including styrene chain was completely unknown. There is no method to observe it directly. Subcritical hydrolysis with alkali enabled to conduct it. The styrene chain could be extracted as the SFC from the thermosetting

polyester resin with no damage. It should be the first time to clarify the molecular structure of thermosetting polyester resin in various FRPs. **Figure 2-3-7** shows the weight-averaged molecular weight (Mw) of the SFC obtained from FRP samples. In SMC samples, it was a range from 35,000 to 54,000 with an average of 46,000. In HL samples, it was a range from 34,000 to 90,000 and averaged 55,000. In BMC samples, it was a range from 23,000 to 30,000 and averaged 27,000. BMC samples showed a relatively smaller Mw.

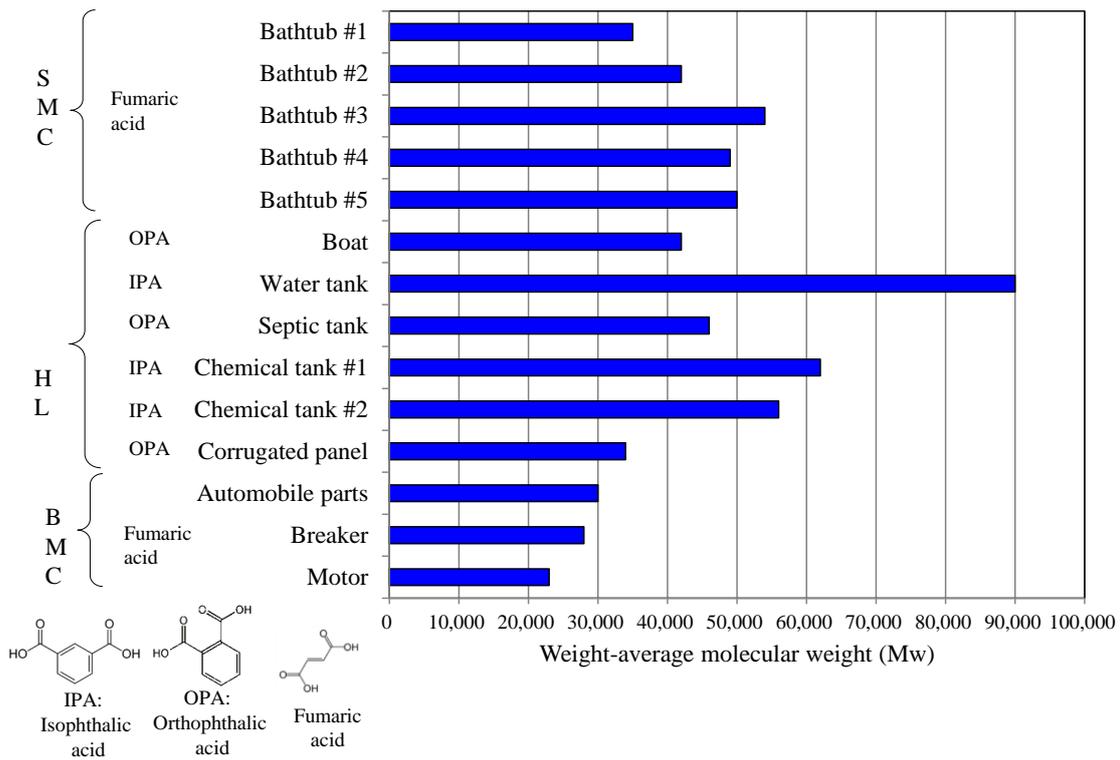


Fig. 2-3-7 Weight-average molecular weight (Mw) of SFC obtained from each FRP sample

Figure 2-3-8 shows the styrene/fumaric acid (S/F) molar ratios of the SFC obtained from each FRP sample. In SMC samples, it was a range from 1.8 to 3.2 and averaged 2.34. In HL samples, it was a range from 2.40 to 3.2 and averaged 2.57. In BMC samples, it was a range from 1.6 to 1.9 and averaged 1.73. BMC samples showed a relatively smaller S/F molar ratio.

Mw and S/F molar ratio are assumed to affect the resin property. The formation of the styrene chains during the curing process must be clarified. This method is also expected to contribute to the fundamental research of thermosetting polyester resins.

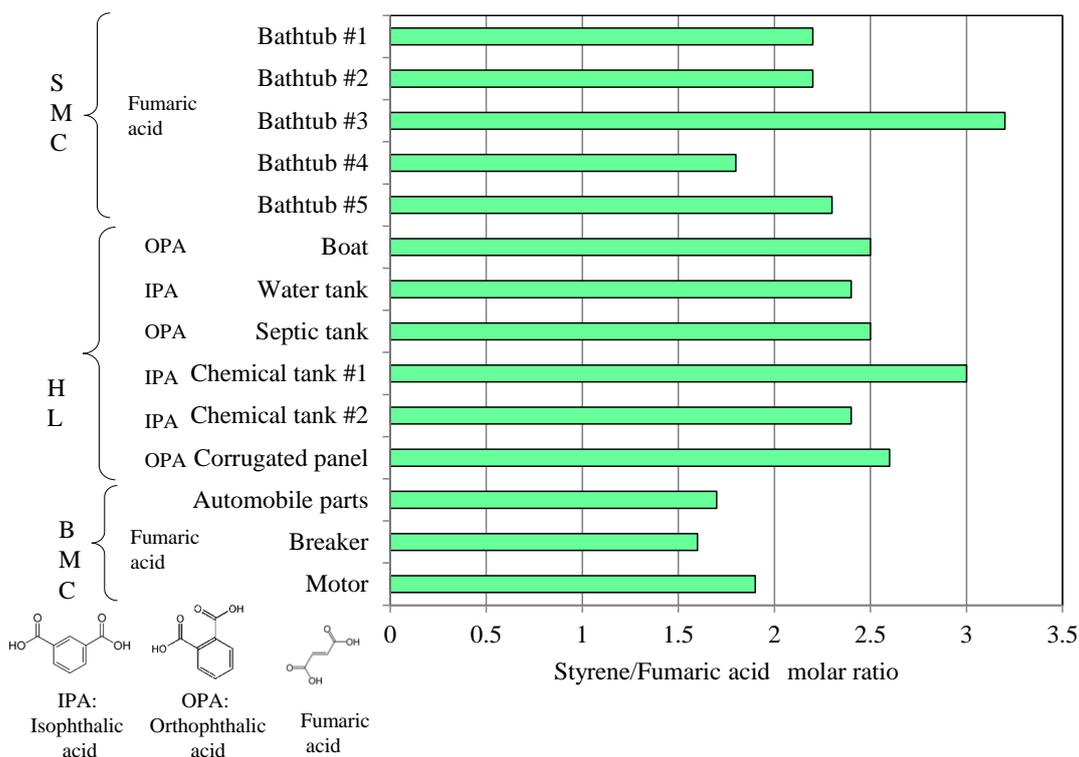


Fig. 2-3-8 Styrene / fumaric acid molar ratio of SFC obtained from each FRP sample

2.3.4. Conclusions

The practicality of this method was verified by evaluating the subcritical hydrolysis applied to various types of commercial FRPs. Reaction conditions were 230 °C and 2 hours with 0.8 mol/L of NaOH. The results were compared with that of bathtub#1 of our company. In all SMC and HL samples, SFC yields per unit weight of FRP were almost same as or higher than bathtub#1. HL process FRPs have an advantage with higher SFC yield based on high content of UP resin. In weight ratio of SFC to initial thermosetting polyester resin, the difference between bathtub#1 and most of FRP samples were less than 20%. Therefore, it was concluded that this method was verified effective for most of FRPs.

The analysis of the recovered products allowed the determination of the chemical composition of the studied materials. In particular it allowed the characterization of the SFC recovered after hydrolysis of the polyester resins. Mw was a range from 23,000 to 90,000. S/F molar ratio was a range from 1.6 to 3.2. The SFCs obtained from various types of commercial FRPs are concluded to have a potential of applying to high performance additives based on the molecular structure. This can also contribute to a better understanding of the formation of the styrene network during the curing process.

2.4 Overall Conclusions

(Subcritical hydrolysis of thermosetting polyester resin)

In recycling thermosetting polyester resin using subcritical water, the hypothesis that subcritical hydrolysis on the reaction condition at a temperature of 230°C or less with alkali catalyst was proposed. Firstly, fundamental verification was conducted using thermosetting polyester resin based on the resin composition of our company's FRP bathtub. Secondly, functional mechanism of alkali catalyst and molecular structure of thermosetting polyester resin were investigated. Thirdly, reaction conditions and catalysts were optimized using real FRP manufacturing waste of our company's bathtub. Lastly, this method was verified the possibility applying to thermosetting polyester resin used in other FRPs than our company's bathtub.

Fundamental verification

Fundamental verification was conducted using thermosetting polyester resin sample. The composition of UP resin used in the sample was based that used in FRP bathtub. On the reaction condition at a temperature of 230°C, at a pressure of 2.8MPa, at a reaction time of 4 hours with KOH, it was demonstrated to dissolve 96% of the initial thermosetting polyester resin in the reaction product liquid as usable matters. SFC was obtained with 75% of the initial thermosetting polyester resin.

It was concluded that the hypothesis was successfully verified to realize almost ideal reaction condition which hydrolysis was dominant and pyrolysis was minimized. Molecular structure analysis showed that the SFC had Mw of 30,000, S/F molar ratio of 2.2, and almost no degradation of carboxylic group. It indicates that the SFC has a high quality as functional polymer. It is considered the first achievement to extract the SFC as functional polymer and to clarify its molecular structure.

Functional mechanism of alkali catalyst and molecular structure of thermosetting polyester resin

Subcritical hydrolysis experiment of thermosetting polyester resin and unsaturated polyester (UP) before curing was conducted on the above reaction condition with various concentration of KOH to clarify functional mechanism of KOH.

Investigation of molecular structure, the share of the polyester chain (i) which has only one glycol was roughly 63% and the polyester chain (ii) which has two glycols was roughly 37%. The hypothesis that there were two different types of ester bonds, "hardly-hydrolysable ester bond" in the polyester chain (i) and "easily-hydrolysable ester bond" for ester bonds other than "hardly-hydrolysable ester bond." More than 1.9 of molar ratio of KOH/carboxylic group of SFC was assumed to be needed to break "hardly-hydrolysable ester bond" to produce SFC. However, this hypothesis should be

verified.

KOH is assumed to be necessary to break “hardly-hydrolysable ester bond.” Other KOH contributions to the reaction acceleration and to the maximization of yield and quality of SFC were also clarified.

Optimization of reaction conditions and catalysts

The optimized conditions of subcritical hydrolysis using manufacturing waste of FRP bathtub based on SFC yield corresponded to either a reaction temperature of 230 °C, reaction time of 2 hours, and KOH concentration of 0.38 mol/L or 230 °C, 1 hour, and NaOH concentration of 0.72 mol/L.

The remarkable data which suggests the hydrolysis reactivity of NaOH and KOH for two different ester bonds were obtained. NaOH (0.72mol/L) showed higher reactivity to break “hardly-hydrolysable ester bonds” than KOH (0.38mol/L) at 200°C for 4 hours and 230°C for 0.5 hours. In terms of SFC yield according to the reaction time, NaOH would be preferable for commercialization.

The hypothesis to explain the difference of the reactivity for the “hardly-hydrolysable ester bonds” between KOH and NaOH was proposed. It is assumed the difference of diffusion rate due to the difference of atomic size to penetrate the narrow polyester chain (i) to access the “hardly-hydrolysable ester bonds.” This hypothesis should also be verified.

Evaluation of subcritical hydrolysis process for various FRPs

To verify this method applying to thermosetting polyester resin used in other FRPs, subcritical hydrolysis experiments for various FRPs were conducted and SFC obtained from each FRP was analyzed.

Reaction conditions were 230 °C and 2 hours with 0.8 mol/L of NaOH. In all SMC and HL samples, SFC yields per unit weight of FRP were almost same as or higher than bathtub#1. HL process FRPs have an advantage with higher SFC yield based on high content of UP resin. It was concluded that this method was verified effective for most of FRPs.

The SFCs obtained from various types of commercial FRPs are concluded to have a potential of applying to high performance additives based on the molecular structure. This can also contribute to a better understanding of the formation of the styrene network during the curing process to improve the property.

3. Application of styrene-fumaric acid copolymer (SFC)

3.1 Introduction

In **chapter 2**, the method of recycling thermosetting polyester resin using subcritical water was established. **Figure 3-1-1** shows concept of this method using NaOH.

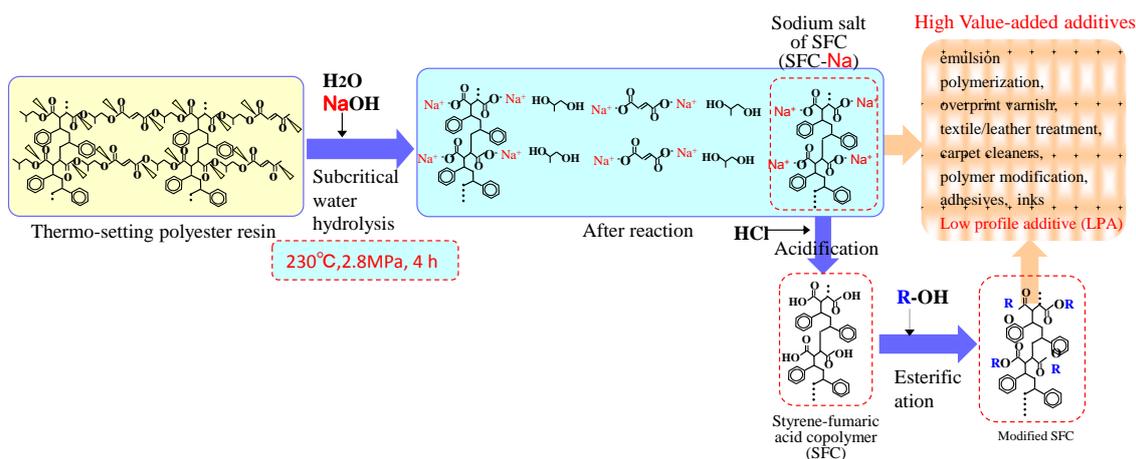
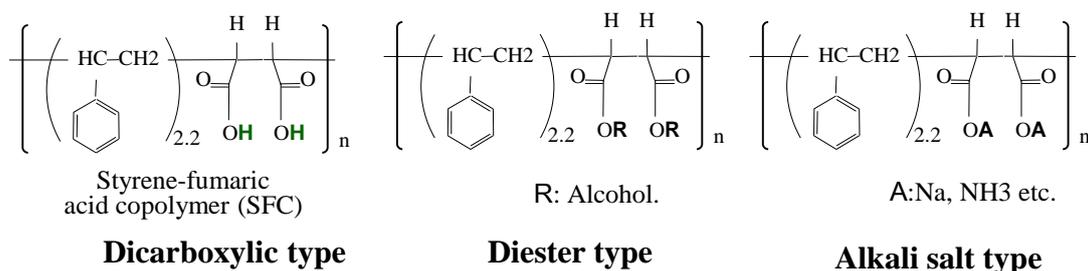


Fig. 3-1-1 Concept of thermosetting polyester resin recycling using subcritical water

In the study of application of SFC obtained, it was verified the possibility of the SFC applying to various high performance additives. SFC has diester type, alkali salt solution type, and dicarboxylic type. **Scheme 3-1-1** shows molecular formula of SFC, SMA, diester type, and alkali salt type.



Scheme 3-1-1 Structure formula of SFC, Diester type, Alkali salt type

In addition, dicarboxylic type and diester type SFC which are not in the market are expected to create new high performance additives and new products based on the new additives.

Firstly, application of diester type, low profile additives (LPA) for FRP forming was selected. The LPA is a key additive to determine product quality such as surface appearance of FRP with controlling shrinkage during curing process. In commercial LPA, polystyrene mainly is used. Styrene skeleton of SFC was expected to create shrinkage control performance.

Secondary, application of alkali salt solution type was aqueous agent. There are various aqueous agent applications. Among them, dispersing agent, detergent builder, and surface sizing agent for papers were selected. They should have hydrophobic region and hydrophilic region. Alkali salt of SFC has styrene skeleton as hydrophobic region and alkali salt of dicarboxyl acid as hydrophilic region. They were expected to contribute to create performance as aqueous agent.

Third application of SFC is dicarboxylic type, SFC itself. Dicarboxylic type, SFC, has higher reactivity than anhydride type, SMA, based on carboxylic acid. SFC has styrene skeleton and carboxylic acid which are hydrolyzed from polyester chain of thermosetting polyester resin. Therefore it was assumed that SFC had a potential to applied to compatibilizing agent for polymer alloy of polystyrene type resin and polyester type resin was selected as application of SFC..

3.2 Low profile additive (LPA)

3.2.1. Introduction

The effectiveness of the LPA is shown in **Fig.3-2-1**. During curing process of FRP, volume shrinkage of FRP board occurred based on the volume change of styrene from liquid to solid without LPA. It caused corrugation and crack. In the case the LPA used, it created voids during curing process to compensate volume shrinkage to prevent corrugation and crack generation as shown in **Fig.3-2-1**.

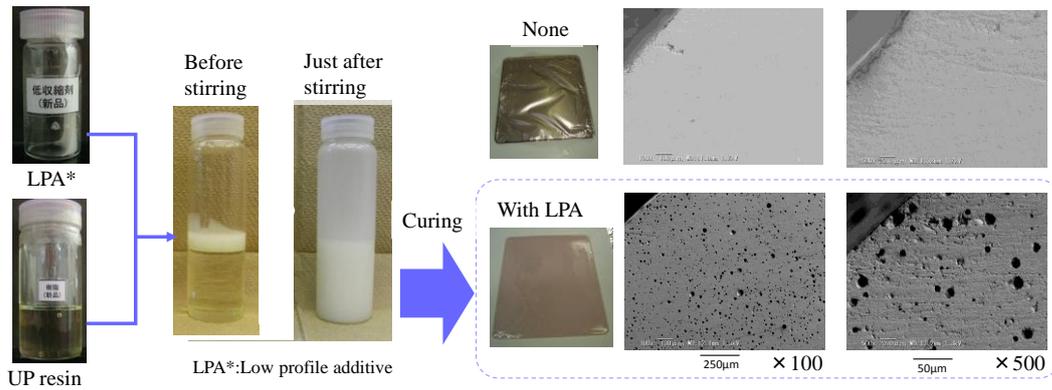


Fig. 3-2-1 Low profile additive (LPA) for FRP forming

In general, polystyrene which has Mw of a range from 150,000 to 250,000 is main component for commercial LPA used in sheet molding compound (SMC) type FRP. SMC is major forming method applying to bathtub and other applications. The SFC was considered to have the possibility to apply to the LPA since it also has styrene skeleton.

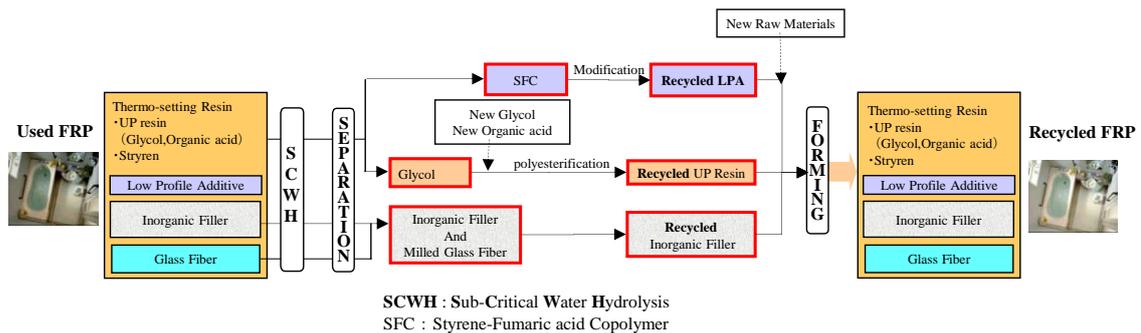


Fig. 3-2-2 Process flow of FRP recycling using subcritical water.

Figure 3-2-2 shows process flow of FRP recycling using subcritical water. Firstly FRP waste was ground and supplied to subcritical hydrolysis process. The thermosetting polyester resin was dissolved by subcritical hydrolysis and then separated from the solid such as glass fibers and inorganic filler. After the reaction, the glass fiber was no longer

the reinforced fiber since it was hydrolyzed severely. Therefore, it cannot recycle to FRP as the glass fiber. However, it could be recycled to FRP with inorganic filler again as used inorganic filler. After the solid separation, resin raw materials and alkali salt of the SFC was dissolved in the reaction product liquid. Acid was added to the reaction product liquid to precipitate the SFC. It was separated from the reaction product liquid and the modified to produce recycled LPA recycling to FRP again. Glycol in the reaction product liquid was recovered and polyesterified with new resin raw materials to produce recycled UP resin and then recycled to FRP again. That is the first application of SFC as diester type.

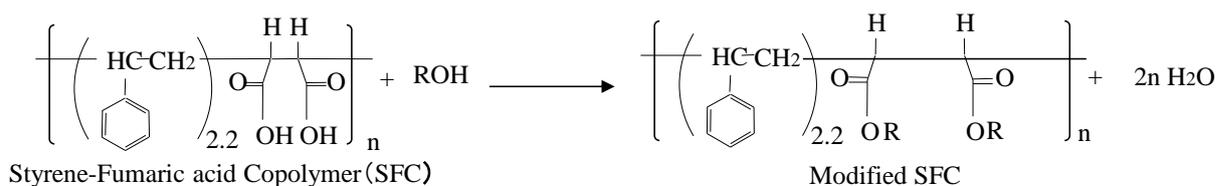
Several subjects were investigated. The SFC is very difficult to be separated from the reaction liquid due to its high hydrophilicity. Water content in the SFC after separation using conventional filter press was 90%. The SFC:Water was 1:9. Water content should be minimized for the next step, esterification process. Efficient separation process was examined.

In enhanced recycling of the SFC, solubility with styrene is required to generate shrinkage control effect. Therefore, the SFC has to be modified to be hydrophobic. Several alcohols were selected to be esterified with SFC to produce the modified SFC. Styrene was added to the modified SFC to produce a recycled LPA and then evaluated the shrinkage control effect. FRP test board was produced using the recycled LAP and a commercial LPA and compared. SFC derived from motor and water tank were also modified to produce recycled LPA and then evaluated.

3.2.2. Materials and methods

3.2.2.1 Optimization of alcohol in esterification of SFC

In esterification of SFC with alcohol, alcohol, 1-butanol, 2-ethyl-1-hexanol, and 1-octanol were selected as esterification agent. Esterification of SFC is described in **Scheme 3-2-1**. They were completely esterified with SFC and the esterified SFC was analyzed by FT-IR. When the peak of ester was observed and the peak of carboxylic group was disappeared, it was defined as complete esterification.



Scheme 3-2-1 Esterification of SFC

Styrene was added to the esterified SFC with a ratio of 7:3 to produce the recycled LPA and observed by visual contact. Viscosity was also measured. The recycled LPA was mixed with styrene and UP resin with a ratio of 1:4. They were stirred and observed by visual contact and optical microscope with time to evaluate solubility. Shrinkage control effect of each modified SFC was also evaluated. Thermosetting polyester resin was prepared with UP resin and each recycled LPA. Content unit of the recycled LPA was varied for 100 units of UP resin and measured volume shrinkage rate. The volume shrinkage rate was calculated according to equation (3-2-1)

$$\text{Volume shrinkage rate (\%)} = 100 \times (Da - Db) / Da \quad (3-2-1)$$

where Da ; density after curing, Db ; density before curing.

3.2.2.2 SFC separation and modification process

In SFC separation experiment, reaction liquid after inorganic materials separation from reaction slurry was used. The reaction slurry was obtained from subcritical water hydrolysis of FRP bathtub manufacturing waste on the reaction condition at 230°C, 2.8MPa, for 2 hours. FRP: 0.8 mol/L NaOH solution was 1:4.

3.2.2.3 Evaluation of the recycled LPA

The selected alcohol was esterified with SFC to produce the modified SFC. Styrene was added to the modified SFC with a ratio of 7:3 to produce a recycled LPA. The recycled LPA and 2 commercial LPAs were mixed with UP resin to be evaluated solubility and compared.

FRP test board sample was produced using the recycled LAP and a commercial LPA. The FRP sample board was evaluated shrinkage control effect and other product quality item. Volume shrinkage ratio after curing was measured based on JIS K6911-1195; Testing method for thermosetting plastics, 5.7. Volume shrinkage rate and heating shrinkage rate (molding compound). In hot water durability test, appearance and color change of the FRP sample board after dipping in 90°C hot water for 120 hours were evaluated. Mechanical strength (pulling and bending strength, impact tenacity) was also tested. FRP test board samples were cut and cross section was observed.

SFCs derived from motor and water tank were modified to produce the recycled LPA. They were also used to produce FRP sample boards and then evaluated shrinkage control.

3.2.3. Results and discussion

3.2.3.1 Optimization of alcohol in esterification of SFC

Table 3-2-1 shows the reaction condition of each alcohol for complete esterification. One- butanol and 1- octanol were same straight chain but the chain length was different. Higher temperature was needed for 1-octanol than that of 1-butanol. Number of carbon for 1-octanol and 2-ethyl-1-hexanol were same. Longer reaction time was needed for 1-octanol than that of 2-ethyl-1-hexanol.

Table 3-2-1 Each alcohol and esterification condition

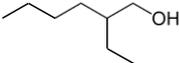
	Molecular formula	Temperature	Reaction time
1-Butanol		140 °C	17 h
2-Ethyl-1-hexanol		175 °C	5 h
1-Octanol		175 °C	17 h

Table 3-2-2 shows the evaluation results of styrene solubility. The SFC esterified with 1-butanol was powdered state. After styrene addition, it became swellheaded. Viscosity was extremely high value of 1,800mPAs. The SFCs esterified with 1-octanol and 2-ethyl-1-hexanol appeared caramel state. They were dissolved in styrene and showed low viscosity.

Table 3-2-2 Solubility test results of the esterified SFC for styrene

Alcohol	Appearance	Styrene solubility	Viscosity (RT:26.7°C)
1-butanol			1800 mPAs
2-ethyl-1-hexanol			65 mPas
1-octanol			69 mPas

Table 3-2-3 shows solubility test results of the recycled LPA using the SFC esterified with 1-butanol and 1-octanol for UP resin. In the recycled LPA using the SFC esterified with 1-butanol, the recycled LPA was phase separated from UP resin with averaged domain diameter of a range from 20 to 50 μm just after stirring. Each domain was gradually combined together and domain size became larger after 15 min. After 1 week, it was no longer dissolved in the UP resin and was separated with agglomeration. On the other hand, the recycled LPA using the SFC esterified with 1-octanol was highly and uniformly dispersed in the UP resin with domain averaged diameter meter of approximately 1 μm just after stirring. The domain size became slightly larger with time. But the domain size seemed be constant after 15 min. and they were kept highly dispersed and dissolved in the UP resin even after 1 week. It was concluded that longer alkyl chain alcohol was effective for solubility for styrene and UP resin. It was expected to show higher shrinkage control effect.

Table 3-2-3 Solubility test results of the recycled LPA for UP resin

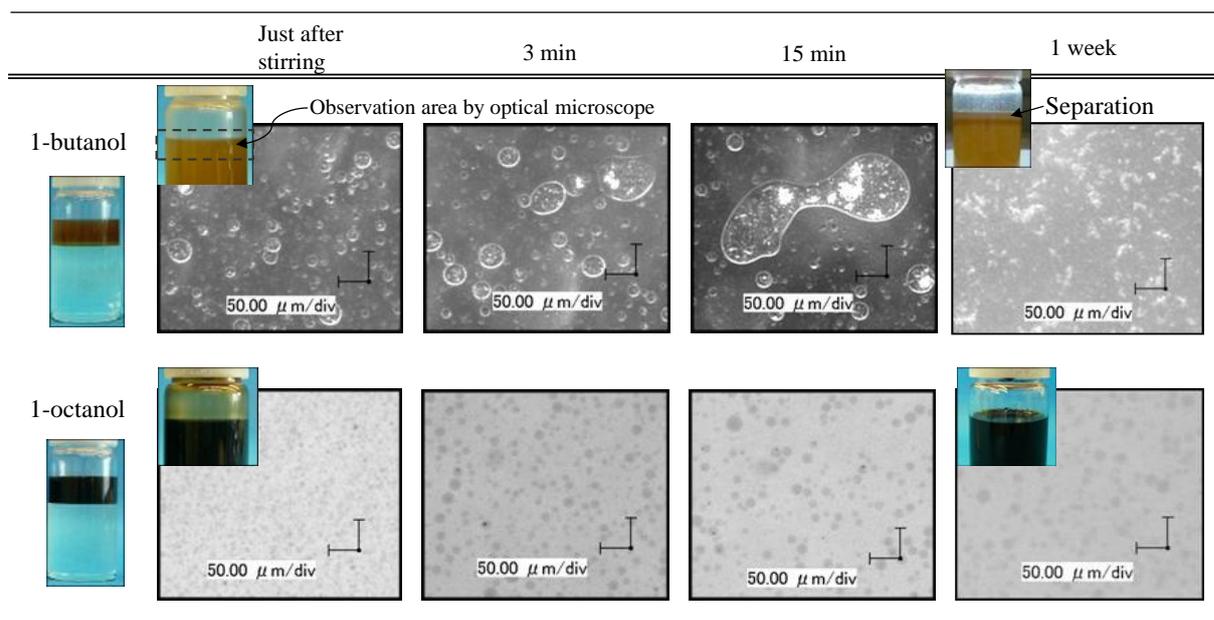


Figure 3-2-3 shows the evaluation results of shrinkage control effect. It shows that the volume shrinkage rate showed lower with increasing content of the recycled LPA. The SFC esterified with 1-octanol showed the best performance. **Scheme 3-2-2** shows the esterification of SFC with 1-octanol.

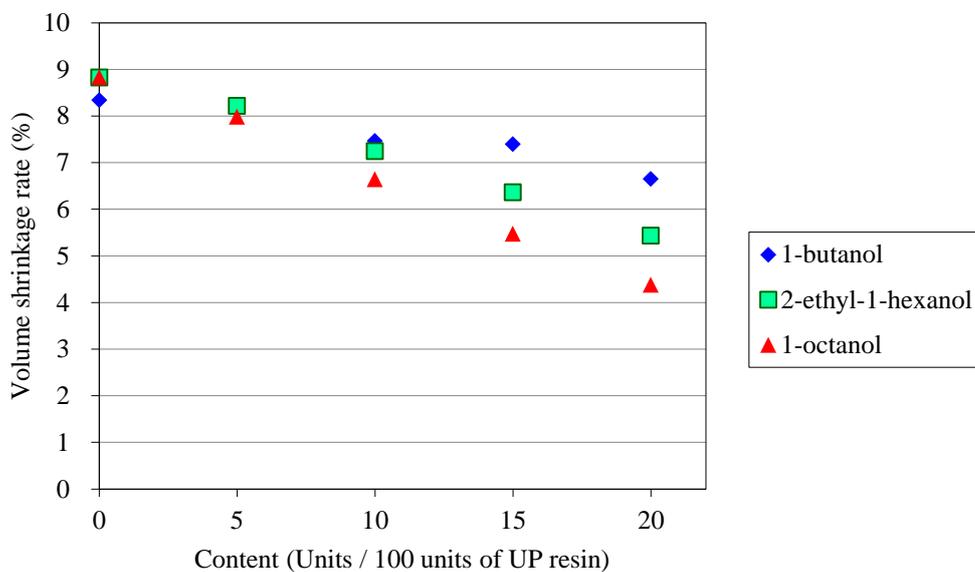
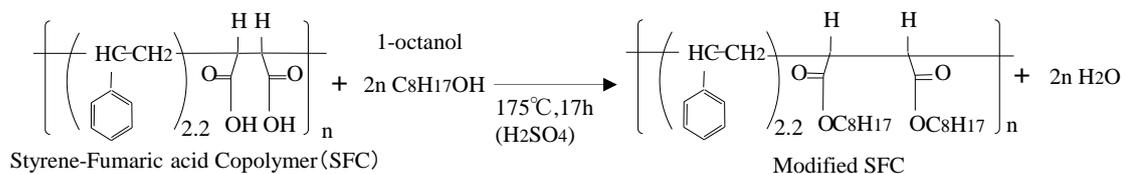


Fig. 3-2-3 Shrinkage control effect of recycled LPA using the modified SFC



Scheme 3-2-2 Esterification of SFC with 1-octanol

SFC and esterification reaction was conducted on the reaction condition at 175°C for 17 hours. Almost 100% of the SFC in 1-octanol was modified. After modification reaction, water was added to the reaction liquid. They were stirred at 80°C for 1 hour to remove impurities such as H₂SO₄. 90% of H₂SO₄ was removed.

3.2.3.2 SFC separation and modification process

In modification of the SFC, 1-octanol was most effective. We focused that 1-octanol has higher solubility for the SFC than water. **Figure 3-2-4** shows the experiment result of the SFC separation and modification processes using 1-octanol. H₂SO₄ was added to the reaction liquid containing styrene-sodium fumarate copolymer to separate out the SFC. They became clouded as shown in **Fig.3-2-4**. 1-octanol was added to the white water. They were stirred at 90°C for 1 hour to extract the SFC to 1-octano. After extraction, it was cooled and left at 25°C for 1 hour. 1-octanol extracting the SFC and aqueous solution were separated as shown in **Fig.3-2-4**. 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. Sulfuric acid was added to 1-octanol phase containing SFC as catalyst and then esterification reaction was conducted to produce modified SFC at 175°C for 17 hours. Styrene was added to the modified SFC with a ratio of 7:3 to produce a recycled LPA.

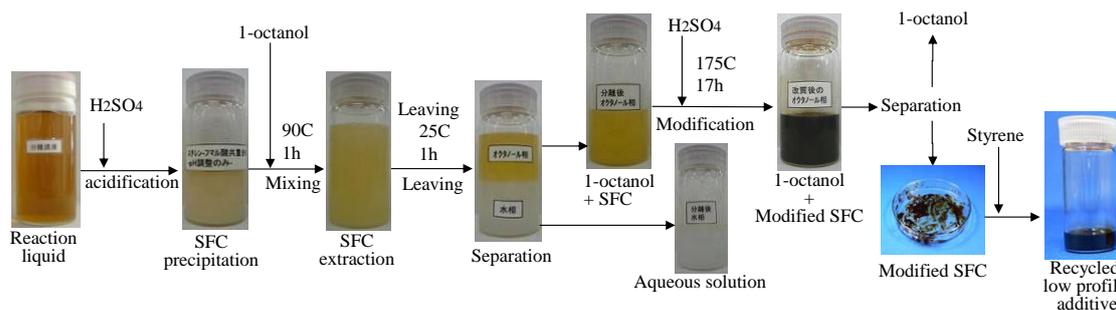


Fig. 3-2-4 SFC separation and modification process experiment

3.2.3.3 Evaluation of the recycled LPA

The recycled LPA obtained from the SFC separation and modification process using 1-octanol was evaluated solubility for UP resin with a commercial LPA and compared. **Figure 3-2-5** shows the evaluation results. Firstly, two phases of the UP resin and the LPA were observed for the commercial LPA and the recycled LPA. Just after stirring, only one phase was observed for the both LPA. They were considered to be dissolved in the UP resin. After 1 week, the recycled LPA was still continuously dissolved in the UP resin, whereas the commercial LPA was separated from the UP resin. It was concluded that the recycled LPA had much higher solubility for the UP resin than the commercial LPA.

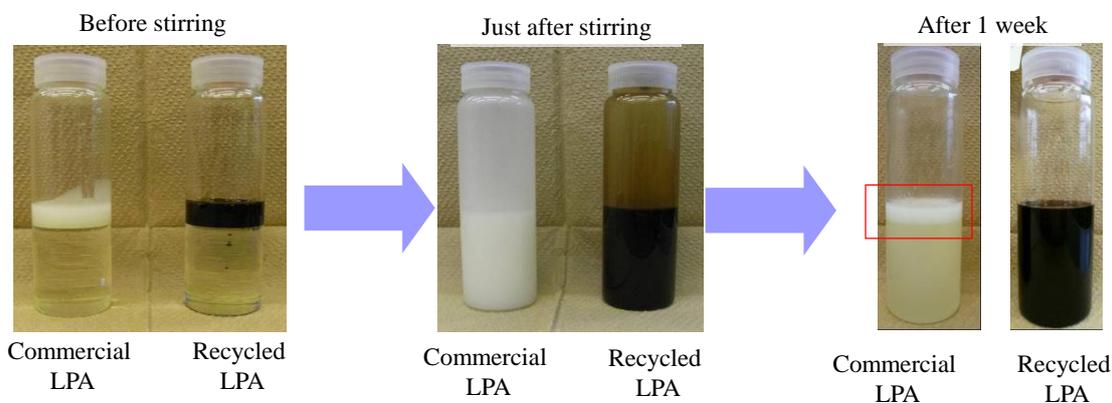


Fig. 3-2-5 Evaluation results of solubility of recycled LPA for UP resin.

The recycled LPA and 2 commercial LPAs were mixed with UP resin to evaluate their solubility to UP resin. **Fig. 3-2-6** shows the evaluation results. General commercial LPA was described in 3.2.1. High performance LPA was block polymer of polyvinyl acetate and polystyrene and much more expensive than general one. Mw was confidential.

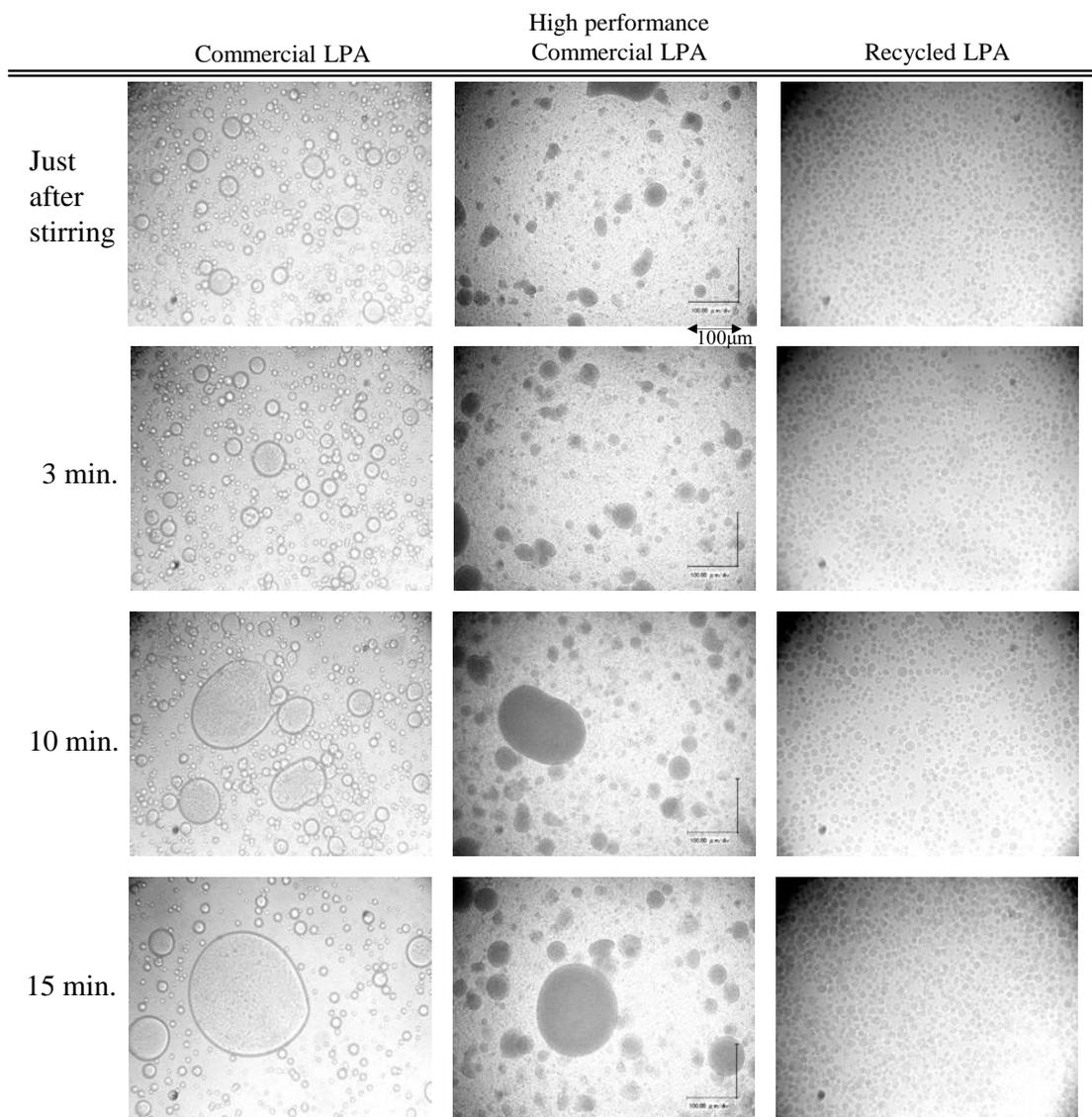


Fig. 3-2-6 Solubility of LPA for UP resin

Just after stirring, commercial LPA and high performance commercial LPA were dispersed as a certain level of small domain (island). However, after 15 min., the domains became much larger which indicated solubility drastically decreased. On the other hand, the recycled LPA was dispersed more uniformly with smaller size of domains than other commercial LPAs. It was remarkable that the domain were kept small even after 15 min. which indicated solubility was highly stable. It was expected to show high performance as LPA.

The recycled LPA and a commercial LPA was used to produce FRP sample boards and tested. **Figure 3-2-7** shows the recycled LPA and the commercial LPA the FRP sample boards. **Table 3-2-4** shows evaluation results. The recycled LPA showed higher shrinkage control effect than the commercial LPA even content was 74% of the commercial LPA. Other product quality items were equivalent to the commercial LPA. It suggested that the recycled LPA had about 69% higher shrinkage control performance per unit weight than that of the commercial LPA. The price of the commercial LPA is from 5 to 10times more expensive than styrene. It suggests “enhanced recycling.”

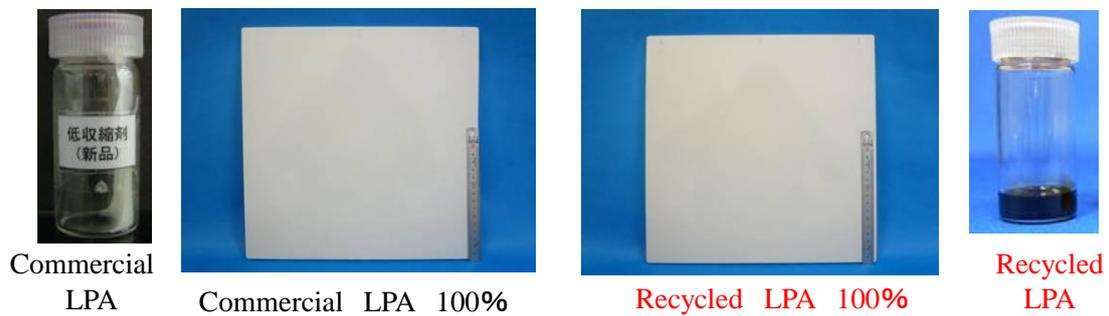


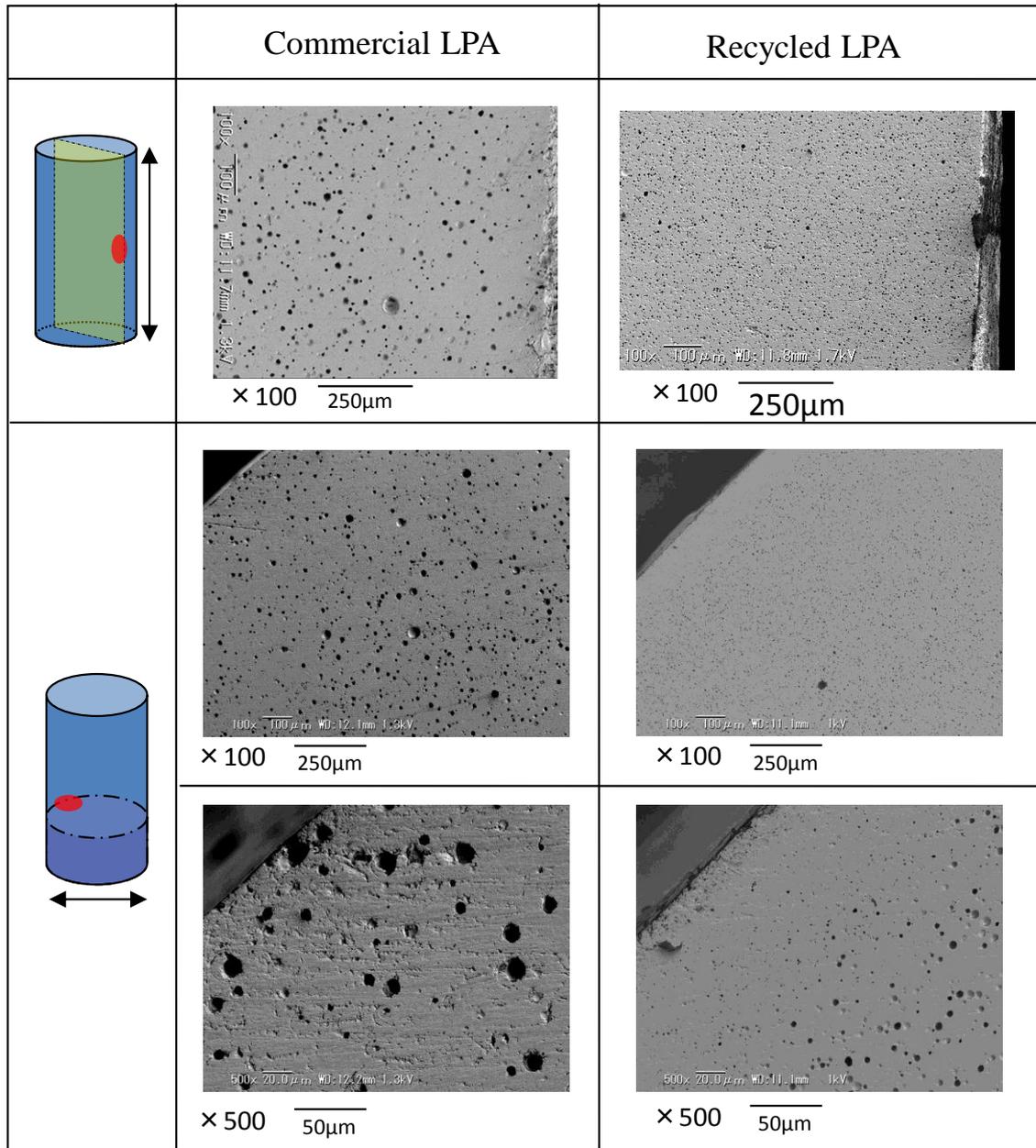
Fig.3-2-7 The recycled LPA, the commercial LPA , and the FRP sample boards.

Table 3-2-4 Evaluation results of the recycled LPA and the commercial LPA

		FRP sample ①	FRP sample ②	FRP sample③
LPA content	Commercial LPA	16.7 unit	8.3 unit	—
	Recycled LPA	—	7.5 unit	12, 4 unit
Quality item	Measurement method and criteria			
Shrinking control	Shrinkage rate (0.15%~0.19%)	0.20 %	0.15 %	0.16 %
Hot water durability	90℃ hot water 115h Color change ($\Delta E \leq 3.5$)	OK $\Delta E = 1.69$	OK $\Delta E = 1.50$	OK $\Delta E = 0.47$
Appearance	Observation (Color heterogeneity)	OK	OK	OK
Mechanical strength	Pulling and Bending strength, Impact tenacity	OK	OK	OK

Figure 3-2-8 shows cross section observation results of FRP sample boards using commercial LPA and recycled LPA. In commercial LPA, larger voids were observed. Whereas, in recycled LPA, many fine voids were uniformly dispersed. It was reasonable to consider that small domains due to higher solubility generated the many fine voids. However, the relationship between shrinkage control performance per unit weight and solubility should be the subject to be investigated. If total volume of all voids is same, many fine voids have higher total surface area. Stress was divided by total surface area. Therefore, FRP using recycled LPA with higher total surface area is expected to have

stronger mechanical strength. In addition, surface appearance and smoothness are also expected to be improved.



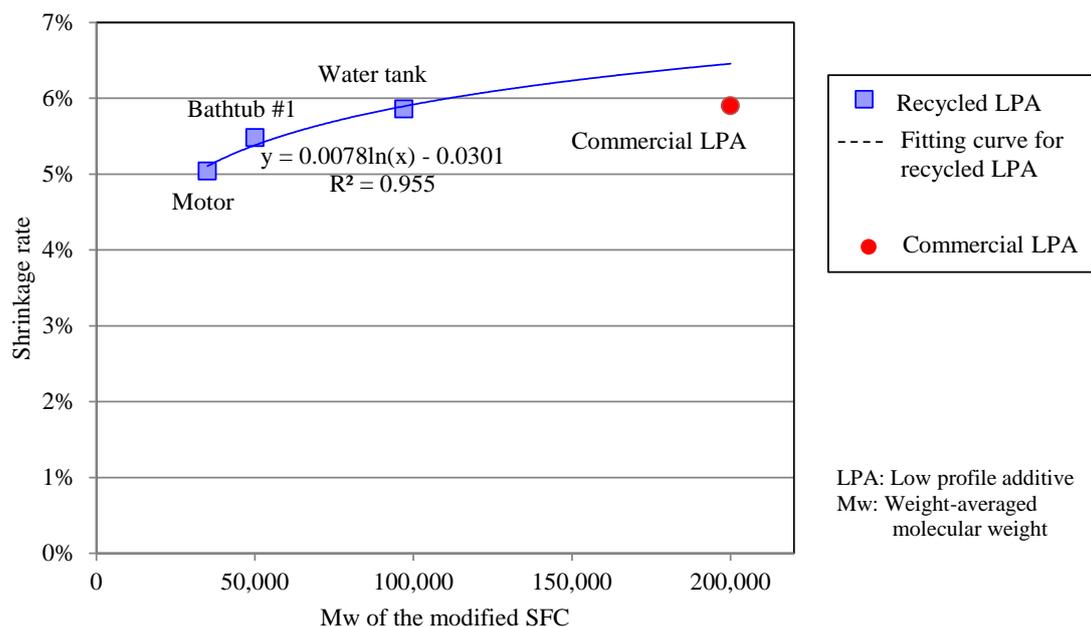
*LPA : Low Profile Additive

Fig. 3-2-8 Cross section observation of FRP sample board using the commercial LPA and the recycled LPA

As mentioned above, the recycled LPA using the modified SFC derived from bathtub showed superior performance to the commercial LPA. The SFCs derived from other FRPs were esterified with 1-octanol to produce the recycled LPA. To examine the

correlation between the shrinkage control effect and the molecular structure, the SFCs derived from the motor and the water tank were selected. The SFC derived from the motor has the smallest Mw with relatively lower styrene/fumaric acid (S/F) molar ratio, whereas the SFC derived from the water tank has the largest Mw with relatively higher S/F molar ratio. The evaluation results were compared with the results for the SFC derived from the bathtub#1 and the commercial LPA.

Figures 3-2-9 A shows the correlation between the shrinkage control effect and the weight-averaged molecular weight (Mw) of the modified SFC after the esterification with 1-octanol. The Mw represent the entire molecular weight not only for the styrene skeleton main chain but also for the branch chains of octyl group. The smaller Mw of the SFC derived from the motor showed the higher shrinkage control effect, whereas the larger Mw of the SFC derived from the water tank in the recycled LPA showed the lower shrinkage control effect and almost equivalent to that of the commercial LPA. In the recycled LPAs, there seems to be a correlation between the shrinkage control effect and Mw of the modified SFC with the fitted curve indicated by the equation described in **Fig.3-2-9 A**. The value of the commercial LPA was not fitted in the fitted curve.



Figures 3-2-9 A The shrinkage control effect and the Mw of the modified SFC after the esterification.

In the commercial LPA, the straight polystyrene having the Mw of a range from 150,000 to 200,000 is generally used. In general, it is considered that the larger Mw shows the higher shrinkage control effect. However, the recycled LPA has the opposite

tendency. The modified SFC derived from the motor showed approximately 17% higher effect than the commercial LPA although the Mw was only about one sixth of that of the commercial LPA. It suggests that the mechanism of expression effect was different between the recycled LPA and the commercial LPA.

Figures 3-2-9 B shows the correlation between the shrinkage control effect and the Mw of the original SFC before the esterification with 1-octanol. The Mw represents only the styrene skeleton main chain in the recycled LPA. It also shows that there seems to be a correlation between the shrinkage control effect and Mw of the original SFC. The original SFC derived from the motor showed approximately 17% higher effect than the commercial LPA although the Mw was only about one ninth of that of the commercial LPA.

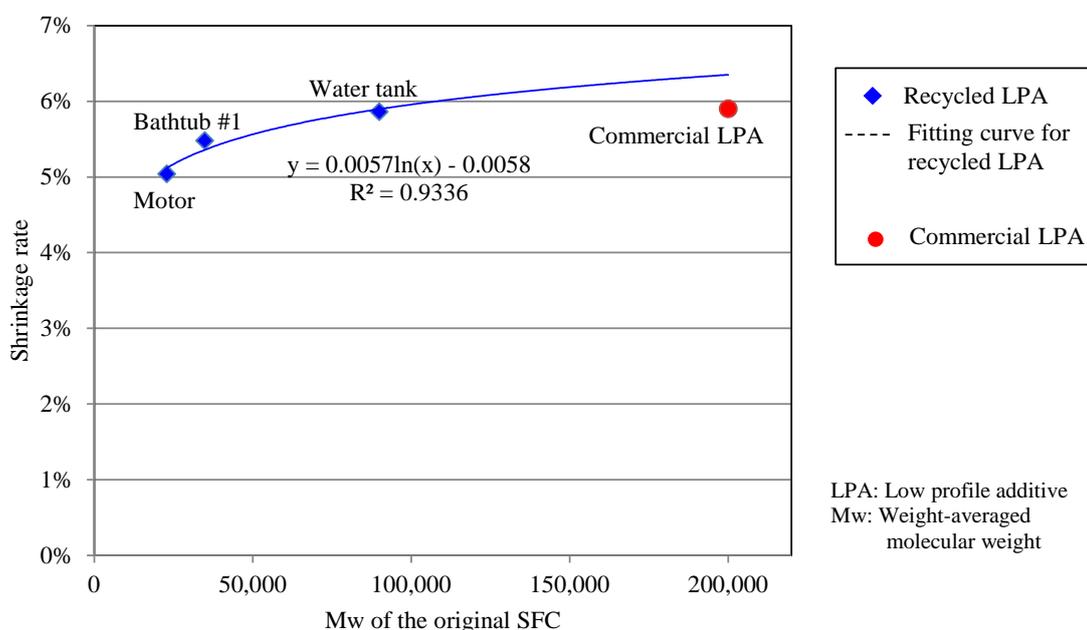


Fig. 3-2-9 B Shrinkage control effect of the original SFC derived from various FRPs before esterification.

Figures 3-2-10 shows the correlation between the shrinkage control effect of the recycled LPA and the styrene/fumaric acid (S/F) molar ratio of the original SFC. It showed the highly linear correlation. The lower S/F molar ratio indicates more branch chains of octyl group. The SFC esterified with 1-octanol showed the higher shrinkage control effect than the SFC esterified with 1-butanol and with 2-ethyl-1-hexanol. It suggests that the branch chain highly affects the shrinkage control effect. More branch chains and longer alkyl chains are assumed to contribute the higher shrinkage control effect.

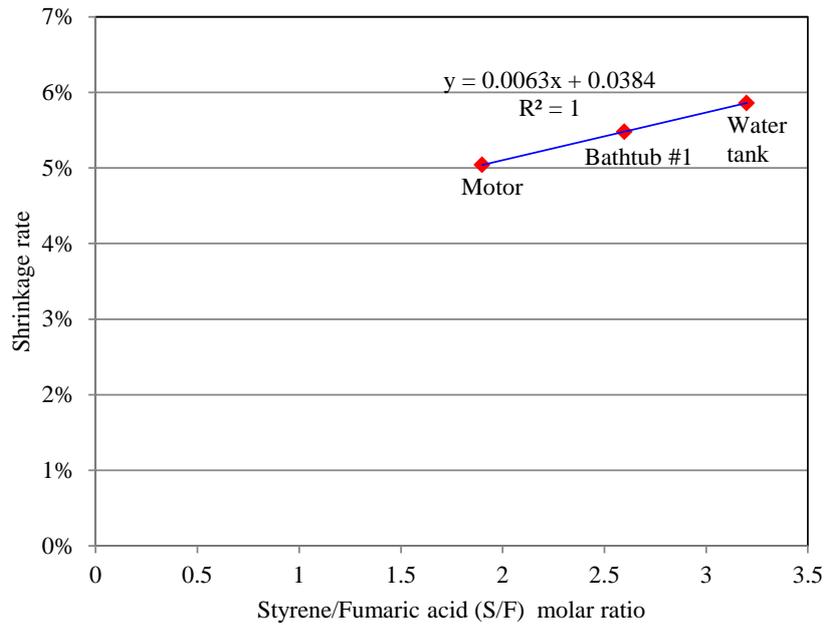


Fig. 3-2-10 Shrinkage control effect and S/F molar ratio of the original SFC derived from various FRPs

As mentioned above, the molecular structure of the recycled LPA highly affects the shrinkage control effect. The mechanism of expression function is assumed different from the commercial LPA. It propose new concept for the LPA. In **Fig. 3-2-8**, the number of voids of the recycled LPA was observed more than that of the commercial LPA. The size of each void of the recycled LPA was smaller than that of the commercial LPA. The smaller Mw is considered to promote the recycled LPA disperse easily and uniformly. The higher dispersion should realize the many smaller agglomerations. The smaller molecular size also contributes to the smaller agglomeration. The size of void produced by the smaller agglomeration must be small. The many smaller voids increase surface area of the interface. The stress per unit surface area should be smaller. It should contribute to provide stronger mechanical strength.

It should be noted that there was no intention to generate the shrinkage control effect in the styrene chain of the thermosetting polyester resin. However, the SFC showed such a superior shrinkage control effect to that of the commercial LPA. This new concept and information obtained can be applied to develop a new LPA which has much superior performance to the best recycled LPA. The new LPA based on this new concept should have a potential to create innovative FRP which has much stronger mechanical strengths. It enables to reduce the material quantity and weight. The light weight can contribute the fuel consumption if it is used in vehicle.

3.2.4. Conclusions

In evaluation of SFC esterified with alcohol, 1-octanol showed the best shrinkage control performance and selected as esterification agent for SFC.

SFC separation and modification processes using 1-octanol was established. Almost 100% of the SFC was extracted from reaction liquid to 1-octanol with extremely less water than conventional method. The SFC extracted was esterified with 1-octanol with H₂SO₄ as catalyst at 175°C for 17 hours to produce the modified SFC with almost 100% conversion. The recycled LPA was produced by styrene addition to the modified SFC.

The recycled LPA showed higher solubility to UP resin than commercial LPA and high performance commercial LPA. The recycled LPA was used to produce FRP sample board and then evaluated with a commercial LPA. The recycled LPA showed about 69% higher shrinkage control performance per unit weight than that of the commercial LPA. Other product quality items were also equivalent to the commercial LPA. Hence, it was concluded that the SFC was successfully verified the possibility of applying to the LPA. It suggests the possibility of from 5 to 10 times “*enhanced recycling*.” In cross section observation, FRP sample board using recycled LPA showed many fine voids uniformly dispersed base on higher solubility to UP resin. It is expected to have stronger mechanical strength and better surface appearance and smoothness.

The recycled LPA using the modified SFC derived from motors and water tank were also evaluated with modified SFC derived from bathtub. The recycled LPA using the modified SFC derived from motors showed the best shrinkage control performance. The correlation between the shrinkage control effect and the molecular size was also examined. The longer alkyl chain, the smaller Mw, and the lower S/F molar ratio showed the higher shrinkage control effect. Based on the results, new concept of the LPA was proposed. It is expected that the superior LPA creates the innovative FRP which has much stronger mechanical strengths.

3.3 Aqueous agent

3.3.1 Introduction

Figures 3-3-1 shows a concept of recycling thermosetting polyester resin using subcritical water with NaOH. After the reaction, SFC is dissolved in the reaction liquid as sodium salt (SFC-Na). SFC-Na has practically the same molecular structure as alkali salt of styrene-maleic anhydride (SMA) which is widely used in various aqueous agents, such as dispersing agent, surface sizing agent, detergent agent, chelating agent, emulsifying agent, and so on [2, 3]. Therefore, the alkali salt of SFC should have a highly potential for applying to such applications.

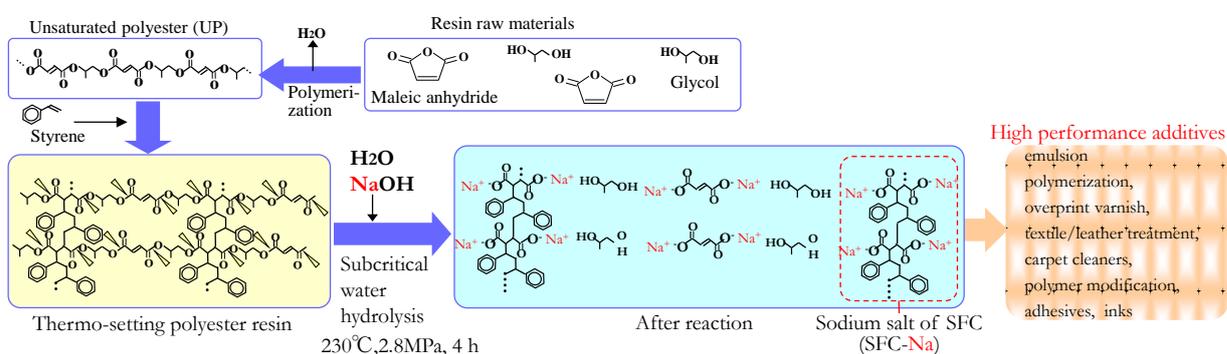


Fig. 3-3-1 Recycling thermosetting polyester resin using subcritical water with NaOH

The dispersing agent is widely needed to increase dispersibility for hydrophilic powder and hydrophobic powder. Kaolin, TiO₂, and CaCO₃ were selected as hydrophilic powders. Phthalocyanine blue, pigment used widely, was selected as hydrophobic powder. The reaction product liquid containing sodium salt of the SFC (SFC-Na) was evaluated with commercial dispersing agent.

The detergent builder is widely used with detergent to prevent the performance loss of detergent caused by calcium (Ca) ion and pH change. Ca ion trapping ability and alkali buffering capacity are required for the detergent builder. They were evaluated for the reaction product liquid and commercial detergent builder. In those applications, the strong merit is to use the reaction product liquid directly with no additional process.

The surface sizing agent is used for papers to prevent bleeding of aqueous ink. The surface sizing agent should have hydrophilic region which contributes to be dispersed on paper surface uniformly and hydrophobic region which contributes to provide hydrophobicity to paper surface to prevent aqueous ink bleeding. Ammonium salt of SFC (SFC-NH₄) was evaluated with commercial surface sizing agent.

Evaluation results of alkali salt solution of SFC were compared with commercial aqueous agent to be verified the possibility of SFC applying to those applications.

3.3.2. Materials and methods

3.3.2.1 Dispersing agent

The target powders were kaolin, titanium oxide (TiO_2) and CaCO_3 as Hydrophilic inorganic pigment, and phthalocyanine blue as hydrophobic organic pigment. Pictures and molecular structure of phthalocyanine blue were described in **Fig. 3-3-2**. To verify the possibility of SFC-Na applying to Dispersing agent, dispersing agent was dissolved in water with 4wt% concentration to produce dispersing agent solution.

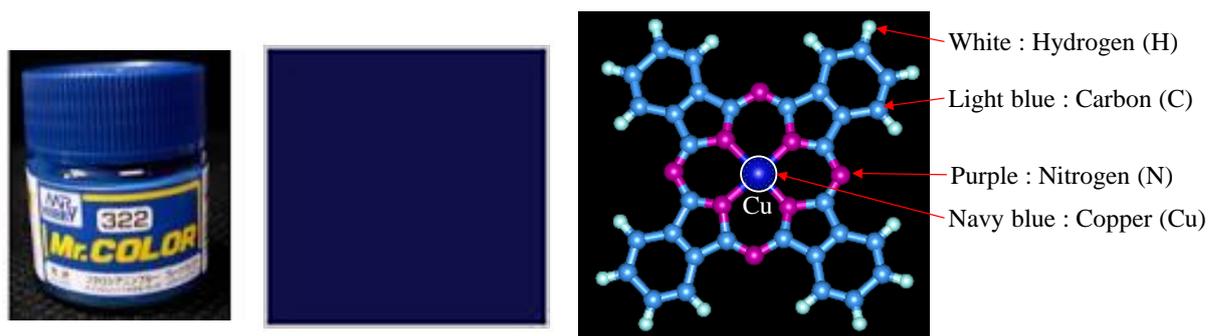


Fig 3-3-2 Phthalocyanine blue

To verify the possibility of SFC-Na applying to dispersing agent, dispersing agent was dissolved in water with 4 wt% concentration to produce dispersing agent solution. In the case of reaction liquid, the SFC-Na in the reaction liquid was defined as dispersing agent. A target powder was mixed with the dispersing agent solution. Target powder: the dispersing agent solution was 1:10. They were stirred for 1 min. at 15,000 rpm by homogenizer (HG-200, AS ONE Corporation). After stirring, the liquid containing the powder was filtered by 0.2 μm mesh membrane filter to remove excessive dispersing agent solution. The filtered powder was dried at 105°C for 1 hour. The dried powder, untreated powder, and dispersing agent solid after drying the dispersing agent solution were evaluated by heat analysis to quantify how much the dispersing agent adsorbed on the powder by calculation based on the weight loss curve of the TG-DTA.

In evaluation of dispersibility, each dispersing agent solution sample with targeting powder after stirring was filtered by different membrane filters designed to filter the powder over 0.45 μm and 1.2 μm . The powder weight filtered by each membrane filter was measured. They were substituted from initial powder weight to obtain the powder weight passed through 0.45 μm membrane filter. More powder weight passed through the membrane filter indicates higher dispersibility. Syringe filter, minisart (Sartrius stedim) was used as membrane filters. Targeting powders were kaolin, TiO_2 , and CaCO_3

as hydrophilic inorganic pigment, and phthalocyanine blue as hydrophobic organic pigment. At first, 0.1 g of powder and 10g of the dispersing agent solution sample with the dispersing agent concentration of 0.5 wt% were put in the 30cc test bottle. Total weight of the dispersing agent was considered to be 0.05 g. They were stirred for 3 minutes by homogenizer with 15,000 rpm. Water was added to them until total weight reached 20 g. After stirring, they were stayed for 5 minutes and then were filtered by membrane filter. Firstly, they were filtered with 1.2 μm membrane filter. The dispersing agent solution sample containing the target powder passed through 1.2 μm membrane filter was stirred again and then filtered with 1.2μm membrane filter.

3.3.2.2 Detergent builder

As detergent builder, calcium (Ca) ion trapping ability and alkali buffering capacity were evaluated. For evaluation of Ca ion trapping ability, 50 mL of aqueous solutions which have 0.05 % of solid content of detergent builder and pure water were prepared at the beginning. In the case of reaction product liquid, SFC-Na content was defined as solid content of detergent builder. Secondary, 0.25 mL of aqueous solution of n-alkyl-benzene sulfonic acid with concentration of 10% was added to them. NaOH or HCl with concentration of 0.1 mol/L was added to them to control pH level to achieve to produce a sample solution. Then calcium acetate solution had been dropped to the sample solution with stirring until they became white. Concentration of calcium acetate was 1% based on calcium acetate monohydrate. The total volume of calcium acetate solution was measured as titer. Ca ion trapping ability is defined as equation 3-3-1.

$$Q = M \frac{v m}{w} \quad (3-3-1)$$

Q : Ca ion trapping ability (CaCO₃ mg/g)

M : Molar mass of CaCO₃

v : total volume of titer (mL)

m : mol of Ca ion per unit volume of titer

w : total weight of detergent builder (g)

For evaluation of alkali buffering capacity, 50 mL of the above detergent builder solutions which have 2% of solid content and pure water were prepared. Secondary, NaOH or HCl of 0.1 mol/L was added to control pH level to achieve pH 10. Then 0.1 mol/L of HCl had been dropped to the solution with stirring until they reached pH 8. The titer was defined as alkali buffering capacity (mL)

3.3.2.3 Surface sizing agent

To verify the possibility of SFC-NH₄ applying to surface sizing agent, the

commercial SA#1 containing styrene skeleton as hydrophobic region as same as the SFC was used. Styrene amount dispersed on the paper surface per unit area is considered to affect water repellency effect. Adsorbed weight of sizing agent per unit area (i) was multiplied with number of moles per unit weight of sizing agent obtained by NMR analysis (ii) to calculate number of moles per unit area (iii).

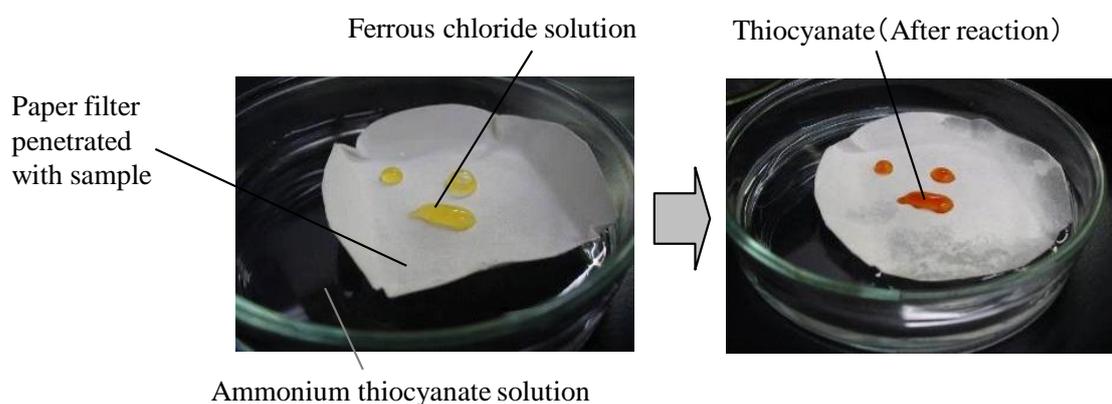


Fig. 3-3-3 Stöckigt sizing method

Surface sizing effect was evaluated based on Stöckigt method (JIS P8812) described in **Fig.3-3-3**. A given amount of surface sizing agent solution sample was penetrated in paper filter and they were dried. The dried paper filter was put on the surface of ammonium thiocyanate solution. Ferrous chloride solution was dropped and then reacted with ammonium thiocyanate solution to be converted to thiocyanate with color changing to red. The transient time of changing color to red was measured as Stöckigt sizing degree and compared with commercial SD#1. Longer transient time indicates higher surface sizing effect base on water repellency.

3.3.3. Results and discussion

3.3.3.1 SFC and commercial aqueous agents

Table 3-3-1 shows molecular formula and Mw in terms of polyethylene glycol of commercial dispersing agent (DA) and reaction product liquid. Polyacrylic sodium salt which has 5,000 of Mw was selected as commercial DA #1 targeting for hydrophilic powders. Styrene-sodium malate-methyl methacrylate copolymer was selected as commercial DA #2 targeting for hydrophobic powders. It also has styrene skeleton which is seemed to be effective for poisoning the surface of hydrophobic powder. Reaction product liquid contains sodium salt of SFC-Na and glycol, fumaric acid and other organic acids derived from degradation of fumaric acid. Mw of SFC-Na was 80,000 in terms of polyethylene glycol and was the largest among samples.

Table 3-3-1 Commercial dispersing agent (DA) , reaction product liquid

Sample	Commercial DA #1	Commercial DA #2	Reaction product liquid (PL)
Material	Polyacrylic sodium salt	Styrene-sodium malate-methyl methacrylate copolymer	Sodium salt of SFC (with glycol, fumaric acid, etc.)
Molecular formula	$\left[\text{CH}_2 - \underset{\substack{ \\ \text{C}=\text{O} \\ \\ \text{ONa}}}{\text{CH}} \right]_n$	$\left(\left[\text{CH} - \text{CH}_2 \right] \left[\underset{\substack{ \\ \text{O}=\text{C} \\ \\ \text{ONa} \\ \text{ONa}}}{\text{CH}} - \underset{\substack{ \\ \text{C}=\text{O}}}{\text{CH}} \right] \text{CH}_2 - \underset{\substack{ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3}}{\overset{\text{CH}_3}{\text{C}}} \right)_n$	$\left(\left[\text{CH} - \text{CH}_2 \right] \left[\underset{\substack{ \\ \text{O}=\text{C} \\ \\ \text{ONa} \\ \text{ONa}}}{\text{CH}} - \underset{\substack{ \\ \text{C}=\text{O}}}{\text{CH}} \right] \right)_{2.2} \left[\text{CH} - \text{CH}_2 \right]_n$
Mw*	5,000	10,000	80,000

Table 3-3-2 shows molecular formula and Mw of commercial detergent builder (DB), commercial surface sizing agent (SA), and SFC-NH₄. Polyacrylic sodium salt which has 22,000 of Mw was selected as commercial DB#1 Styrene-ammonium acrylate copolymer was selected as commercial SA#1. It has both hydrophilic region of ammonium acrylate and strong hydrophobic region of styrene skeleton.

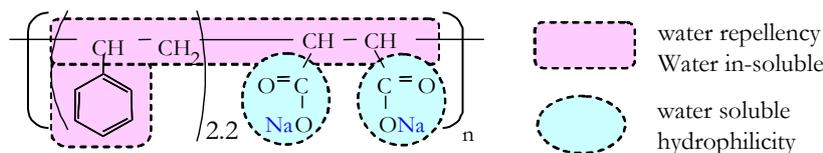
Table 3-3-2 Commercial detergent builder(DB) and surface sizing agent (SA), SFC-NH₄

Sample	Commercial DB #1	Commercial SA #1	SFC-NH ₄
Material	Polyacrylic sodium salt	Styrene-ammonium acrylate copolymer	Ammonium salt of SFC
Molecular formula	$\left[\text{CH}_2 - \underset{\substack{ \\ \text{C}=\text{O} \\ \\ \text{ONa}}}{\text{CH}} \right]_n$	$\left(\left[\text{CH} - \text{CH}_2 \right] \left[\underset{\substack{ \\ \text{O}=\text{C} \\ \\ \text{ONH}_4}}{\text{CH}} - \text{CH}_2 \right] \right)_n$	$\left(\left[\text{CH} - \text{CH}_2 \right] \left[\underset{\substack{ \\ \text{O}=\text{C} \\ \\ \text{ONH}_4 \\ \text{ONH}_4}}{\text{CH}} - \underset{\substack{ \\ \text{C}=\text{O}}}{\text{CH}} \right] \right)_{2.2} \left[\text{CH} - \text{CH}_2 \right]_n$
Mw*	22,000	40,000	80,000

Mw*:Weight averaged molecular weight (in terms of polyethylene glycol)

3.3.3.2 Dispersing agent

Molecular formula of sodium salt of the SFC (SFC-Na) is described in **Scheme 3-3-1**. SFC-Na has styrene skeleton as a hydrophobic region and sodium carboxylate as a hydrophilic region. **Figure 3-3-4** shows hypothetical mechanism of SFC-Na as dispersing agent. Powders tend to be agglomerated each other by intermolecular force. Surface of powder is charged positive. Carbonyl ion of SFC-Na is negatively charged and is attached to positive charge powder surface. Powder surface is covered by SFC-Na which has negative charge. Electrostatic repulsion is developed between each negatively charged powder. The electrostatic repulsion is expected to prevent agglomeration and to increase dispersibility. Steric hindrance caused by SFC-Na is also expected to prevent agglomeration.



Scheme 3-3-1 Molecular formula of sodium salt of SFC (SFC-Na)

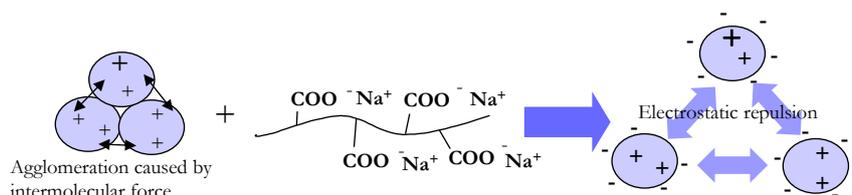


Fig. 3-3-4 Hypothetic mechanism of SFC-Na as dispersing agent

Figure 3-3-5 shows hypothesis for mechanism of SFC-Na as dispersing agent for hydrophobic powder. Hydrophobic powder cannot be dispersed in water since hydrophobic surface has no affinity to water molecule. Hydrophobic materials tend to be agglomerated each other since water molecule cannot access the surface. Dispersing agent should have hydrophobic region and a hydrophilic region. Hydrophobic region of SFC-Na is poised on the surface of hydrophobic powder. Hydrophilic region of SFC-Na is expected to provide water solubility acting like cilium.

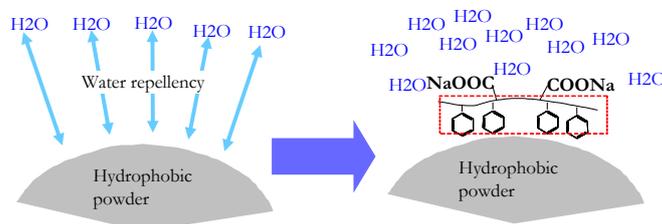


Fig. 3-3-5 Hypothesis for mechanism of SFC-Na as dispersing agent for hydrophobic powder

Table 3-3-3 shows evaluation results of dispersing agent adsorption on each powder. As described in **Figs.3-3-4** and **3-3-5**, the dispersing agent is required to adsorb the powder surface to express dispersing effect. The adsorbed amount of SFC in reaction product liquid was more than that of both commercial DA#1 and DA#2. Therefore, the reaction product liquid is expected to have a dispersing effect for both powders.

Table 3-3-3 Dispersing agent (DA) adsorption on each powder (mg/g)

Powder	Reaction liquid	Commercial DA #1	Commercial DA #2
Kaolin (hydrophilic pigment)	8.1	2.5	-
CaCO ₃ (hydrophilic pigment)	5.1	3.1	-
Phthalocyanine blue (hydrophobic pigment)	11.1	-	7.5

Filtering test result for kaolin, TiO₂, CaCO₃, and phthalocyanine blue were described in **Figs 3-3-6 (a), (b), (c), and (d)**, respectively. In case of all targeting powder, particle size of most of powder without the dispersing agent was over 1.2μm. If the dispersing agent is effective, the weight of particle size over 1.2μm should be decreased. Total weight of the dispersing agent was 0.05g. Most of them were considered to have particle size less than 0.45μm.

In filtering test result for kaolin described in **Fig. 3-3-6 (a)**, the reaction product liquid almost didn't show a dispersing effect for kaolin even weight of particle size range between 0.45μm and 1.2μm was slightly increased. Commercial DA#1 showed a slight dispersing effect.

In filtering test result for TiO₂ described in **Fig. 3-3-6 (b)**, the reaction product liquid showed a slight dispersing effect. However, the dispersing effect of commercial DA#1 was larger than reaction liquid.

In filtering test result for CaCO₃ described in **Fig. 3-3-6 (c)**, reaction product liquid showed a slight dispersing effect. Commercial DA#1 almost didn't show a dispersing effect. It was concluded that the dispersing effect of the reaction product liquid for hydrophilic powders were small.

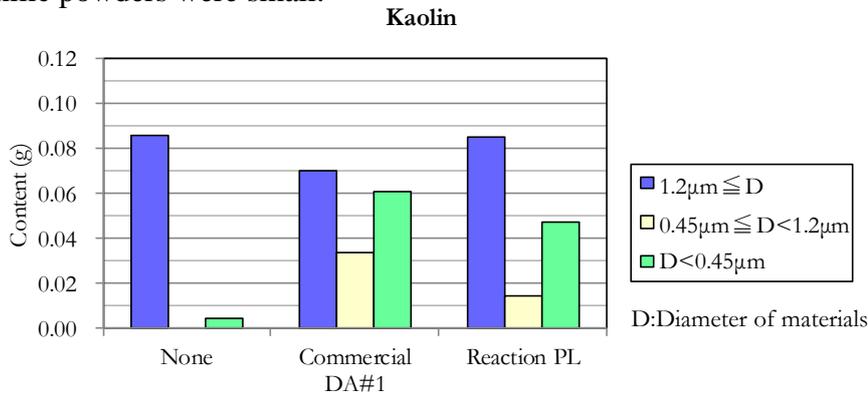


Fig. 3-3-6 (a) Filtering test result (Kaolin)

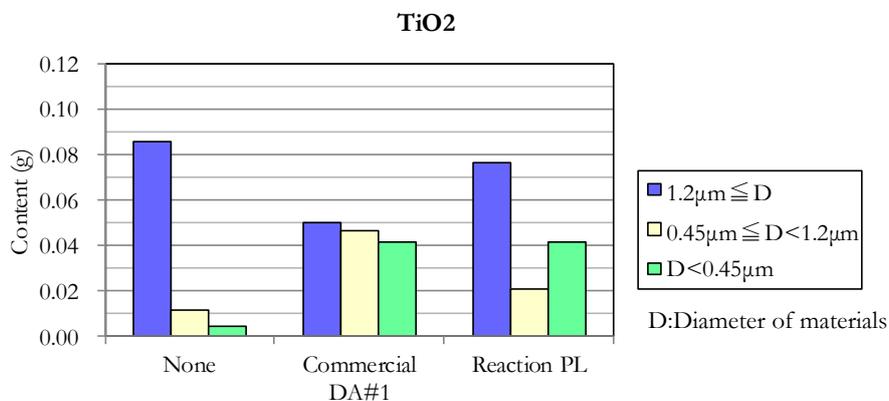


Fig. 3-3-6 (b) Filtering test result (TiO₂)

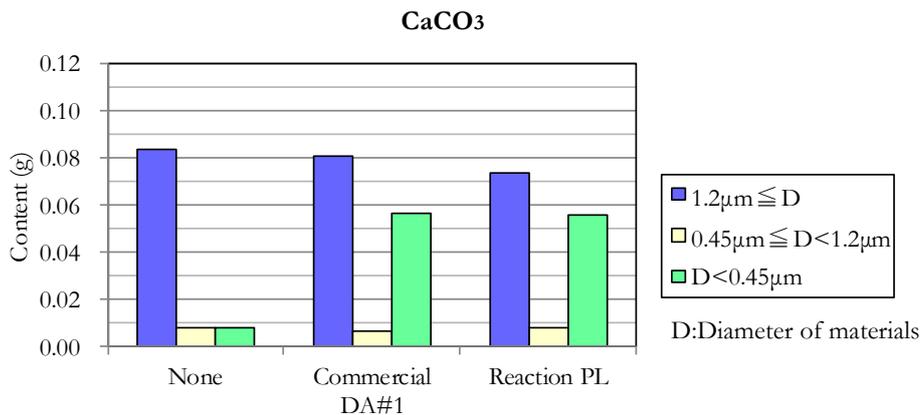


Fig. 3-3-6 (c) Filtering test result (CaCO₃)

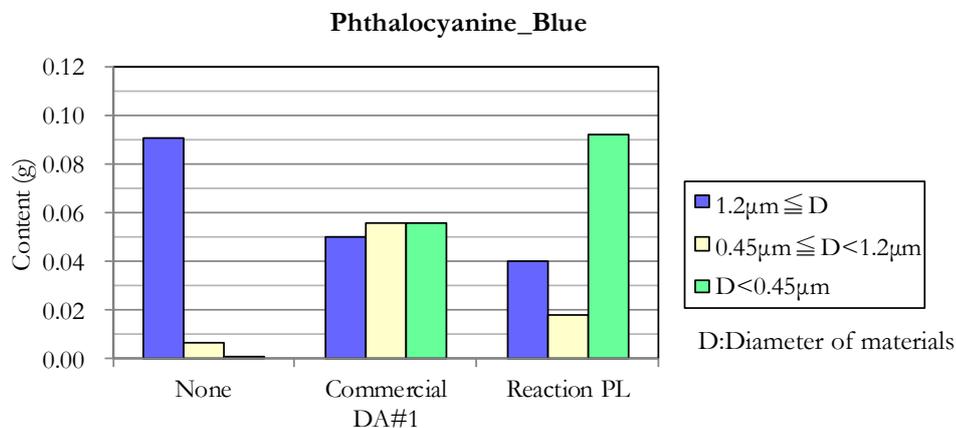


Fig. 3-3-6 (d) Filtering test result (Phthalocyanine Blue)

The dispersing effect mechanism by SFC-Na for hydrophilic powders is considered electrostatic repulsion and steric hindrance. Amount of carbonyl ion per unit weight of SFC-Na is less than that of commercial DA#1. It is assumed insufficient although its adsorption amount was more than commercial DA#1. Mw is also suggested to be important factor for uniform distribution on powder surface. Mw of SFC-Na is assumed to be too large to be distributed uniformly to create the dispersing effect.

Figure 3-3-6 (d) shows filtering test result of phthalocyanine blue. It was obvious that the weight of particle size over 1.2µm was decreased by reaction liquid to indicate the dispersing effect. The weight of particle size over 1.2µm of commercial DA#2 was also decreased. However, the weight of particle size less than 0.45µm of the reaction product liquid was much more than that of commercial DA#2. The reaction product liquid has the powder finer than commercial DA#2. Styrene skeleton of the SFC-Na seemed to have sufficient affinity with styrene skeleton of the phthalocyanine blue. Dicarboxylic sodium salt of the SFC-Na seemed to provide the powder with

dispersibility on water. Commercial DA#2 also has styrene skeleton and dicarboxylic sodium salt. However, their ratio is unknown. It is suggested that the ratio of hydrophobic region and hydrophilic region affected to dispersing effect. Mw might be also another factor for dispersing effect.

The reaction product liquid successfully demonstrated the superior dispersing effect for phthalocyanine blue to commercial SD#2. It was concluded that the reaction product liquid was verified the possibility for applying to the dispersing agent for hydrophobic powders.

3.3.3.3 Detergent builder

Figure 3-3-7 shows hypothesis for mechanism of SFC-Na trapping Ca ion as dispersing agent. Dicarboxyl sodium salt is expected to trap Ca^{2+} effectively.

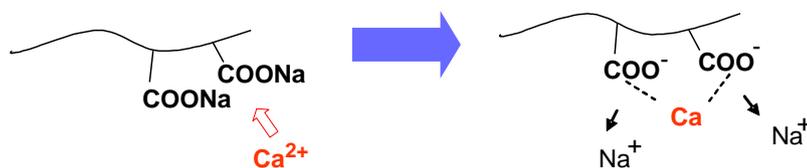


Fig.3-3-7 Hypothesis for mechanism of SFC-Na for trapping calcium (Ca) ion

Figure 3-3-8 shows the evaluation result of Ca ion trapping ability. The reaction product liquid showed higher Ca ion trapping ability than pure water with no detergent builder. Carbonyl ion of SFC-Na seemed to trap Ca^{2+} effectively. Commercial DB#1 showed higher performance than the reaction product liquid. The commercial DB#1 has the higher molar ratio of carbonyl ion per unit weight than SFC-Na. It is assumed to affect the higher Ca ion trapping ability.

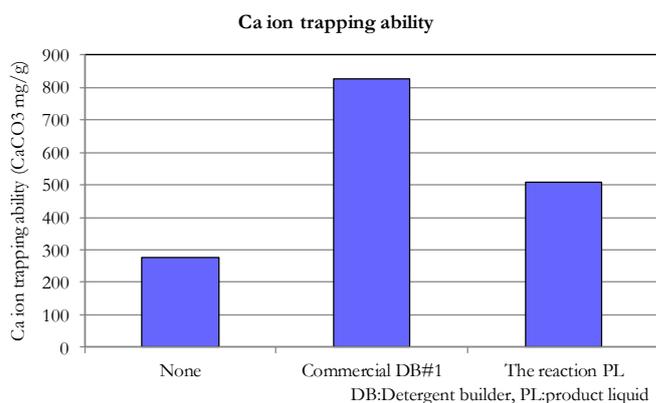


Fig.3-3-8 Evaluation result of Ca ion trapping ability

Figure 3-3-9 shows the evaluation result of alkali buffering capacity. The reaction product liquid showed significant performance. Alkali buffering capacity of the reaction

product liquid was about 6.6 times higher than that of commercial DB#1. In the reaction product liquid, there were certain amounts of carboxylic acid sodium salt other than the sodium salt of SFC. Sodium salt of fumaric acid and other carboxylic acid such as maleic acid, glycolic acid, acetic acid, and so on. It was suggested that they also contributed to buffer alkali.

The reaction product liquid successfully demonstrated the superior alkali buffering capacity to commercial DB#1. It also showed Ca ion trapping ability. It was concluded that the reaction product liquid was verified the possibility for applying to the detergent builder.

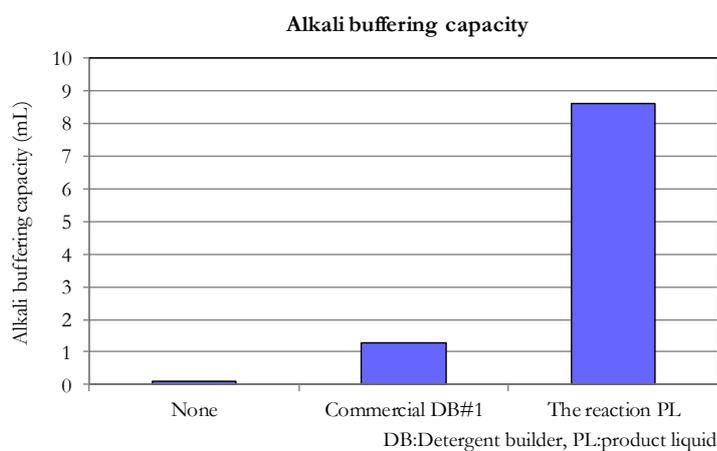


Fig.3-3-9 Evaluation result of alkali buffering capacity

3.3.3.4 Surface sizing agent

In the case of surface sizing agent, ammonia was used as alkali of SFC instead of Na. **Figure 3-3-10** shows hypothetical mechanism of SFC-NH₄ as surface sizing agent. Paper surface is hydrophilic due to OH group of cellulose. Firstly, SFC-NH₄ is dispersed uniformly on paper surface due to its hydrophilic ammonium carboxylate. After dispersion, ammonia is vaporized to produce carboxyl acid which is less hydrophilic than ammonium carboxylate then SFC is fixed on paper surface. Hydrophobic region of the SFC is expected to provide water repellency.

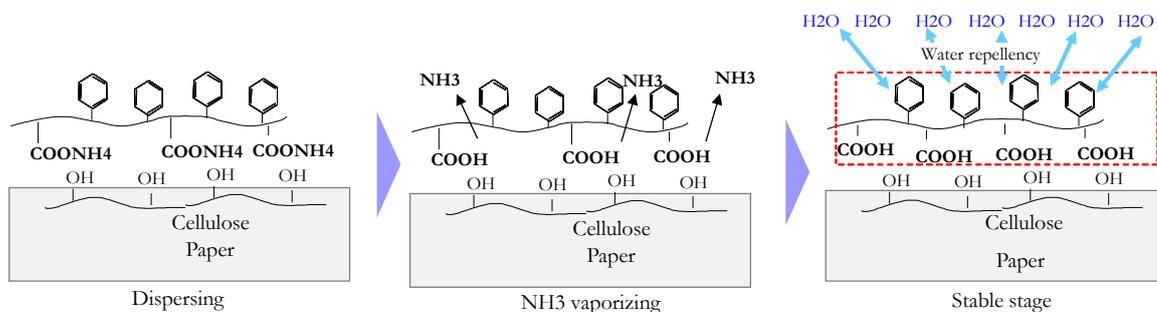


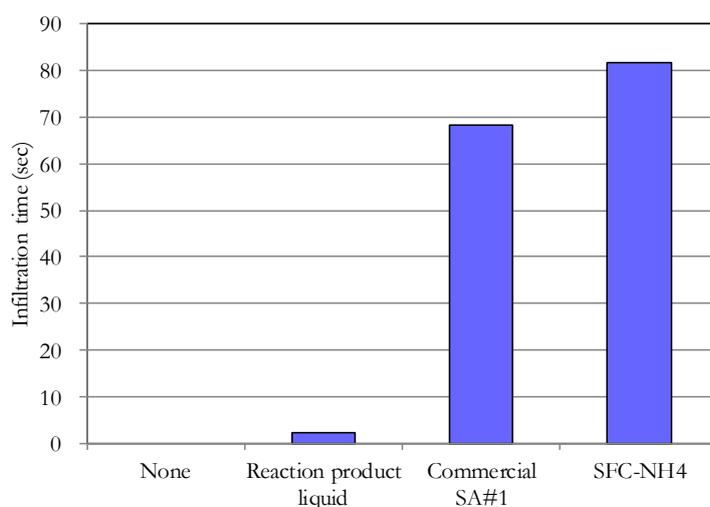
Fig. 3-3-10 Hypothetic mechanism of SFC-NH₄ as surface sizing agent

Table 3-3-4 Surface sizing agent (SA) adsorption comparison

		Reaction liquid	Commercial SA #1
(a) Sizing agent adsorption amount per unit area	($\times 10^{-4}$ g/cm ²)	10.0	7.8
(b) Styrene (mol) per unit weight of sizing agent	($\times 10^{-3}$ mol/g)	6.4	7.3
(c) Styrene (mol) per unit area (= (a) \times (b))	($\times 10^{-6}$ mol/cm ²)	6.4	5.7

Table 3-3-4 shows the evaluation result of number of styrene moles per unit area in paper. Styrene (mol) per unit weight of the reaction liquid was less than that of commercial SD#1. However, adsorption amount per unit area of the reaction product liquid was larger than that of commercial SD#1. The difference was assumed to be caused by the molar ratio of carbonyl ion and styrene. SFC has di-carbonyl ion and commercial SD#1 has mono-carbonyl ion. The higher molar ratio of carbonyl ion provides higher hydrophilicity to contribute to increase adsorption amount on paper. SFC-NH₄ totally provided more amount of styrene to paper than commercial SA#1. Therefore, it was expected to create a surface sizing effect equivalent to commercial SA#1.

Figure 3-3-11 shows the Stöckigt sizing test result. In the case of no additive, dropped ferrous chloride solution was immediately reacted with ammonium thiocyanate solution, thus infiltration time was 0 sec. In the case that the paper filter was penetrated with the reaction product liquid containing mainly SFC-Na, it showed a slightly sizing effect due to its styrene skeleton although SFC-Na itself was hydrophilic entirely. In the case of SFC-NH₄, it showed about 20% higher sizing effect than that of commercial SD#1. It was assumed that larger amount of styrene per unit area of SFC-NH₄ than commercial SD#1 contributed the higher sizing effect.

**Fig. 3-3-11** Stöckigt sizing test result

The SFC-NH₄ successfully demonstrated the superior surface sizing effect than commercial SD#1. It is concluded that the SFC-NH₄ was verified the possibility to be applied to surface sizing agent. However, in the case of SFC-NH₄, paper was slightly colored by unknown impurities. It has to be improved.

3.3.4. Conclusions

In verification of applying to dispersing agent, the reaction product liquid showed less dispersing effect than commercial DA#1 for hydrophilic powder such as kaolin, TiO₂, and CaCO₃. On the other hand, the reaction product liquid showed superior dispersing effect to commercial DA#2 for phthalocyanine blue. Styrene skeleton of SFC-Na is assumed to contribute to increase the dispersing effect. The reaction product liquid has the possibility for applying to the dispersing agent for hydrophobic powders.

In verification of applying to detergent builder, the reaction product liquid showed about 6.6 times higher alkali buffering capacity than that of commercial DB#1. It also showed Ca ion trapping ability. The reaction product liquid has the possibility for applying to the detergent builder.

In verification of applying to surface sizing agent, SFC-NH₄ showed about 20% higher sizing effect than that of commercial SA#1. SFC-NH₄ has possibility to be applied to surface sizing agent.

It was concluded that SFC alkali salt has a potential to substitute to the commercial high performance aqueous agents. The SFC is expected to be applied to other applications widely.

3.4 Compatibilizing agent for polymer alloy

3.4.1 Introduction

3.4.1.1 SFC applying to reactive compatibilizing agent for polymer alloy

Compatibilizing agent for polymer alloy was selected as a candidate for application of SFC. Polymer alloy has been attracted attention to improve the resin property. The property improvement of each polymer is considered to have a limitation. Polymer alloy is expected to break through the limitations to create innovative polymer and its applied products [34-37]. Polymer alloy is also considered effective for recycling plastic waste [34].

In polymer alloy of two incompatible polymers, compatibilizing agent should be essential. **Figure 3-4-1** shows an example of compatibilizing agent for polymer alloy of immiscible polymer A and B. Block polymer is described as an example of compatibilizing agent. When immiscible polymer A and B were mixed, “sea-island” structure will appear as shown in **Fig.3-4-1**.

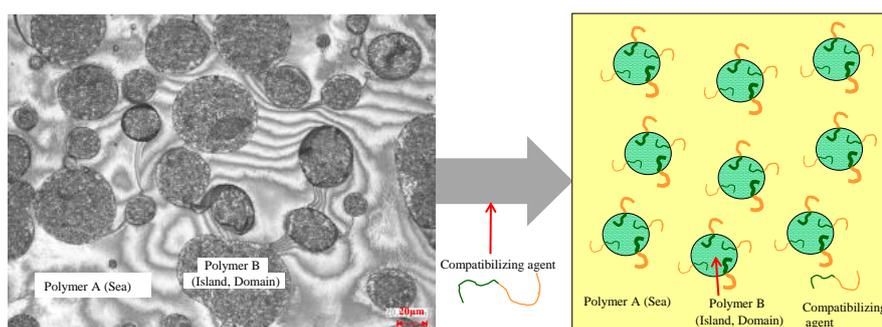


Fig. 3-4-1 Example of compatibilizing agent for polymer alloy

“Sea” structure consists of Polymer A and island (domain) structure consists of polymer B. Domain size represents compatibility. In considering mechanical strength of polymer alloy, stress adding to the polymer alloy is divided by total surface area of interface between polymer A and B since the interface should be weak in strength. If the domain size is not small, total surface area becomes small. Consequently, the mechanical strength should be low since the stress per unit surface area is high. Therefore, high compatibility indicating small domain size is required for polymer alloy. To increase compatibility, compatibilizing agent is essential for polymer alloy. Compatibilizing agent such as block polymer or graft polymer has two parts which are compatible with polymer A and B. Each part grasps the polymer respectively to increase the compatibility described in **Fig.3-4-1**.

In polymer alloy, reactive processing for immiscible polymers is expected to create new innovative materials [36-38]. Reactive processing requires reactive compatibilizing

agent which reacts with polymer during kneading. **Figure 3-4-2** shows reactive processing using reactive compatibilizing agent for polymer alloy of immiscible polymer A and B. In general, content of reactive compatibilizing agent is less than that of non-reactive compatibilizing agent. It is usually more effective to compatibilize immiscible polymers due to reaction with one of the polymers. Non-reactive compatibilizing agent is considered difficult to be dispersed effectively since they tend to be agglomerated.

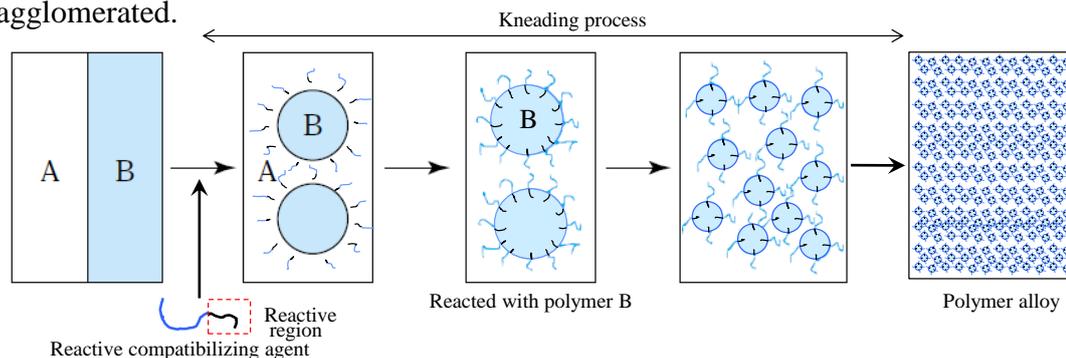


Fig. 3-4-2 Reactive processing for polymer alloy [36]

Reactive region of reactive compatibilizing agent reacts with one polymer to grasp the polymer. Another region should have the affinity with another polymer. An anchoring effect is produced by both regions. It contributes to make the domain size smaller to increase the compatibility during kneading process.

Block polymer or graft polymer which has reactive monomer is generally used as the reactive compatibilizing agent. Maleic anhydride is applied to the reactive monomer for graft polymer. Random copolymer is also applied to the reactive compatibilizing agent although it doesn't have 2 different parts like block polymer or graft polymer [34, 37]. Styrene-maleic anhydride copolymer (SMA) which has a similar molecular structure to SFC is most often used as the reactive compatibilizing agent in the random copolymers such as polymer alloy for nylon and polyphenylwne ether [34]. Maleic anhydride in the SMA has been widely used in graft reactions for various polymers due to its high reactivity with various functional groups [38]. The SMA is also applied to polymer alloy for polystyrene and polyamide 6 [44], acrylonitrile-butadiene-styrene (ABS) and poly (ethylene terephthalate) (PET) [45], ABS and poly (butylene terephthalate) (PBT) [46] and PET and polystyrene (PS) [47, 48].

SFC has a similar molecular structure to the SMA including styrene skeleton. Therefore, it was assumed that SFC also had a potential to be applied to reactive compatibilizing agent for polymer alloy of polystyrene type resin and polyester type resin. It should have higher reactivity with PET than SMA since its carboxylic group can easily react with OH group of polymers. SMA was reported to have low reactivity with PET without

the presence of catalyst [37]. Therefore, complex dual compatibilizing system of SMA and other materials were proposed [47, 48]. Tetra-glycidyl ether of diphenyl diamino methane (TGDDM) [47] or poly (methylene (phenylene isocyanate)) (PMPI) [48] was added to PET and PS with the SMA and it reacts with PET and SMA at the interface to produce copolymer. It is considered a kind of a block copolymer of SMA and other compound.

3.4.1.2. PET/SPS polymer alloy for film capacitor

It was reported that new polymer alloy of polyethylene naphthalate (PEN) and Syndiotactic polystyrene (SPS) improved the voltage resistance and processability for stretched thin film for film capacitor [40, 41]. Film capacitor is widely used in various kinds of products such as lighting fixtures, home appliances, and so on. **Figure 3-4-3** shows an example of film capacitor. Stretched thin film of thermoplastic and aluminum (Al) deposited film are laminated. Thickness of the film is approximately sub μm . Electricity is stored in the gap between Al deposited films.

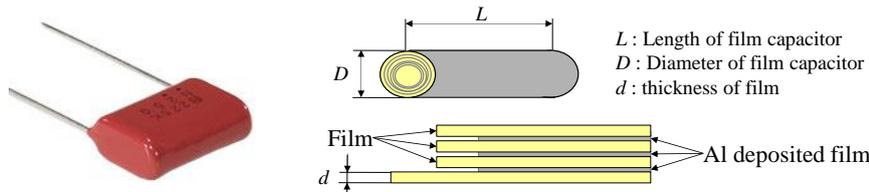


Fig. 3-4-3 Film capacitor

It has a potential to substitute aluminum (Al) electrolytic capacitor [49]. Al electrolytic capacitor is much smaller than film capacitor. Therefore, it is widely used in most of electronics products such as lighting fixtures, home appliances, car electronics, and so on. However, the biggest disadvantage of Al electrolytic capacitor is life. Its life is a range from 5 to 7 years, whereas life of film capacitor is approximately 20 years [49]. In addition, life of Al electrolytic capacitor depends on ambient temperature. If the temperature is 10°C higher than prospected, the life should be a half.

In most of electronics products using Al electrolytic capacitor, the shortest life of each component or device used in the products is that of Al electrolytic capacitor. Therefore, the life of the electronics products is subject to the life of Al electrolytic capacitor. Much longer life of film capacitor enables to provide much longer life to electronics products which should cause the cost reduction not for only products replacement, but also for maintenance fee.

Film capacitor was started to be supply to hybrid electric vehicles (HEV) several years ago instead of Al electrolytic capacitors due to its longer life and superior electric properties [49, 50]. The mass volume of film capacitor for HEV contributed to reduce the cost. It caused the increasing of demand for film capacitor to substitute Al

electrolytic capacitors for many applications such as converter of photovoltaic generation (PV) systems.

However, the film capacitor size is still larger than Al electrolytic capacitor. Further size reduction is required to expand applications. The size of film capacitor depends on electrostatic capacity. The electrostatic capacity is described as equation (3-4-1).

$$C = \frac{\epsilon S}{d} \quad (3-4-1)$$

where C : Electrostatic capacity [F], ϵ : Dielectric constant

S : Surface area of film [m²], d : Thickness of film [m]

Equation (3-4-1) indicates the following points of relationship between each factor and the surface area (S) which represents the size of the film capacitors if the electrostatic capacity is set up the constant value.

- Higher *dielectric constant* (ϵ) requires smaller S
- Smaller *thickness of film* (d) requires smaller S

Thickness of film highly affects the size of capacitor. If the thickness becomes a half, surface requires a half for the given electrostatic capacity. In Fig.3-4-3, for simplifying the size estimation, length of film capacitor (L) should be a half. Diameter of film capacitor (D) also should be a half since the diameter depends on the film thickness mainly. Thickness of Al deposited film is negligibly thin. Hence, the size should be one-fourth generally [49]. It is roughly estimated the size should be proportion to the square of thickness.

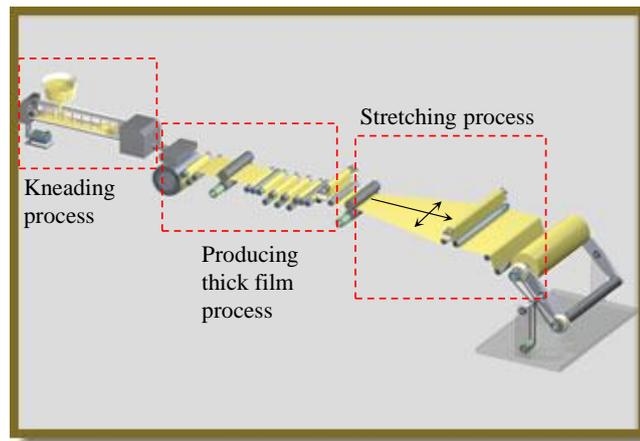


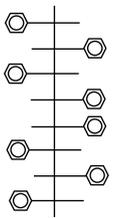
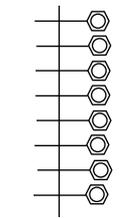
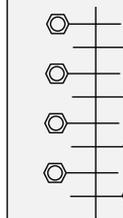
Fig 3-4-4 Example of 2 axes stretching machine [51]

However, thickness of film is subjected to voltage resistance and processability for production process of stretched thin film. Sub μm order of stretched thin film requires high mechanical strength to prevent tearing during the stretching process. **Figure 3-4-4** shows an example of 2 axes stretching machine [51]. Polymer is supplied to this

machine and then is kneaded to produce thick film. The thick film is stretched to both of vertical direction and horizontal direction to produce the stretched thin film with sub μm order. If mechanical strength is in sufficient, the film should be tore up during the stretching process or manufacturing process of capacitor. Therefore, extremely high mechanical strength should be required for the polymer.

SPS is a high performance engineering plastic and has higher thermal stability [39]. Molecular structure and thermal property of SPS and other type of polystyrene are described in **Table 3-4-1**. Its higher thermal stability is considered to be based on its unique molecular structure.

Table 3-4-1 Syndiotactic polystyrene [39].

Steric alignment and thermal stability		
Atactic	Isotactic	Syndiotactic
		
T _g =100°C T _m : —	T _g =100°C T _m =240°C	T _g =100°C T _m =240~270°C



SPS

In film capacitor, polypropylene (PP) and polyethylene terephthalate (PET) are generally used for the thermoplastic resin. **Table 3-4-2** shows the comparison of film capacitors.

Table 3-4-2 Comparison of film capacitors

	PP		PET		SPS(neat resin)		PET/SPS (Assumption)	
Dielectric constant (ϵ)	✗	2.2	⊙	3.2	△	2.6	⊙	3.0
AC Voltage Resistance(kV/mm)	⊙	200 ~ 400	✗	120 ~ 280	⊙	(Assumption)	⊙	Improved by SPS
Temperature dependence of electric property	⊙	Independent	△	Dependent	⊙	(Assumption)	⊙	Improved by SPS
Processability for thin film	✗	Thick	⊙	Thinner than PP	—	N/A	⊙	Thinner than PP
Size	✗		△		—	N/A	⊙	Improved by SPS

PET:SPS=70%:30%

The surface area (S) of PET requires only about two-thirds of PP since dielectric constant (ϵ) of PET (3.2) is about 1.5 times higher than that of PP (2.2). It indicates that the size of PET film capacitor requires only about two-thirds of PP film capacitor. PET can be produced thinner film than PP. The size of capacitor is roughly proportion to the square of film thickness. It should be remarkable advantage. However, PET has a lower

limit of thickness since AC voltage resistance is lower than PP. Another disadvantage of PET is temperature dependence of electric property. Once the temperature increases in some reason, there is a possibility that a negative cycle starts and then cause thermal runaway phenomenon at the worst case. PP doesn't depend on temperature and has a highly thermal stability. These disadvantages of PET are expected to be improved by SPS. The same disadvantage of PEN stretched thin film was verified to be improved by SPS [40, 41]. If PET/SPS polymer alloy film could realize to improve disadvantage of PET, it was assumed to decrease the film thickness to the minimum size which is realized in terms of processability. The film capacitor size is roughly proportion to the square of film thickness. It suggests the possibility to achieve the same size as Al electrolytic capacitor. It is expected the revolutionary impact for electronic products.

As mentioned above, in exploring the application of SFC, the compatibilizing agent for polymer alloy of polyethylene terephthalate (PET) and syndiotactic polystyrene (SPS) was selected to create new innovative film capacitor which has extremely small size as same as Al electrolytic capacitor.

3.4.1.3 Hypothesis of SFC applying to the reactive compatibilizing agent

Figure 3-4-5 shows PET and SPS after kneading at a temperature of 300°C and a rotation speed at 35 rpm with no compatibilizing agent. “Sea” area consists of PET and island (domain) consists of SPS. Averaged diameter of domain was 40.6µm. The averaged diameter seemed to be too large. The stretched thin film with thickness of sub µm order requires extremely high compatibility. It is obvious that superior compatibilizing agent should be needed.

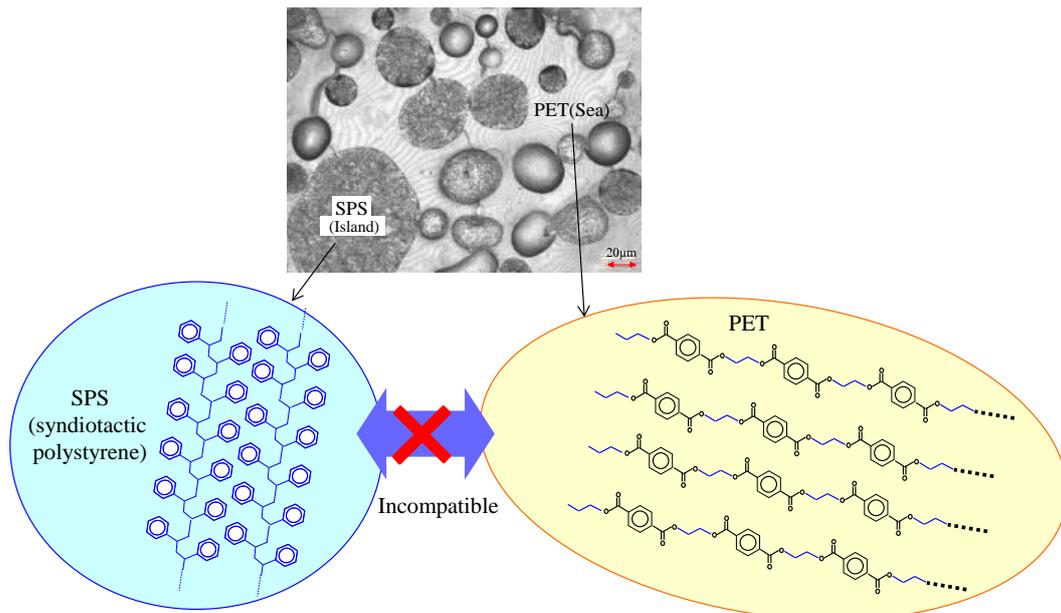


Fig. 3-4-5 SPS and PET (Kneading condition, 300°C, 35rpm)

Hypothesis of SFC applying to compatibilizing agent for PET/SPS polymer alloy is described in **Fig. 3-4-6**. Firstly, carboxylic acid of SFC reacts with OH group at the end of PET polymer to generate ester bond to be integrated. The SFC integrated with PET polymer is dispersed on the interface of PET agglomeration. Styrene skeleton of SFC should be affinitive for SPS agglomeration. Hence, compatibility should be increased.

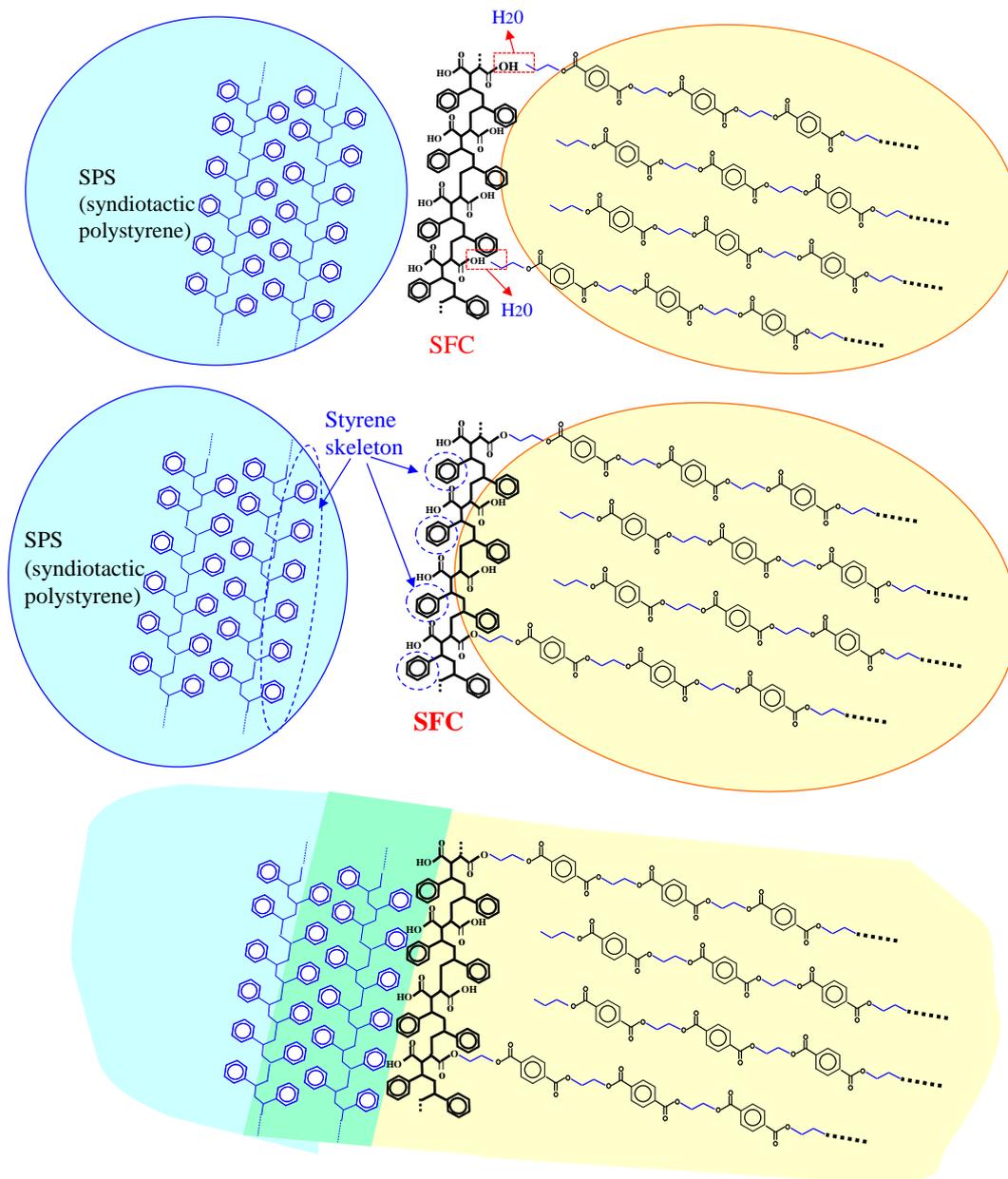


Fig. 3-4-6. Hypothesis of SFC applying to compatibilizing agent for PET/SPS polymer alloy

PET/SPS polymer alloy has a potential to improve the PET film capacitor to solve its disadvantage resulting to create new smaller film capacitor. In future, it is proposed to

realize same size film capacitor as Al electrolytic capacitor with semi-permanent life. It suggests that it might provide semi-permanent life to most of electronic products. It is expected the revolutionary impact for electronic products in world wide

In this study, fundamental verification of the hypothesis which SFC could be applied to compatibilizing agent for PRT/SPS polymer alloy described above was conducted. PET, SPS were mixed with SFC or other commercial compatibilizing agent and then were kneaded by kneading machine to produce PET/SPS polymer alloy. The PET/SPS polymer alloy using various compatibilizing agents were evaluated the compatibility. To investigate the mechanism of compatibilizing effect and to improve the hypothesis, thermal stability analyses of SFC and SFC esterified with 1-octanol were conducted. To identify the molecular structure of compatibilizing agents in PET/SPS polymer alloy after kneading process, separation process was examined and then the solid obtained was analyzed by FT-IR and Diffusion Ordered Spectroscopy (DOSY) NMR.

3.4.2 Materials and methods

PET (SK Chemical: Skypet-BB8055) and SPS (Idemitsu Kosan Co., Ltd.; Xarec, S105) were used to produce polymer alloy sample. Content ratio of PET, SPS, and compaibilizing agent were 69wt%, 30wt%, and 1wt%, respectively. In the case of no compaibilizing agent, Content ratio of PET and SPS were 70wt%, 30wt%, respectively. **Figure 3-4-7** shows kneading experiment to produce polymer alloy. Two-axes kneading machine (Imoto Machinery Co., Ltd.; IMC-168D) was used. Kneading condition was at a temperature of 300°C with rotation speed was 35 rpm.

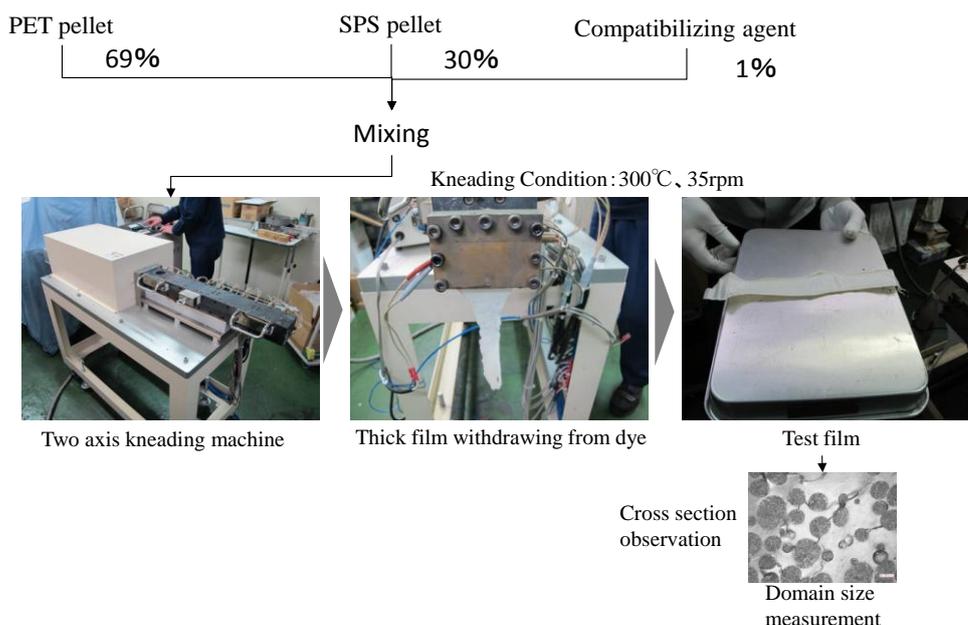


Fig. 3-4-7 Kneading experiment of polymer alloy

Test film was cut and cross section was observed by laser microscope (Keyence;VK-9510) and software (Keyence;VK-viewer). Domain size in graphic data obtained was measured by Mac-View (Mountech Co., Ltd.)

Various products of SMA (Kawahara Petrochemical Co., Ltd.) were tested with SFC for comparison. Commercial compatibilizing agent described in [40], Epocros (Oxazolyn type polystyrene, Nippon Shokubai Co., Ltd.; RPS-1005) [52] and styrene-acrylic acid copolymer (Seiko PMC Corporation; RS-1192), were also tested. They are defined as the best compatibilizing agents for PEN/SPS polymer alloy [40]. Epocros is a graft polymer which has polystyrene skeleton with oxazolyn group. It has a compatibility with polystyrene and PPE. Its oxazolyn group can react with PET, PBT, PPS, PC [53]. Detail molecular structure is confidential. RS1192 is styrene-acrylic acid copolymer which has Mw of 11,800 and styrene/acid molar ratio is 0.84. It should be equivalent to 1.68 as S/F molar ratio since acrylic acid is mono carboxylic acid.

In thermal stability analyses, TG-DTA, TG at constant temperature, Thermogravimetry Mass Spectrometry (TG-MS), Trap GC/MS were conducted. TG-DTA and TG at constant temperature were analyzed by SII Nano Technology Inc., TG/TDA6300. TG-MS was analyzed by Shimadzu Corporation, TG-40 type GC/MS QP2010. Trap GC/MS was analyzed by Shimadzu Corporation, GC/MS QP5050A.

SFC and styrene acrylic acid copolymer were extracted from polymer alloy after kneading process and analyzed. **Figure 3-4-8** shows a separation process flow in the case of SFC after kneading process. It was extremely difficult to extract the compatibilizing agent which has a similar structure of both polymers at content ratio of only 1wt%. Firstly, PET/SPS polymer alloy sample using SFC was frost shattered. Secondly, 8 g of Potassium hydrate (KOH) and 100mL of pure water were added to the polymer alloy sample powder and then stirred at a temperature of 100°C for 16 hours. PET was hydrolyzed to ethylene glycol (EG) and potassium terephthalate (TPA-K). SFC should become potassium salt (SFC-K). They were dissolved into water since they were water soluble. SPS was not hydrolyzed and remained as solid. It was filtered to be separated from the solution containing EG, TPA-K, and SFC-K.

Next, 200mL of hydrochloric acid solution at a concentration of 0.2mol/L was added to the filtrate and the stirred. TPA-K and SFC-K were acidified to terephthalic acid (TPA) and SFC, respectively and then precipitated. They were filtered to be separated from the solution. After filtering TPA and SFC, 30mL of glacial acetic acid was added to them to separate TPA and SFC. SFC could be dissolved in glacial acetic acid, whereas TPA could not be dissolved. TPA was filtered as solid to be separate from glacial acetic acid solution containing SFC. The glacial acetic acid solution was vacuum evaporated

to vaporize acetic acid and then the precipitated sample was obtained.

The precipitated sample obtained was analyzed by FT-IR to clarify to have carboxylic acid and styrene skeleton. After FT-IR analysis, Diffusion Ordered Spectroscopy (DOSY) ^{13}C NMR (^{13}C DOSY analysis) was conducted to identify that the carboxylic acid and the styrene skeleton existed in same one molecule to verify that it was SFC originally. In identification of each compound among mixture sample, DOSY method enables to obtain ^{13}C NMR spectrums of each compound without separation them from mixture sample due to the difference diffusion rate in the solution based on the size of molecule. It has been applied to analyze various complex mixtures as a powerful tool [53-56].

Firstly of pre-treatment for ^{13}C DOSY analysis, 10 mL of methanol was added to the precipitated sample to dissolve it. Secondly, 2 mL of hexane solution containing trimethylamine diazomethane at a concentration of 10% was added to the methanol solution. Then, the methanol solution became cloudy with generating nitrogen gas and SFC esterified with methanol was precipitated. The solution was naturally evaporated at room temperature for 12 hours. Finally, 0.5 mL of deuterated chloroform was added to the evaporated sample to prepare a sample solution for DOSY analysis.

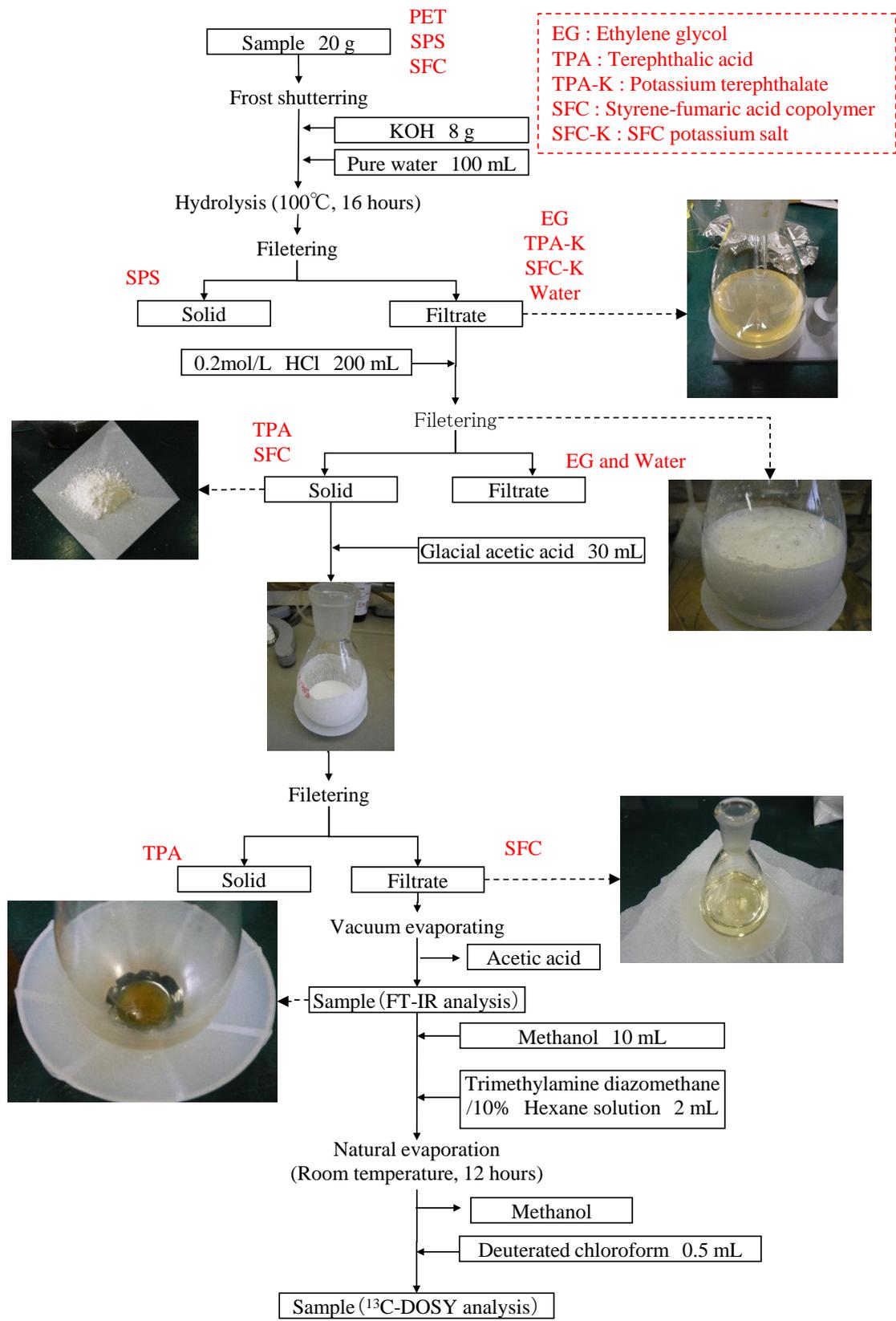


Fig. 3-4-8 Process flow of extracting compatibilizing agent (In case of SFC)

3.4.3 Results and discussion

Tables 3-4-3A and 3-4-3B show kneading experimental results of PET/SPS polymer alloy using various compatibilizing agents. Kneading condition was at a temperature of 300°C. The graphic data was cross section observation of test film. Scale factor is 1,000 times. Their order is based on averaged diameter (μm).

Table 3-4-3 A Kneading experimental results of PET/SPS polymer alloy

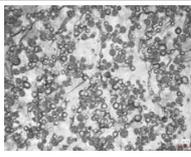
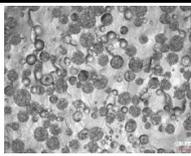
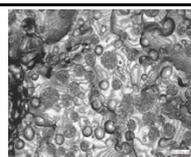
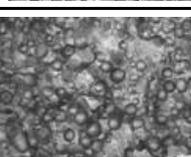
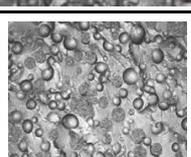
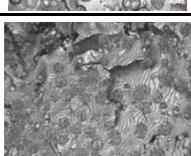
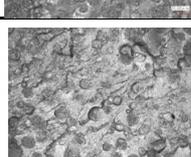
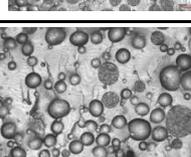
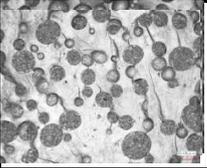
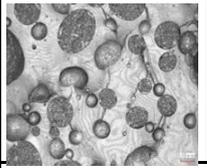
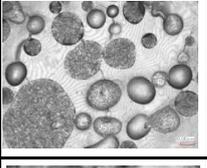
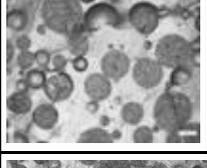
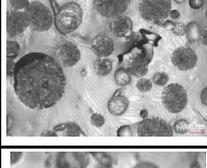
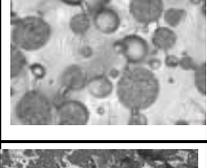
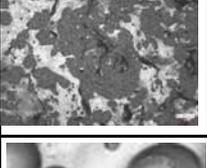
Sample	Mw	S/F molar ratio	Averaged diameter [μm]	$\times 1,000$
SFC (Dicarboxylic acid type)	30,000	2.2	8.6	
SMA 3000P (Anhydride type)	9,500	3.0	17.8	
SMA 2625P (Half-ester type)	9,000	2.0	18.7	
RS1192 (Styrene-acrylic acid copolymer)	11,800	0.84	19.8	
SMA 2000I (Imide type)	4,000	2.0	20.0	
SMA 17352P (Half-ester type)	7,000	1.0	20.8	
SMA 2000P (Anhydride type)	7,500	2.0	21.3	
EF-30 (Anhydride type)	9,500	3.0	25.6	

Table 3-4-3 B Kneading experimental results of PET/SPS polymer alloy

Sample	Mw	S/F molar ratio	Averaged diameter [μm]	$\times 1,000$
1440 (Half-ester type)	7,000	1.0	31.4	
3840F (Half-ester type)	10,500	4.0	37.0	
None	—	—	40.6	
EF-40 (Anhydride type)	11,000	4.0	41.3	
SMA-1000P (Anhydride type)	5,000	1.0	48.3	
EF-60 (Anhydride type)	11,500	6.0	63.4	
RPS-1005 Epocross Oxazolyn type Polystyrene	—	—	70.6	
EF-80 (Anhydride type)	14,000	8.0	80.3	

In graphic data, domain (island) was SPS and “sea” was PET. SFC showed the best performance for compatibilizing PET and SPS with averaged domain size of $8.6\mu\text{m}$. The second best was SMA3000P with $17.8\mu\text{m}$ which was twice as SFC. SMA has a similar molecular structure to SFC. One reason was assumed the different of reactivity

of dicarboxylic acid type and anhydride type. SFC, dicarboxylic acid type, should have higher reactivity. Another reason was assumed that Mw of SMAs was a range from 4,000 to 14,000. As described in Fig.3-4-1, a certain length of molecules represented by Mw might be needed to grasp each polymer to create compatibilizing effect. Mw of SFC was 30,000. Mw of SMAs was assumed to be too small.

Epocross (Oxazolyn type polystyrene) was not effective and showed larger averaged diameter than no compatibilizing agent (None) although it was described as effective compatibilizing agent for PEN/SPS polymer alloy in patent [32].

Relationship between averaged diameter and Mw or S/F molar ratio of compatibilizing agents were examined. **Fig.3-4-9** shows the relationship between averaged diameter and Mw. No compatibilizing agent (None) and Epocross (Oxazolyn type polystyrene) was plot at Mw=0. Molecular structure of Epocross was unknown due to confidentiality. In Mw at a range less than 14,000, it seemed to have a tendency that averaged diameter increase with increasing Mw. However, Mw of SFC was 30,000. It should not be able to consider as same extension. Styrene-acrylic acid copolymer showed small averaged diameter even Mw was 11,800.

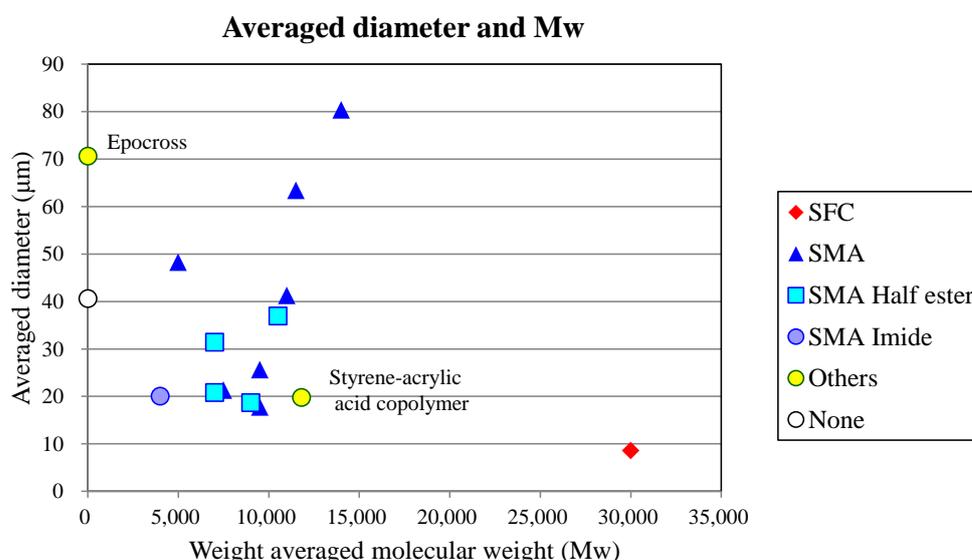


Fig.3-4-9 The relationship between averaged diameter and Mw

Fig.3-4-10 shows the relationship between averaged diameter and Styrene/Acid (S/A) molar ratio. No compatibilizing agent (None) and Epocross (Oxazolyn type polystyrene) was plot at S/A molar ratio=0. In S/A molar ratio is over 2.9, averaged diameter became larger with increasing S/A molar ratio. At S/A molar ratio is around 1.0, compatibilizing agents have averaged diameter at a range from 20 to 48. SFC has S/A molar ratio of 2.2. It is seemed to contribute small averaged diameter consisting with other compatibilizing agents.

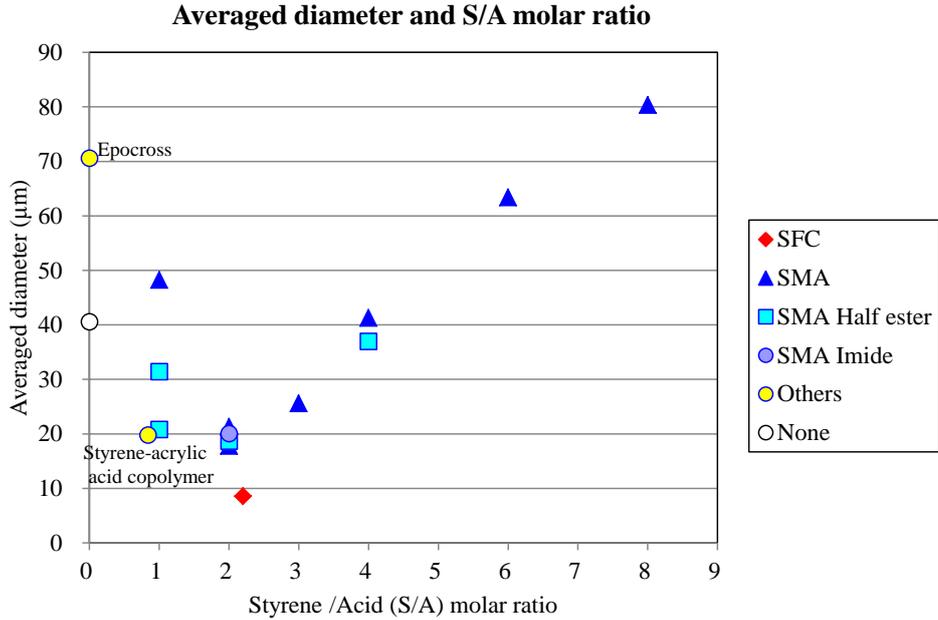


Fig.3-4-10 The relationship between averaged diameter and S/A molar ratio

The above evaluation results suggested that Mw and S/A molar ratio affected the compatibility represented by averaged diameter. To clarify the each independent effectiveness of Mw and S/A molar ratio, the relationships between averaged diameter and S/A molar ratio at a similar Mw and Mw at a similar S/A molar ratio were examined.

Fig.3-4-11 shows the relationship between averaged diameter and S/A molar ratio in Mw at a range from 9,000 to 14,000. Averaged diameter became smaller with decreasing S/A molar ratio until S/A molar ratio=3.0. In S/A molar ratio was less than 3.0, averaged diameters were same level around 20µm.

Mw at a range from 9,000 to 14,000

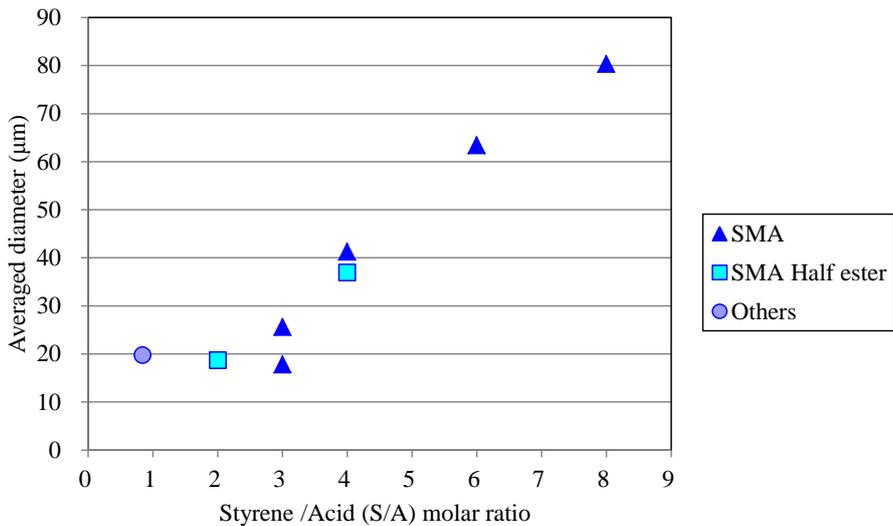


Fig.3-4-11 The relationship between averaged diameter and S/A molar ratio.

Fig.3-4-12 shows the relationship between averaged diameter and Mw in S/A molar ratio at a range from 0.8 to 1.0. Averaged diameter became smaller with increasing Mw.

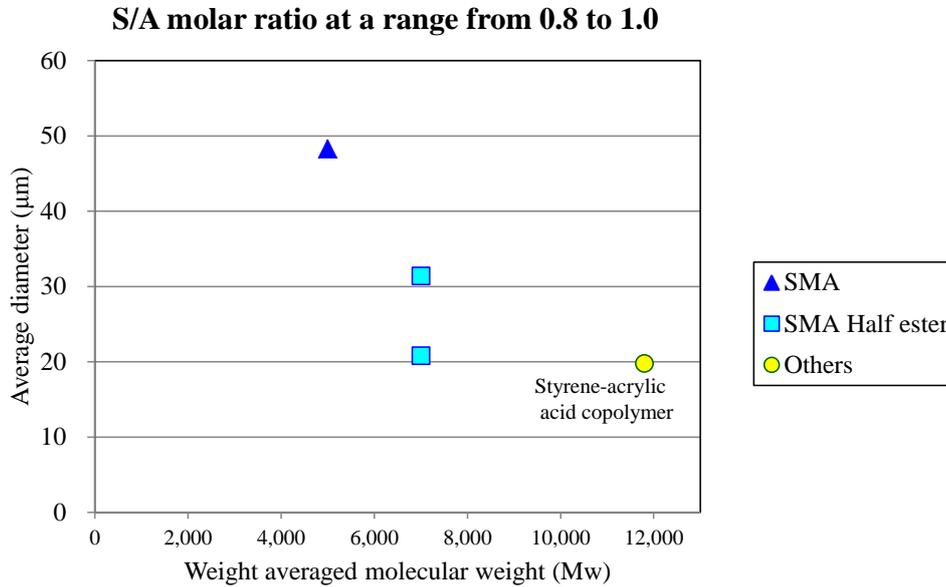


Fig.3-4-12 The relationship between averaged diameter and Mw

Fig.3-4-13 shows the relationship between averaged diameter and Mw in S/A molar ratio at a range from 2.0 to 2.2. Averaged diameter also became smaller with increasing Mw. It seemed that SFC was an extension of tendency of SMAs. In S/A molar ratio was less than 2.2, averaged diameter became smaller with increasing Mw for dicarboxylic acid type, anhydride type, half ester type, and imide type.

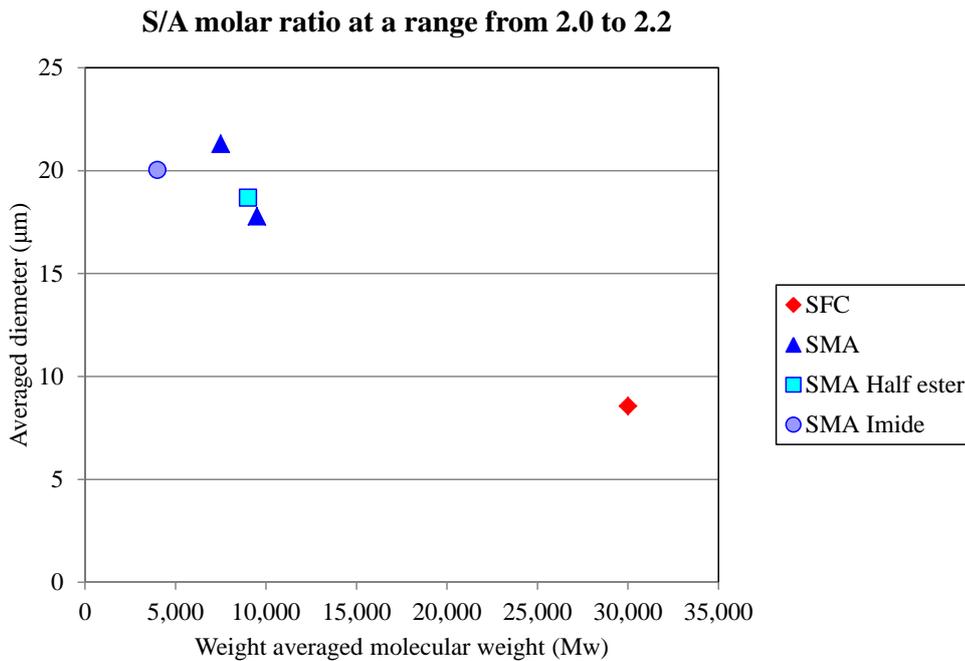


Fig.3-4-13 The relationship between averaged diameter and Mw

Whereas, in S/A molar ratio was over 3.0, the tendency was opposite described in **Fig. 3-4-14**. Averaged diameter became larger with increasing Mw.

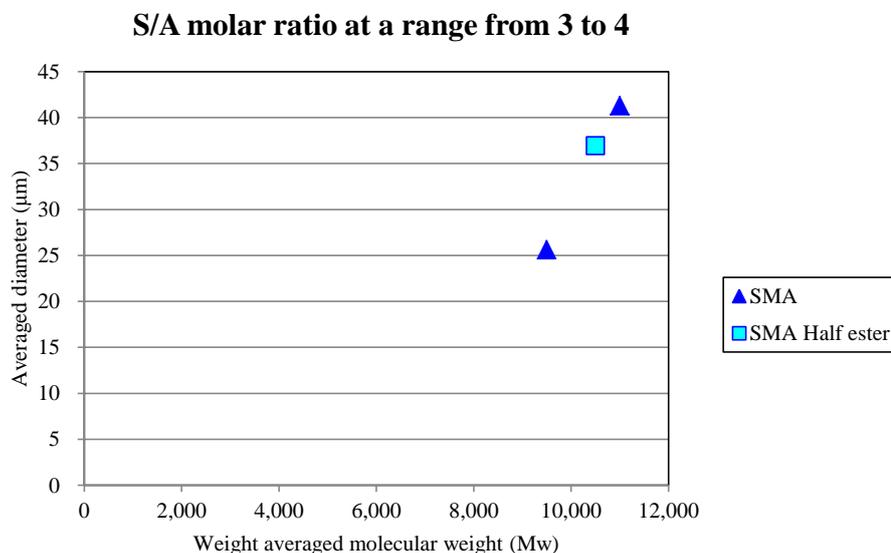


Fig.3-4-14 The relationship between averaged diameter and Mw

It was assumed that Mw and S/A molar ratio affected to compatibility for PET/SPS polymer alloy. In S/A molar ratio was less than 2.2, averaged diameter became smaller with increasing Mw. Mw of 30,000 for SFC seemed to contribute the best performance of compatibility. In Mw was around 30,000, the effectiveness of S/A molar ratio were unknown since there was no compatibilizing agent which had same level of Mw. However, In Mw at a range from 9,000 to 14,000, S/A molar ratio of 2.0 or less seemed to be effective. Therefore, both of the higher Mw and the lower S/A molar ratio of SFC were concluded to contribute to generate the compatibilizing effect.

Mechanism of compatibilizing effect for SFC was seemed to be explained by the hypothesis of dehydration condensation between carboxylic acid of SFC and OH group at the end of PET described in Fig.3-3-4. However, it was assumed that the hypothesis should be improved. Unreacted carboxylic acid should be converted to be hydrophobic. Based on previous literature and the evaluation result of thermal stability test of SFC and SFC esterified with 1-octanol, the hypothesis was re-considered to explain the compatibilization mechanism.

M. Swaitala-Zeliazkow conducted the TG-DTA analysis of SMA, styrene-maleic acid copolymer (SMAC) and styrene-fumaric acid copolymer (SFC) [57 58]. It was reported that SMA showed thermal stability, but SMAC and SFC were thermally unstable. **Fig.3-4-15** shows TG-DTA result of SMA and SMAC [57]. SMA was stable up to around 300°C and then decreasing. SMAC, dicarboxylic type, started to decrease at around 100°C.

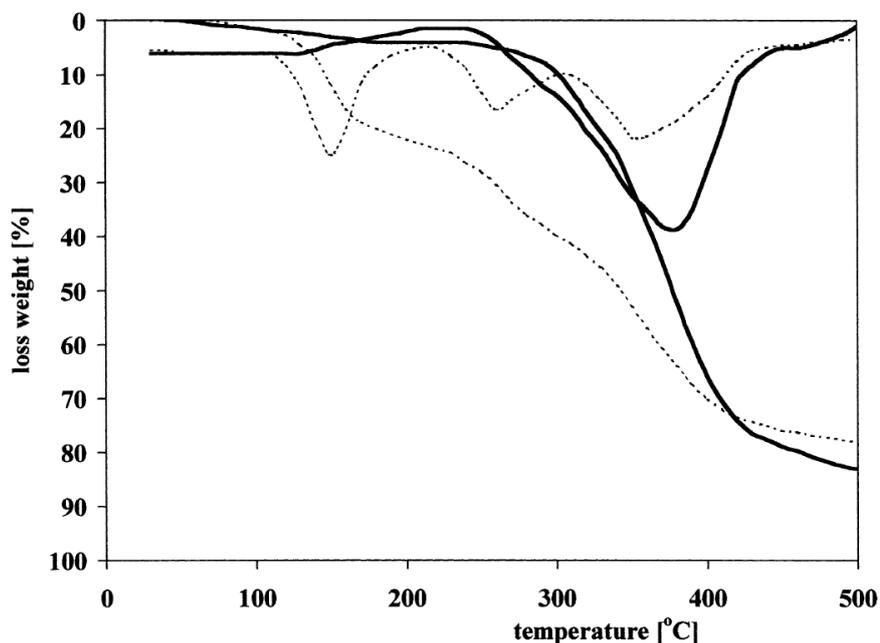


Fig. 1. TG and DTG curves of St-MAn copolymer (—) and hydrolysed St-MAn copolymer (.....).

Fig.3-4-15 TG-DTA of SMA and SMAC [57]

Fig. 3-4-16 shows TG-DTA of SFC and SFC esterified with 1-octanol (SFC-C8). SFC also started to degrade at around 100°C. SFC-C8 was very stable up to around 350°C.

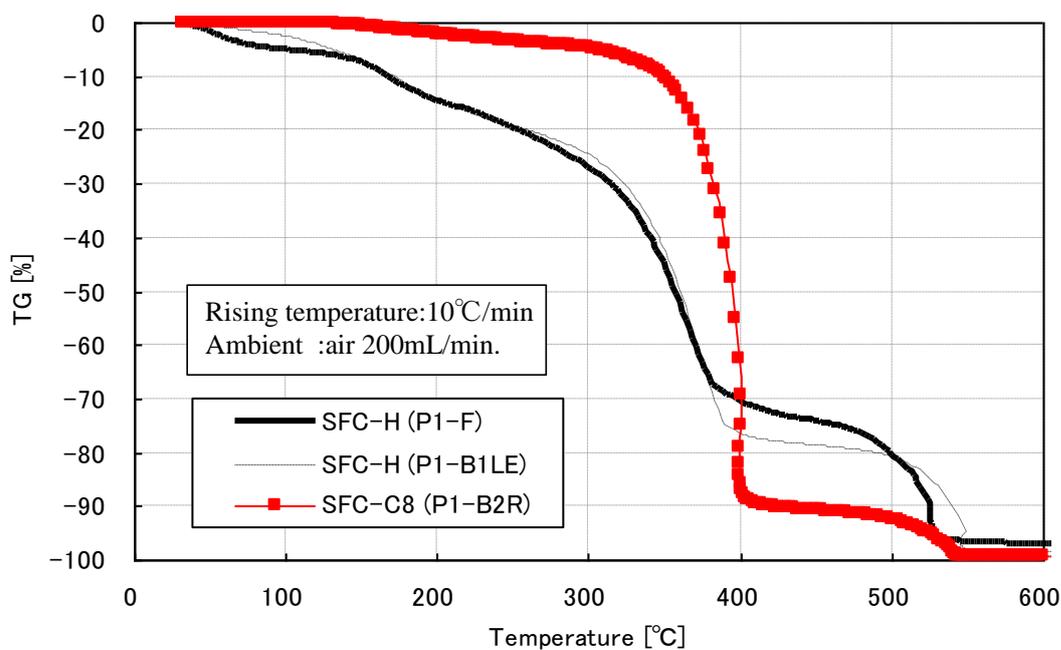


Fig.3-4-16 TG-DTA of SFC and SFC-C8

Figure 3-4-17 A, B shows TG curve at temperature of SFC and SFC-C8. SFC decreased with 20% at 180°C. Whereas, SFC-C8 decreased with only 5% at a temperature range from 140°C to 180°C for 3 hours. It suggests that SFC thermal stability should become higher once esterified.

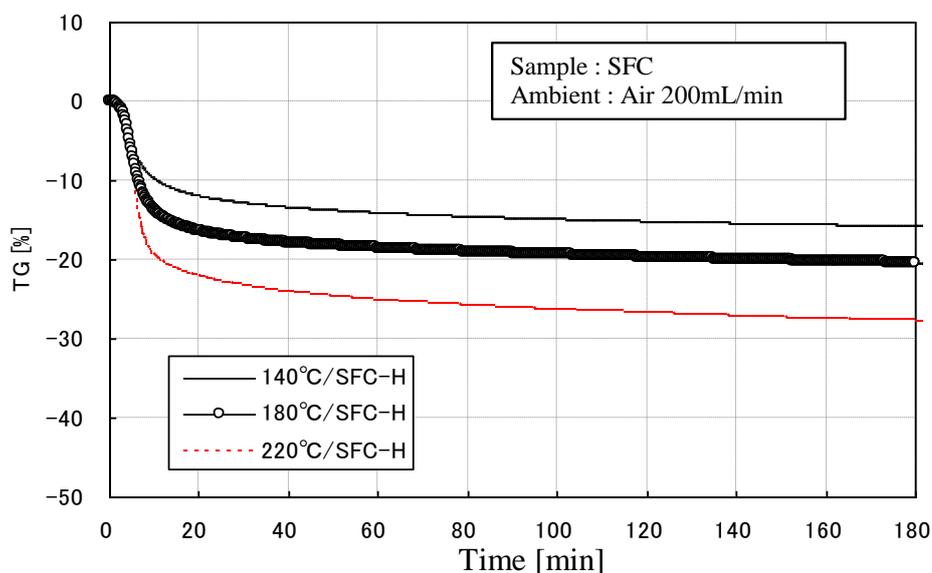


Fig. 3-4-17 A TG at constant temperature (SFC)

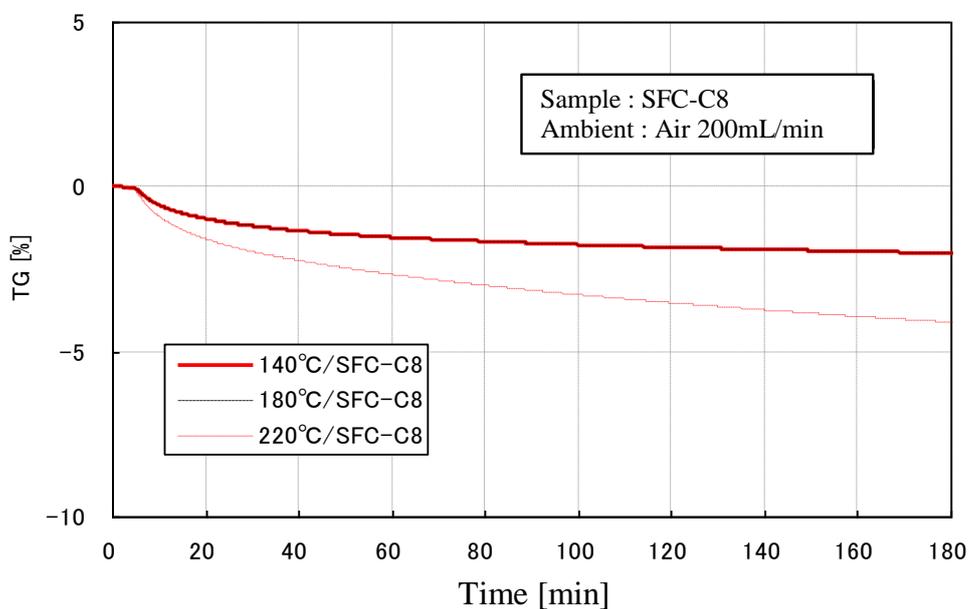


Fig. 3-4-17 B TG at constant temperature (SFC-C8)

Fig. 3-4-18 A shows TG-DTA results of SFC. **Fig. 3-4-18 B** shows TG-MS results of SFC which indicates various gas generations. **Fig. 3-4-18 C** shows TG-MS results which indicate accumulation of gas generated.

Water started to generated around 150°C and had a peak around 210°C and then decrease. It suggests that dicarboxylic acid converted to anhydride. CO₂ started to generated around 210°C and had a maximum generation around 280°C. It suggests that decarbonization of carboxylic acid. Styrene had the first peak around 180°C and then slightly generated and had the second small peak around 250°C. After 300°C, it generated explosively. It suggests that demolition of styrene skeleton. C₁₀H₁₄O had the first peak around 180°C and had the second peak around 250°C. Both peaks of styrene and C₁₀H₁₄O at 180°C were assumed vaporization of styrene remaining. Both peaks at 250°C were assumed to be derived from the pyrolysis of styrene chain. It should be supported by the Kubota's report which indicated the pyrolysis of styrene chain started around 230°C in glycolysis of thermosetting polyester resin [13, 15].

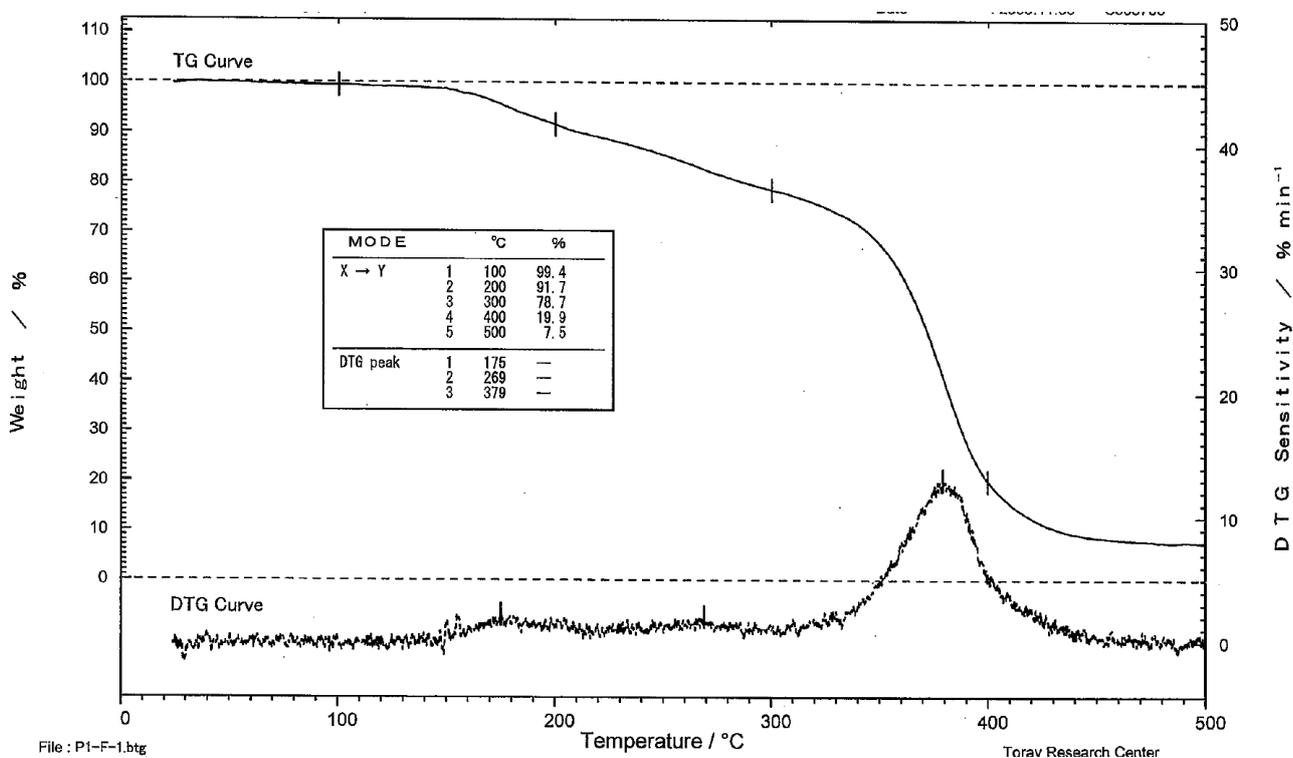


Fig. 3-4-18 A TG-DTA results of SFC.

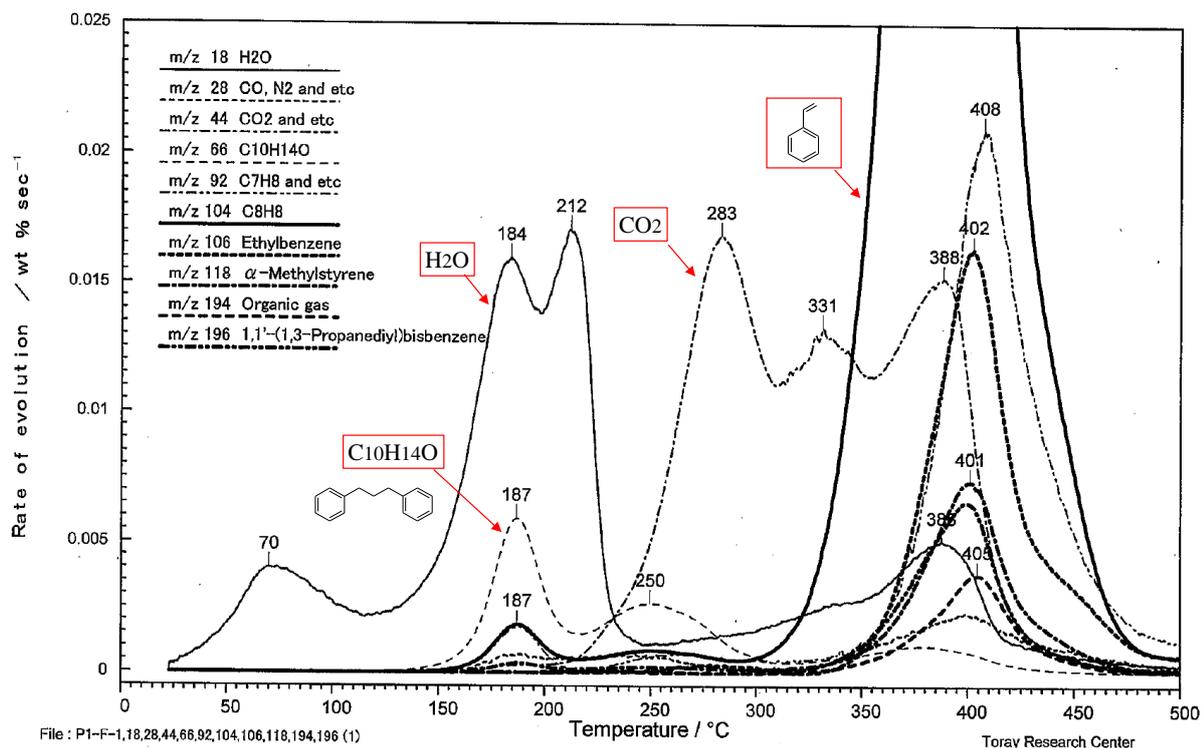


Fig. 3-4-18 B TG-MS results of SFC

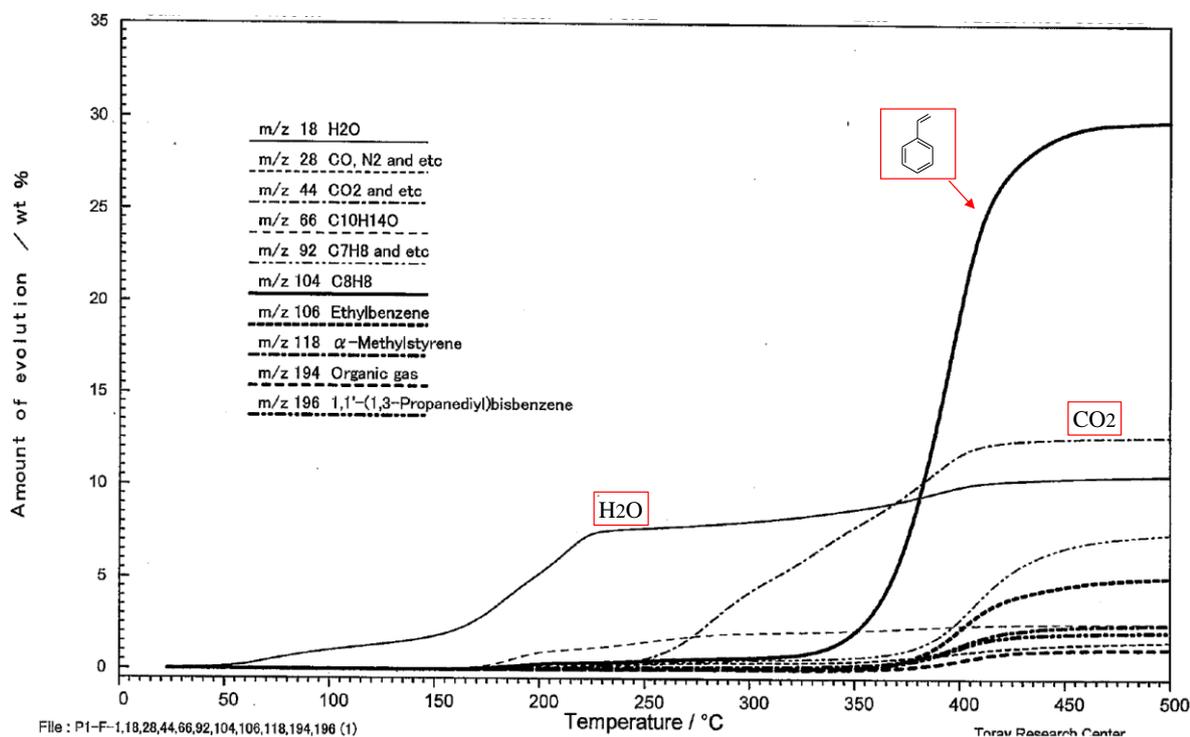


Fig. 3-4-18 C TG-MS results of SFC

The sample after vacuum evaporation to remove acetic acid in process flow described in **Fig.3-4-8** was analyzed by FT-IR. **Fig. 3-4-19** shows the result of FT-IR spectrum for a sample extracted from PET/SPS polymer alloy using SFC. Peaks which indicated styrene skeleton and carboxylic group were observed. However, it was not identified that styrene skeleton and carboxylic group existed in a same molecule. There is a possibility that both peaks were derived from two different molecules.

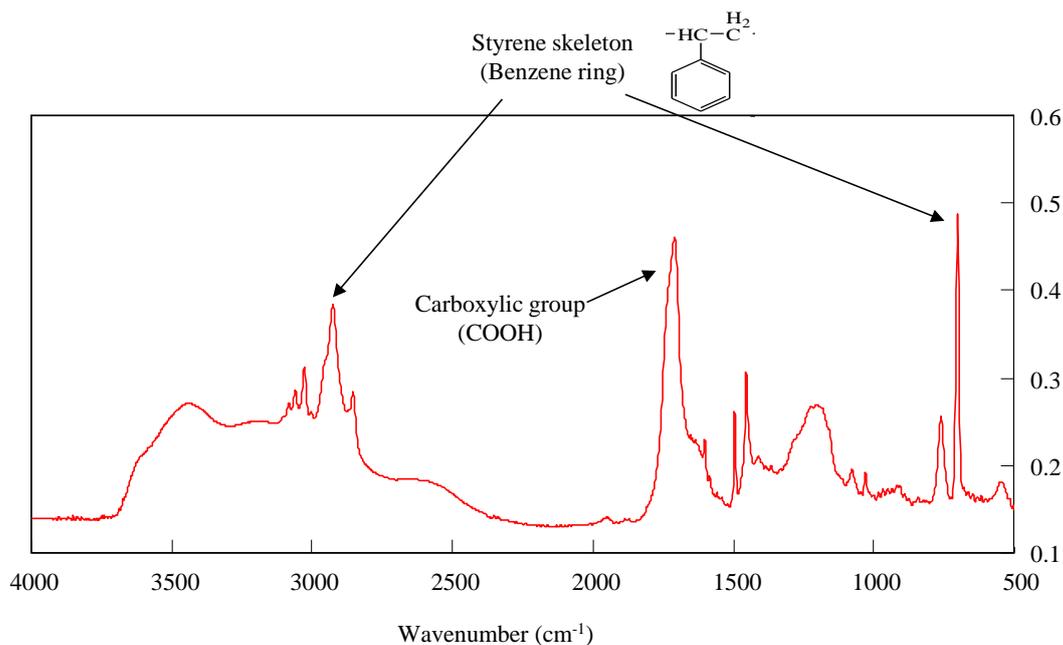


Fig. 3-4-19 FT-IR spectrum for a sample extracted from PET/SPS polymer alloy using SFC

To identify that the sample has the styrene skeleton and the carboxylic acid in one molecule, ¹³C DOSY analysis was conducted. This identification indicates the sample should be the SFC. **Fig.3-4-20** shows the spectrum chart of ¹³C DOSY for the sample extracted from PET/SPS polymer alloy using SFC. The ¹³C DOSY spectrums described in **Fig.3-4-20** are separated based on diffusion coefficient. The upper spectrum indicates the large molecule with low diffusion coefficient, whereas the lower spectrum indicates the small molecule with high diffusion coefficient. **Figure 3-4-21 A** shows square of the peak strength of each diffusion coefficient for ester, benzene circle of styrene, and chloroform as analyzing agent. Peak of ester indicates carboxylic acid since the carboxylic acid was esterified with methanol in the pre-treatment described in **the section 3.4.2**. **Figure 3-4-21 B** shows the standardized square of peak strength of each diffusion coefficient. The square of peak strength of each diffusion coefficient was divided by the square of peak strength of the fastest diffusion coefficient.

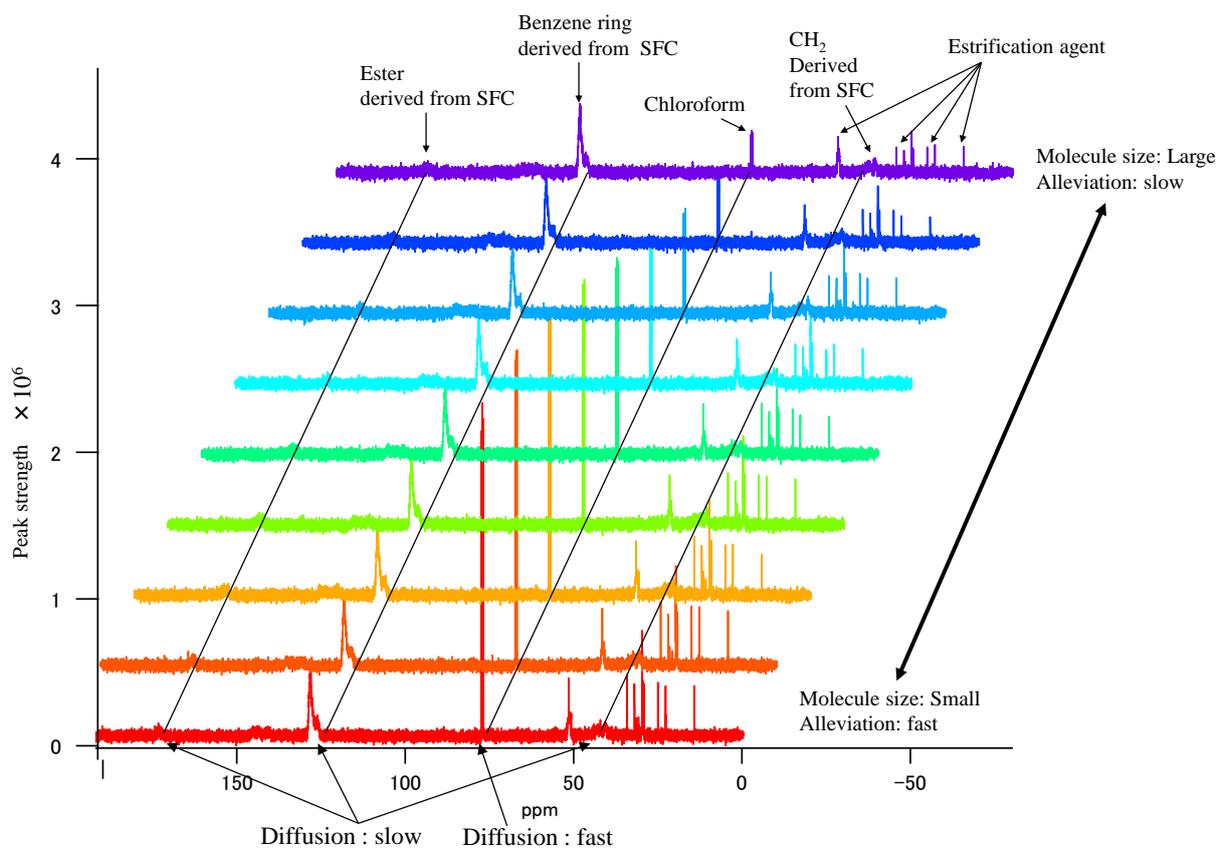


Fig.3-4-20 Spectrum charts of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using SFC

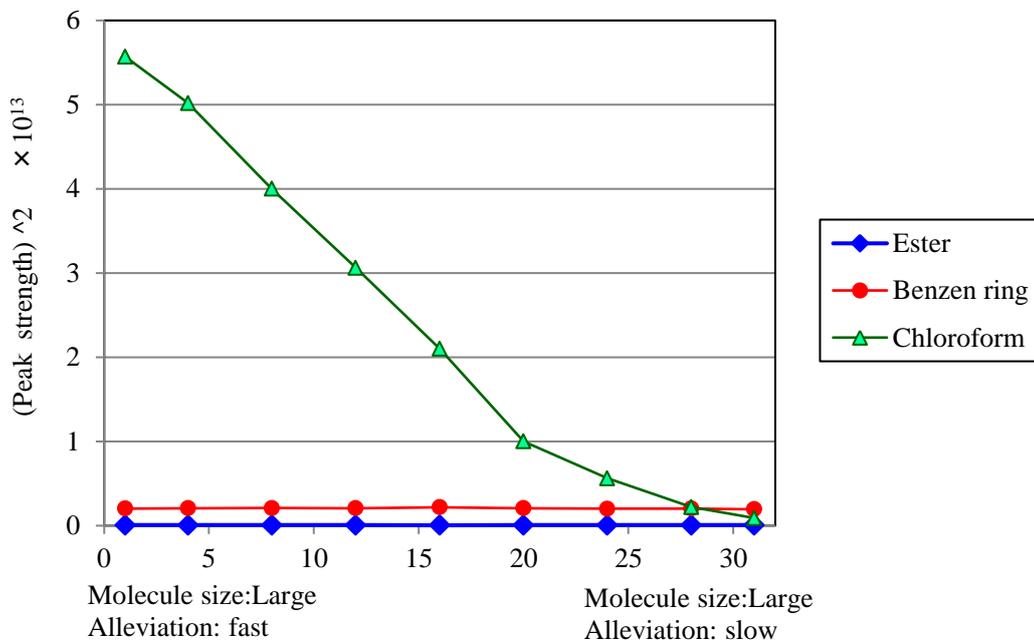


Fig.3-4-21 A Square of peak strength of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using SFC.

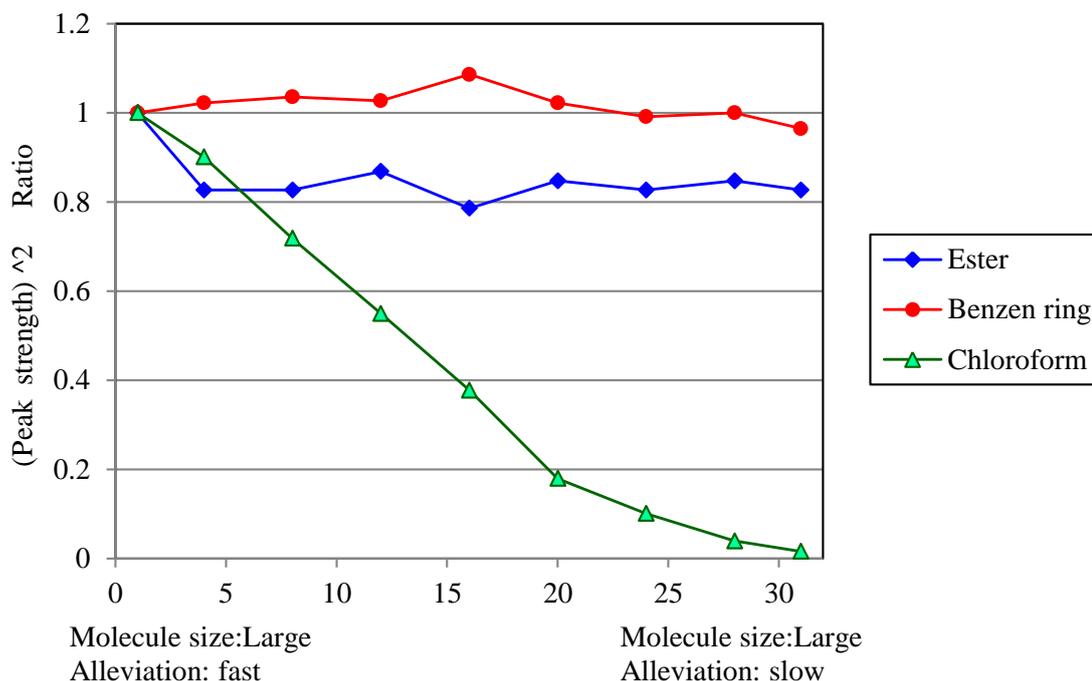


Fig.3-4-21 B The standardized Square of peak strength of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using SFC.

The peak of chloroform became smaller with increasing the diffusion rate and the size of molecules. On the other hand, the peaks of ester and benzene circle were constant in all diffusion coefficients. Even in the lowest diffusion coefficients, the squares of peak strength for ester and benzene circle were almost same level of that in the fastest diffusion coefficient although that of chloroform the lowest diffusion coefficient was only 1.6% on that in the fastest diffusion rate. There is no other organic compound than the SFC which has the ester in large molecules with the lowest diffusion rate. Therefore, it was concluded that the sample must be the SFC.

The PET/SPS polymer alloy using styrene-acrylic acid copolymer (RS1192) was also analyzed in the same procedure as the case for the SFC. **Fig.3-4-22** shows the spectrum chart of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using RS1192. As same as the case for the SFC, the peaks of ester and benzene circle were almost constant although peak of chloroform decrease with increasing diffusion coefficient. **Figure 3-4-23 A** shows square of the peak strength of each diffusion coefficient for ester, benzene circle, and chloroform. **Figure 3-4-23 B** shows the standardized square of peak strength. The results indicated that the sample extracted has ester and benzene circle. Therefore, it was concluded that the sample must be the RS1192.

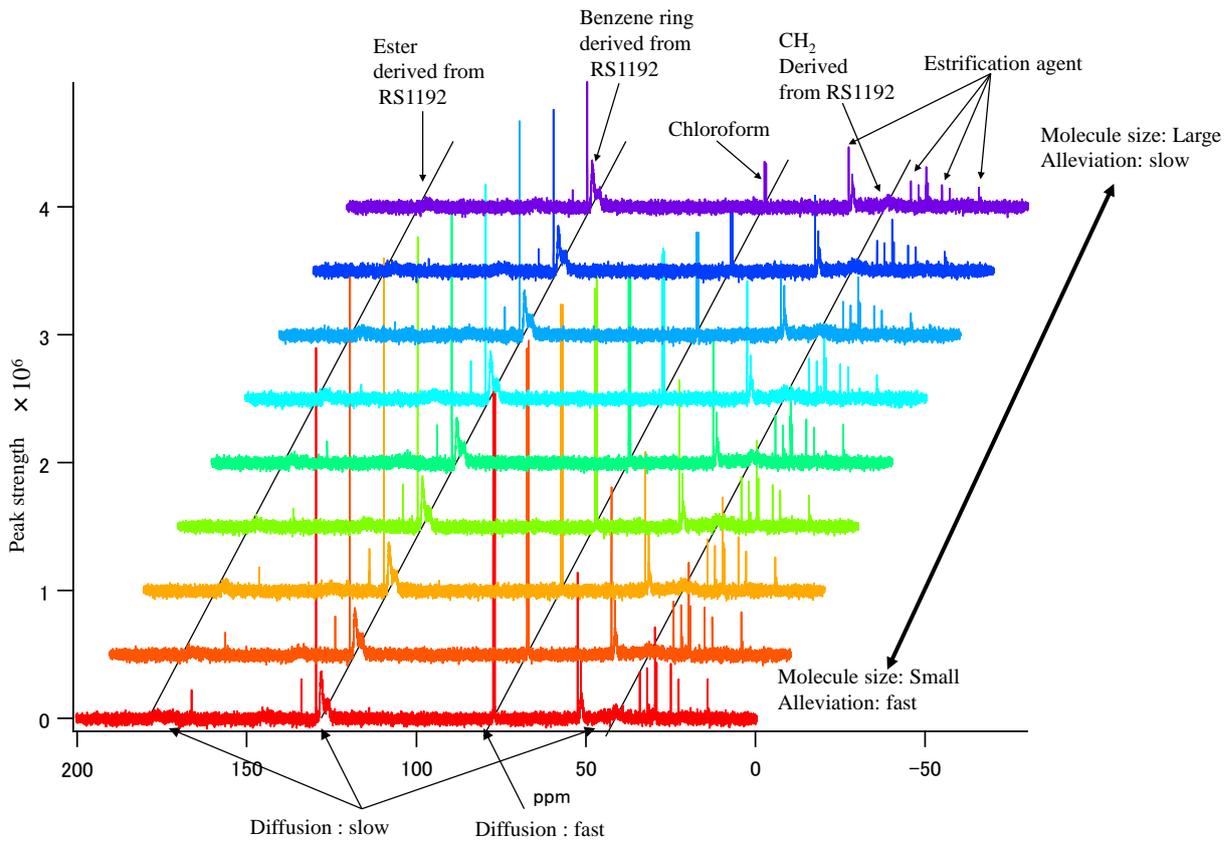


Fig.3-4-22 Spectrum chart of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using RS1192.

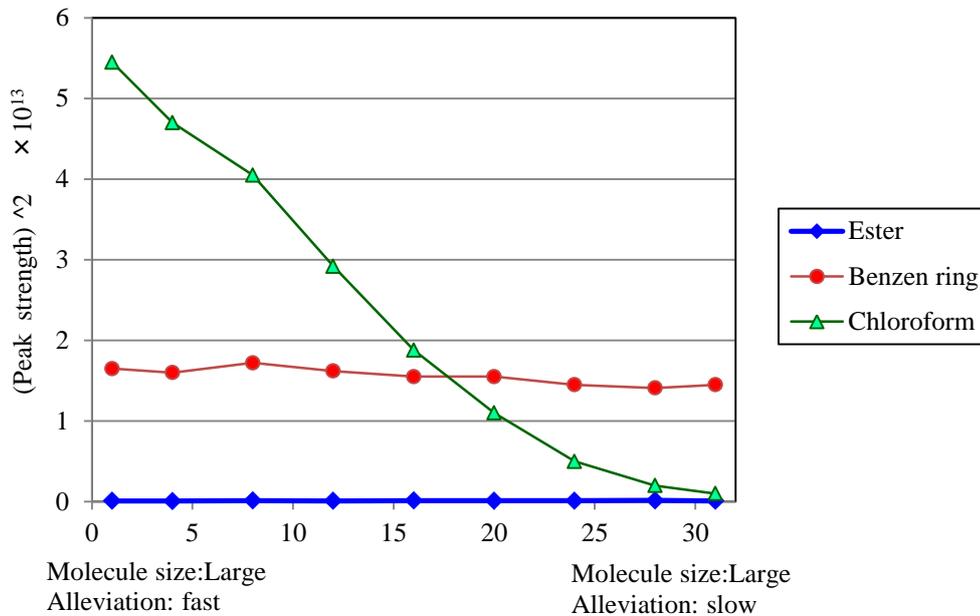


Fig.3-4-23 A Square of peak strength of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using RS1192.

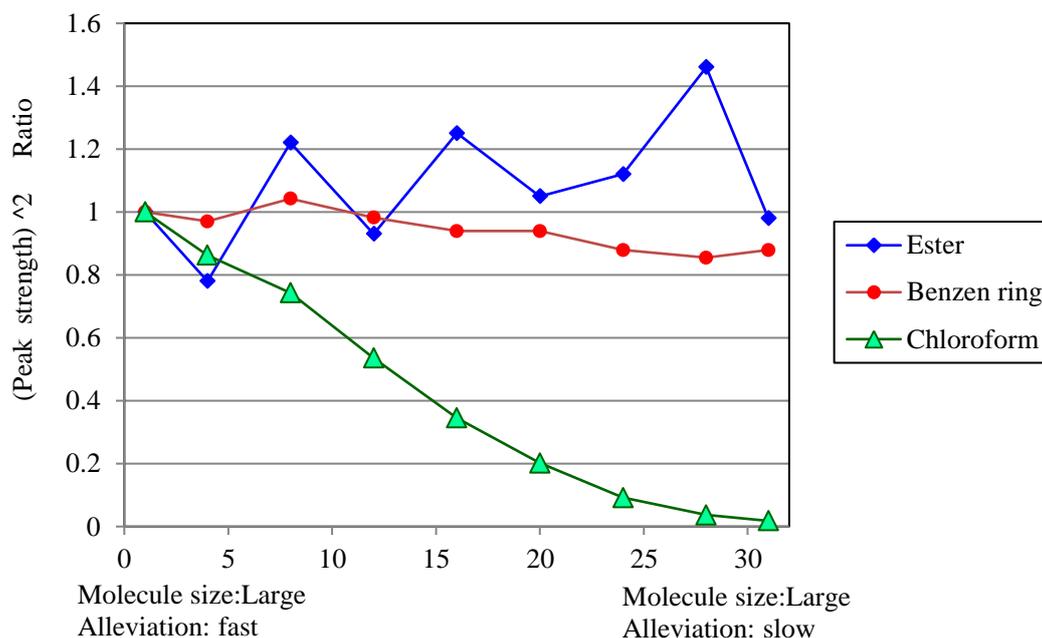


Fig.3-4-23 B The standardized Square of peak strength of ^{13}C DOSY for the sample extracted from PET/SPS polymer alloy using RS1192.

Based on the information described as above, the new hypotheses of the SFC which creates compatibilizing effect for PET/SPS polymer alloy was proposed. **Figures 3-4-24 A and B** show the first hypothesis. **Figure 3-4-24 A** shows the first stage of compatibilizing effect until 200°C. After the dehydration condensation between OH group at the end of PET polymer and carboxylic acid of SFC, rest of unreacted carboxylic acid was assumed not to have affinity with SPS. If all of them are react with PET, PET would surround SFC to prevent SFC accessing to SPS. In such situation, compatibilizing effect is not expected. Around 150°C, dehydration of dicarboxylic was assumed to occur. Dicarboxylic acid should be converted to anhydride. It is assumed to have stronger hydrophobicity than carboxylic acid. Dehydration of dicarboxylic acid is assumed to be continued until 200°C. For this period, dehydration condensation between OH group of PET and carboxylic acid of SFC is also assumed to be continued. They should be competitively occurred until 200 °C.

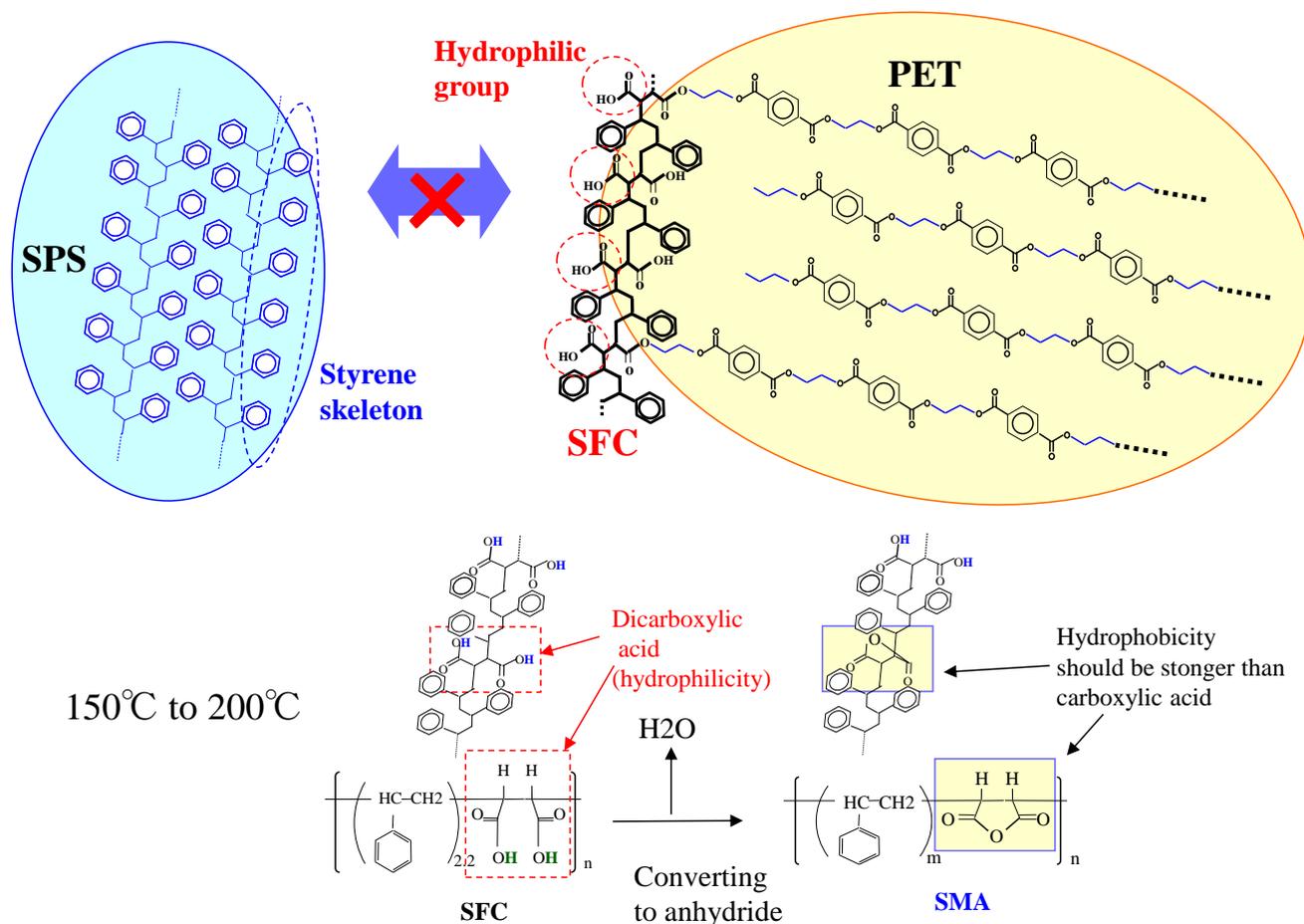


Fig. 3-4-24 A The first hypothesis of compatibilization mechanism of SFC(1st stage)

Fig. 3-4-24 B shows the second stage of compatibilizing effect above at 200°C. Around 200°C, decarbonizing of carboxylic acid starts to occur. Ester bond between PET and SFC should be stable. Anhydride also should be stable. Therefore, carbonating is considered to be occurred only in unreacted carboxylic acid. In this stage, dehydration condensation between PET and SFC may still occur. The decarbonization should provide hydrophobicity to the region. Hence, all hydrophilic carboxylic acids of SFC were disappeared by esterifying with PET or being dehydrated or being decarbonized. SFC is assumed to grasp PET and to exist at interface of PET. SFC on the interface of PET should have sufficient affinity with SPS. This is the new hypothesis.

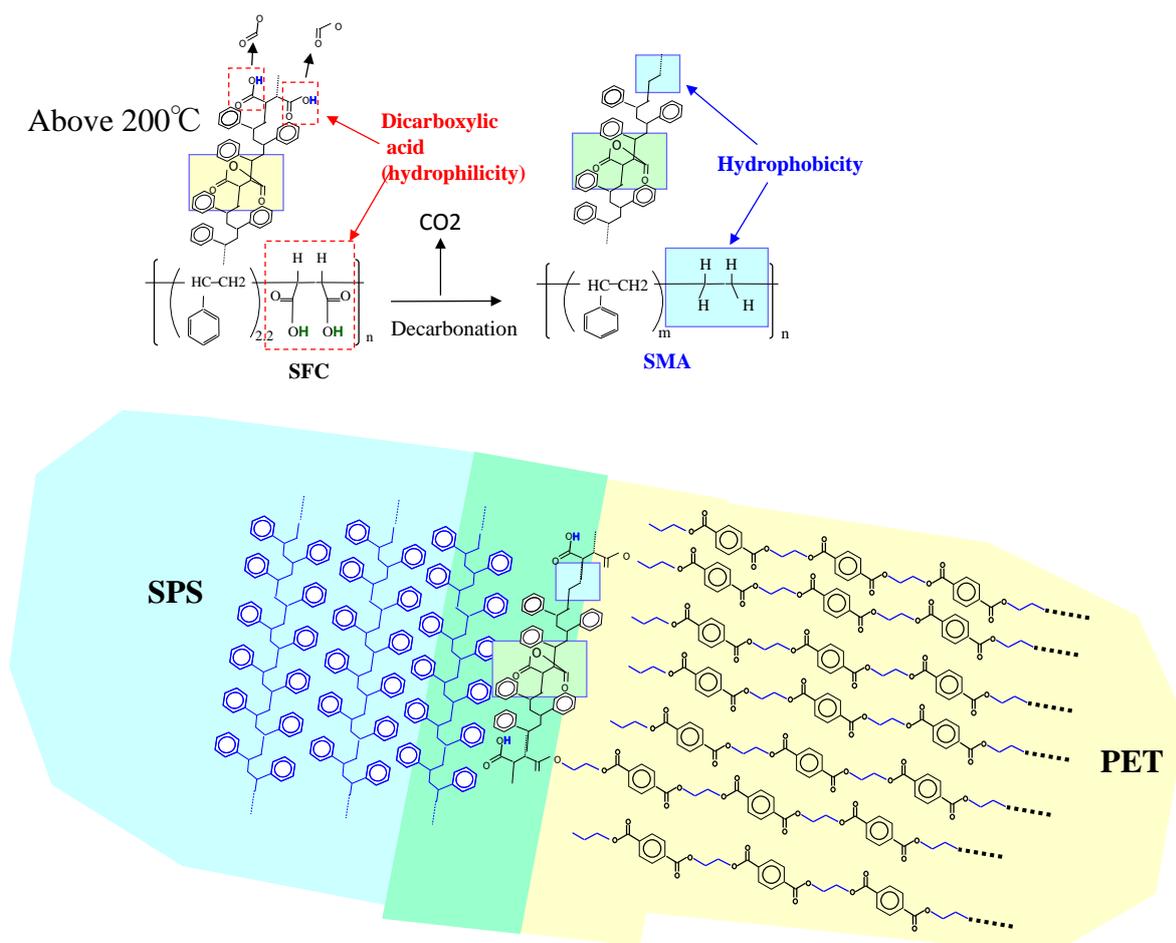


Fig. 3-4-24 B The first hypothesis of compatibilizing mechanism of SFC(2nd stage)

The kneading experimental results described in **Tables 3-4-3A and 3-4-3B** suggested that a certain length of molecules might be needed to grasp each polymer to create compatibilizing effect as described in **Fig.3-4-1**. To explain it, the new concept was introduced to the first hypothesis to propose the second hypothesis. **Figs. 3-4-25 A ,B, and C**.

Firstly, carboxylic acid of SFC reacts with OH group at the end of PET polymer to generate ester bond to be integrated as same as the first hypothesis described in **Fug.3-4-25A**.

Lower part (in figure) of SFC is outside of the body of PET. At a temperature range from 150°C to 200°C, dicarboxylic acids were converted to anhydrides to be hydrophobic. Affinity with SPS is becoming higher.

Thirdly, all carboxylic acids in the upper part of SFC are esterified with PET. It is completely drawn into the body of PET and is well-integrated with PET. In lower part of SFC, decarbonization of rest of carboxylic acid occurs over 200°C. All carboxylic acids in lower part of SFC were converted to anhydride or were decarbonized and then converted to be hydrophobic entirely. It penetrates into the body of SPS to grasp it as described in **Fig. 3-4-25 C**.

Hence, SFC was assumed to show significant compatibilizing effect for PET and SPS. In this hypothesis, a certain level of molecular length (Mw) is needed. Shorter molecule cannot grasp the polymer sufficiently. In addition, lower S/A molar ratio indicates higher molar ratio of carboxylic acid. It should be effective to be integrated with PET to grasp it.

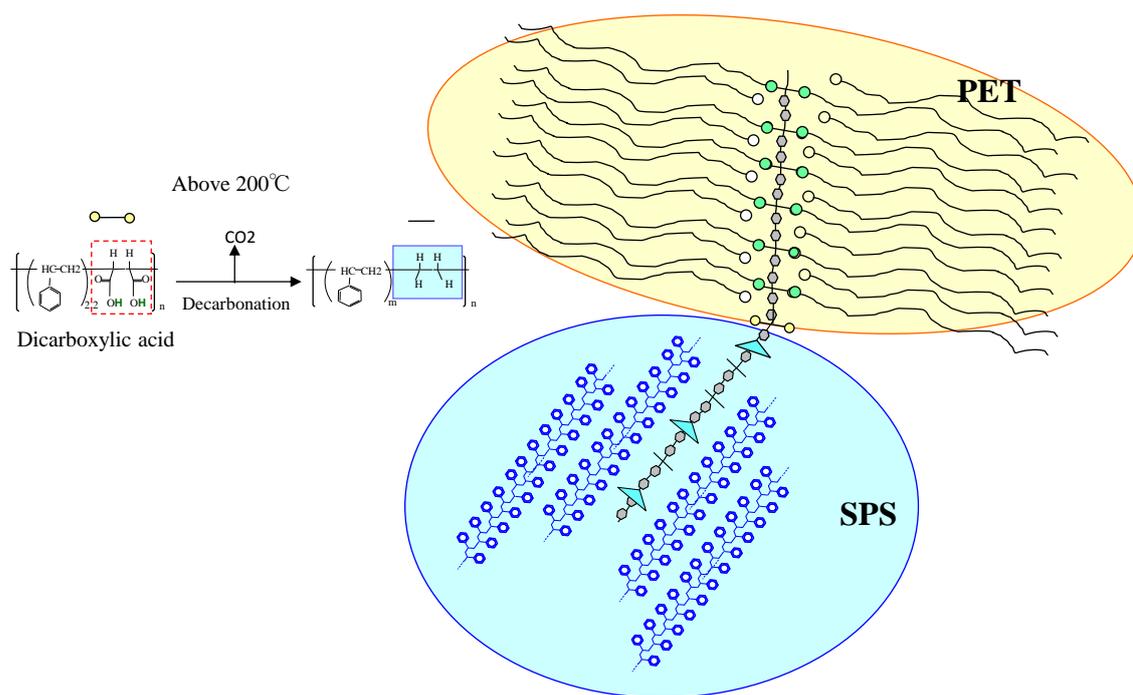


Fig. 3-4-25 C The second hypothesis of compatibilization mechanism of SFC (3rd stage)

Figure 3-4-11 showed that averaged diameter became smaller with decreasing S/A molar ratio at Mw of a range from 9,000 to 14,000. In **Fig. 3-4-12** and **Fig.3-4-13**, in S/A molar ratio was less than 2.2, averaged diameter became smaller with increasing Mw. Based on this 2nd hypothesis, in the case S/A molar ratio is low, the compatibilizing agent should have enough carboxylic acid to be integrated with PET to

grasp the body of PET for generating compatibilizing effect. For the compatibilizing agent which have enough carboxylic acid to be integrated with PET, in the case the Mw is small, it was assumed that the compatibilizing agent should not have a sufficient molecular length outside the body of PET to grasp the body of SPS for generating compatibilizing effect.

In **Fig. 3-4-14**, averaged diameter became larger with increasing Mw at S/A molar ratio at a range from 3 to 4. It was the opposite tendency. The 2nd hypothesis seemed to be difficult to be applied. The first hypothesis is considered applicable. In this case, the first step of integration with PET seemed to be rate-limiting reaction due to lower ratio of carboxylic acid. The shorter molecules should have an advantage to be dispersed on interface between PET and SPS.

In the second hypothesis, SFC was assumed to be defined as block polymer. The SFC as random copolymer was transformed to block polymer during the kneading process. In general, block polymer or graft polymer is applied to the reactive compatibilizing agent since two different parts should be needed to grasp the body of each incompatible polymer. SMA, as a random copolymer, is rarely applied to the reactive compatibilizing agent. However, the application is limited. It is assumed that SMA could not be transformed to block polymer structure like SFC case since anhydride has highly thermal stability until 300°C. In TG-DTA results of SMA described in **Fig.3-4-15** showed almost no weight loss until 300°C. It indicates that no dehydration or decarbonization occurred. It is assumed that integration with PET is low due to low reactivity of anhydride. Therefore, it should be still SMA itself. On the other hand, SFC could be converted to block polymer structure due to thermal instability and high reactivity of carboxylic acid.

In addition, during the kneading process, the reactive compatibilizing agent needs to be dispersed in viscous polymer. It is assumed the rate-controlling step. The block polymer is originally designed that each part should have sufficient reactivity or affinity with each polymer, respectively. Therefore, the reactivity of one part should be higher than averaged reactivity of SFC. However, reactivity and dispersion is conflicted each other. At the beginning of kneading process, the bulk of the reactive compatibilizing agent is mixed with two incompatible polymers. It is not reasonable to consider the three polymers could be mixed simultaneously and uniformly. The mixing should be applied to two polymers initially. At that time, one part of the reactive compatibilizing agent easily reacts with one polymer and then most of the reactive compatibilizing agent should be trapped by the polymer. After the trapping, it should be hard for the reactive compatibilizing agent to be dispersed to have a chance to react with another polymer. If

the affinity or the integration is too high, the agent bulk should be drawn to the bulk of one polymer.

On the other hand, reactivity or affinity of a certain part of SFC is lower than that of block polymer. In another words, SFC doesn't have sufficient reactivity or affinity for both polymers. Therefore, both polymers reject SFC and then SFC tends to be existed interface between two polymers. SFC gradually reacts with PET and then trapped continuously. Rest of them could be dispersed in interface between two polymers since affinity with SPS is still insufficient. After all SFC is dispersed uniformly, not integrated part is transformed to high affinity part for SPS by hydration and decarbonization. In terms of initial dispersion, SFC is assumed to have advantage over block polymer or graft polymer.

It suggests that these results propose a concept of the reactive compatibilizing agent using random copolymer transforming to block polymer during kneading process. Random copolymer applying to the reactive compatibilizing agent is reported only SMA [33]. SMA could not be transformed to block polymer. Other random copolymers have not been studied intensively. If the random copolymer has functional group which has highly reactivity and thermal instability like SFC, it should have the possibility applying to this concept reactive compatibilizing agent. It is proposed to name "*transforming reactive compatibilizing agent*." In general, block polymer and graft polymer are very expensive, whereas random copolymer is affordable. Moreover, the SFC is obtained from thermosetting polyester resin waste which is now landfilled. It is expected to open the door for less expensive existing random copolymer and random copolymer obtained from the resin waste, SFC, to apply to reactive processing to create new polymer alloy for many innovative applications.

3.4.4 Conclusions

In polymer alloy of PET and SPS, SFC successfully showed the best performance for compatibilizing effect among commercial compatibilizing agent. It was verified the possibility applying to compatibilizing agent for PET/SPS polymer alloy. Compatibilizing mechanism was investigated based on thermal analysis of SFC and two new hypotheses were proposed. The first hypothesis is that carboxylic acid of SFC reacts with OH group at the end of PET polymer to be integrated and dehydration and decarbonization of dicarboxylic acid provides hydrophobicity to SFC to generate higher affinity to SPS. They should contribute to increase compatibility of PET/SPS polymer alloy.

The second hypothesis is that all carboxylic acids of the first half part of SFC were

esterified to be well-integrated with PET. All carboxylic acids of the second half part of SFC were dehydrated or decarbonized to generate higher affinity to SPS. The structure seemed to be similar to that of block polymer. In general, block polymer or graft polymer is applied to the reactive compatibilizing agent. These results suggest that it is proposed a new concept named “*transforming reactive compatibilizing agent*” of random copolymer transforming to block polymer during kneading process. It is suggested that there is a possibility of random copolymer to have advantage over expensive block polymer or graft polymer. It is expected that less expensive existing random copolymer and random copolymer obtained from thermosetting polyester resin waste, SFC, applying to the reactive processing for creating new polymer in many innovative applications.

The correlations between the molecular structure and the compatibilizing effect was also examined. It suggests that the optimization of the molecular structure can increase compatibilizing effect. It is expected the new compatibilizing agent based on the new concept realize the PET/SPS polymer alloy film capacitor and other new innovative materials and products.

3.5 Overall Conclusion

(Application of styrene-fumaric acid copolymer (SFC))

As described as above, SFC was verified the possibility applying to various high performance additives.

Low profile additive (LPA)

In evaluation of SFC esterified with alcohol, 1-octanol showed the best shrinkage control performance and was selected as esterification agent for SFC. SFC separation and modification processes using 1-octanol was established. The recycled LPA was produced by adding styrene to the modified SFC.

The recycled LPA showed about 69% higher shrinkage control performance per unit weight than that of the commercial LPA. It was concluded that the SFC was successfully verified the possibility of applying to the LPA. It suggests the possibility of a range from 5 to 10 times “*enhanced recycling.*” In cross section observation, FRP sample board using recycled LPA showed many fine voids uniformly dispersed base on higher solubility to UP resin. It is expected to have stronger mechanical strength.

The correlation between the shrinkage control effect and the molecular size was also examined. The longer alkyl chain, the smaller Mw, and the lower S/F molar ratio showed the higher shrinkage control effect. Based on the results, new concept of the LPA was proposed. It is expected that the superior LPA creates the innovative FRP which has much stronger mechanical strengths.

Aqueous agent

In verification of applying to dispersing agent, the reaction product liquid showed superior dispersing effect to commercial DA#2 for phthalocyanine blue. In verification of applying to detergent builder, the reaction product liquid showed about 6.6 times higher alkali buffering capacity than that of commercial DB#1. In verification of applying to surface sizing agent, SFC-NH₄ showed about 20% higher sizing effect than that of commercial SA#1.

It was concluded that SFC alkali salt has a potential to substitute to the commercial high performance aqueous agents. The SFC is expected to be applied to other applications widely.

Compatibilizing agent for polymer alloy

It was verified the possibility of the SFC applying to compatibilizing agent for PET/SPS polymer alloy. Investigation of compatibilizing mechanism based on thermal analysis of SFC suggests two new hypotheses. The first hypothesis is that carboxylic acid of SFC reacts with OH group at the end of PET polymer to be integrated and dehydration and dicarbonization of diacid provides hydrophobicity to SFC to

generate higher affinity to SPS.

The second hypothesis is that all carboxylic acids of the first half part of SFC were esterified to be well-integrated with PET. All carboxylic acids of the second half part of SFC were dehydrated or decarbonized to generate higher affinity to SPS. The structure seemed to be similar to that of block polymer. These results suggest to propose a new concept of the reactive compatibilizing agent named “*transforming compatibilizing agent*” of random copolymer transforming to block polymer during kneading process. It suggests that there is a possibility of random copolymer to have advantage over expensive block polymer or graft polymer. However, this hypothesis should be verified. It is expected that less expensive existing random copolymer and random copolymer obtained from thermosetting polyester resin waste, SFC, applying to the reactive processing for creating new polymer alloy using this new concept compatibilizing agent in many innovative applications.

Evaluation results suggest that the optimization of the molecular structure is suggested to increase compatibilizing effect. It is expected the new compatibilizing agent based on the new concept realize the PET/SPS polymer alloy film capacitor and other new innovative materials and products.

4. Overall Conclusions

(Study on Recycling Thermosetting Polyester Resin into High Performance Additives Using Subcritical Water)

4.1. Subcritical hydrolysis of thermosetting polyester resin

In recycling thermosetting polyester resin using subcritical water, the hypothesis that subcritical hydrolysis on the reaction condition at a temperature of 230°C or less with alkali catalyst was proposed.

Fundamental verification

The hypothesis was successfully verified and demonstrated. On the reaction condition at a temperature of 230°C, at a pressure of 2.8MPa, at a reaction time of 4 hours with KOH, 96% of the initial thermosetting polyester resin was dissolved in the reaction product liquid as usable matters. SFC was obtained with 75% of the initial thermosetting polyester resin. The SFC had Mw of 30,000 and a S/F molar ratio of 2.2.

It was the first time to demonstrate to extract the SFC as functional polymer which has a similar molecular structure to the SMA widely applied as high performance additives. The SFC obtained should also have a potential to be applied to the high performance additives.

Functional mechanism of alkali catalyst and molecular structure of thermosetting polyester resin

Investigation of molecular structure suggests that there are two types of polyester chains, the polyester chain (i) which has only one glycol and the polyester chain (ii) which has two glycols. The share of them is roughly 63% and 37%, respectively. It is considered the first achievement to clarify the molecular structure of styrene chain and polyester chain in the thermosetting polyester resin. The hypothesis is proposed that there are “hardly-hydrolysable ester bond” in the polyester chain (i) and “easily-hydrolysable ester bond” for ester bonds other than “hardly-hydrolysable ester bond.” More than 1.9 of molar ratio of KOH/carboxylic group of SFC was assumed to be needed to break “hardly-hydrolysable ester bond” to produce SFC. However, this hypothesis should be verified.

KOH contributions to the reaction acceleration and the maximization of yield and quality of SFC were concluded as i) accelerating to break “hardly-hydrolysable ester bonds”, ii) preventing secondary reaction, iii) making the separation process efficiently, and iv) providing solubility in subcritical water. However, iv) should be verified since solubility of SFC in subcritical water at 230°C are unknown.

Optimization of reaction conditions and catalysts

The optimized conditions of subcritical hydrolysis using manufacturing waste of FRP bathtub based on SFC yield were concluded as follows:

	Concentration	Temperature	Reaction time	Conversion	SFC production rate
KOH	0.38 mol/L	230 °C	2 hours	92 %	99.6 %
NaOH	0.72 mol/L	230 °C	1 hours	82 %	90 %

The results suggest that NaOH would be preferable for commercialization in terms of SFC yield according to the reaction time.

The hypothesis to explain the difference of the reactivity for the “hardly-hydrolysable ester bonds” between KOH and NaOH based on the difference of diffusion rate due to atomic size was proposed. This hypothesis should also be verified.

Evaluation of subcritical hydrolysis process for various FRPs

The experimental results of subcritical hydrolysis for various FRPs showed almost equivalent reactivity and the SFC yield to those of the bathtub#1. The difference is considered to be within the acceptable range. Therefore, it was verified the possibility of this method applying to other various FRPs.

It was also the achievement to clarify the molecular structure of the styrene chain in various FRPs. They are expected to be utilized to improve the property. The SFCs obtained from various FRPs were also verified the possibility of applying to high performance additives based on the molecular structure.

4.2. Application of styrene-fumaric acid copolymer (SFC))

SFC was successfully verified the possibility applying to various high performance additives.

Low profile additive (LPA)

The recycled LPA using the SFC esterified with 1-octanol showed about 69% higher shrinkage control performance per unit weight than that of the commercial LPA. Other product quality items were also equivalent to the commercial LPA. Hence, it was concluded that the SFC was successfully verified the possibility of applying to the LPA. It suggests the possibility of a range from 5 to 10 times “*enhanced recycling.*” Many fine voids produced by the recycled LPA are expected to have stronger mechanical strength and better surface appearance and smoothness.

The correlation between the shrinkage control effect and the molecular structure was also examined. The longer alkyl chain, the smaller Mw, and the lower S/F molar ratio showed the higher shrinkage control effect. Based on the results, new concept of the LPA was proposed. It is expected that the new LPA based on the new concept creates the innovative FRP which has much stronger mechanical strengths.

Aqueous agent

In verification of applying to dispersing agent, the reaction product liquid showed less dispersing effect than commercial DA#1 for hydrophilic powder, whereas it showed superior dispersing effect to commercial DA#2 for phthalocyanine blue as hydrophobic powder. In verification of applying to detergent builder, the reaction product liquid showed about 6.6 times higher alkali buffering capacity than that of commercial DB#1. It also showed Ca ion trapping ability. In verification of applying to surface sizing agent, SFC-NH₄ showed about 20% higher sizing effect than that of commercial SA#1.

It was concluded that SFC alkali salt has a potential to substitute to the commercial high performance additives. The SFC is also expected to be applied to other applications widely.

Compatibilizing agent for polymer alloy

In polymer alloy of PET and SPS, SFC successfully showed the best performance for compatibilizing effect among commercial compatibilizing agent. It was verified the possibility applying to compatibilizing agent for PET/SPS polymer alloy. Two new hypotheses were proposed. The first hypothesis is that carboxylic acid of SFC reacts with OH group at the end of PET polymer to be integrated and dehydration and decarboxylation of dicarboxylic acid provides hydrophobicity to SFC to generate higher affinity to SPS. The second hypothesis is that all carboxylic acids of the first half part of SFC were esterified to be well-integrated with PET. All carboxylic acids of the second half part of SFC were dehydrated or decarboxylated to generate higher affinity to SPS. The structure seemed to be similar to that of block polymer. These results suggest that it is proposed a new concept of the reactive compatibilizing agent named “*transforming compatibilizing agent*” of random copolymer transforming to block polymer during kneading process.

The optimization of the molecular structure is considered to increase compatibilizing effect. It is assumed that the new compatibilizing agent based on the new concept realize the PET/SPS polymer alloy film capacitor.

4.3 Future prospect

Most of SFC in thermosetting polyester resin waste is now wastefully landfilled although it has a potential to apply to high performance additives. This method proposes a new concept of “enhanced recycling” which can recycle the resin waste into higher value product than raw materials. It is expected that this study contributes to accelerate the study of recycling thermosetting resin.

This study could firstly provide many valuable information of the molecular structure

of the thermosetting polyester resin which has been unknown. This method was verified very effective for the molecular structure analysis. The molecular structure information and this analyzing method are expected to be utilized to improve the property of the thermosetting polyester resin.

SFC has a potential not only to substitute for existing high performance additives, but also to create new type of high performance additives based on unique molecular structure which existing commercial additives don't have. It is expected to be utilized to create new innovative materials and products.

In addition, this study proposed new concept of high performance additives. It should be noted that there was no intention for the SFC to generate the function for the high performance additives. However, it showed the superior performance in the LPA, some of the aqueous agent, and the compatibilizing agent to the commercial additives. The new concept of the LPA having smaller molecular size with alkyl branches has a potential to create new innovative FRP which has much stronger mechanical strength. Another new concept of compatibilizing agent named "*transforming compatibilizing agent*" proposed the possibility of less expensive random copolymer applying to compatibilizing agent substituting the expensive block polymer or graft polymer. It is also expected to develop new type compatibizing agent to create new innovative materials and products.

Acknowledgements

I wish to express my sincere appreciation to Dr. Motonobu Goto, professor of Nagoya University for his continuous guidance and encouragement throughout the entire development of this thesis. My deep appreciation goes to Drs. Tomohiko Tagawa, Hiroyuki Asanuma, and Susum Nii of Nagoya University for having valuable advices on this thesis. It is my pleasure to record a special note of appreciation to Dr. Hiroyuki Yoshida, former Professor of Osaka Prefecture University for giving me the opportunity to start the study of subcritical water hydrolysis and guidance of fundamental research. I am also grateful to Mr. Tamaki Fujimoto, former executive officer of Eco Solutions Company of Panasonic Corporation for giving me the opportunity to start this study in Nagoya University. My deep appreciation goes to Messrs. Toshiaki Tokizane, Koichi Kobayashi, and Masahiro Fukiage of Eco Solutions Company of Panasonic Corporation for supporting the study of compatibilizing agent in management. I also wish to express my sincere appreciation to Messrs. Hiroshi Kikuchi, Yoshiro Kagami, Toru Fujioka, Masashi Yamada, Masahiro Asahida, Mitsuru Maeda, and Kiyotaka Waki for supporting this study in management.

I wish to express my deep gratitude to Messrs. M. Hidaka, T. Shimokage, H.Takeoka, R. Majima, K. Shibata, T. Urabe, T. Yoshimura, M. Sato, and Ms. M. Saimoto for sincere cooperation and supporting this study. I am also grateful to Messrs. T. Maekawa, T. Itoh, T. Izumitani, T. Miyazaki, S. Matsugi, S. Hirota, H. Yano, K. Sawada, N. Yabunouchi, Y. Yasuda, Mses. J. Nakajima(Matsui), N.Imanari, and N.Nakajima for having cooperation in this study.

The research on the investigation on the proposed subcritical hydrolysis was supported by the Ministry of Economy, Trade and Industry, as a part of joint research project with the International Center for Environmental Technology Transfer (ICETT). The research on the evaluation of subcritical hydrolysis applied to various FRPs was supported by the New Energy and Industrial Technology Development Organization (NEDO). We also received cooperation from Showa Denko K.K. (formerly Showa High Polymer Co., Ltd.) to obtain FRP samples.

Lastly, I wish to express my deepest gratitude to my wife for supporting me to concentrate this study for the last three years. I probably would not be able to complete this study without her help.

References

- [1] Curtis LG, D. Edwards L, Simons RM, Trent PJ, Von Brame PTr. Investigation of Maleate-Fumarate Isomerization in Unsaturated Polyesters by Nuclear Magnetic Resonance. *Ind. Eng. Chem. Prod. Res. Dev.* 1964; 3 (3): 218–21
- [2] Kawahara Petrochemical Co., Ltd. Home Page, SMA resin, <http://www.kawahara.co.jp/sma.html>
- [3] [Cray Valley USA, LLC, Home Page, SMA], <http://www.crayvalley.com/products/sma-styrene>
- [4] Ukai T, Influence of Shale Revolution on Chemical Industry. *Information Sensor* 2014; 93:12-3
<http://www.shinnihon.or.jp/shinnihon-library/publications/issue/info-sensor/pdf/info-sensor-2014-05-04.pdf>
- [5] Asokan P, Osmani M, Price ADF. Assessing the recycling potential of glass fibre reinforced plastic waste in concrete and cement composites. *J Cleaner Production* 2009; 17 :821–9.
- [6] Nakai S, Tokumou Y, Tsukawaki S, Okuda T, Nishijima W, Okada M. Recycling of waste FRP as filler for new FRP products. 6th International Symposium on Feedstock Recycling of Polymeric Materials 2011:165-6.
- [7] Ribeiro MCS, Fiúza A, Dinis ML, Castro ACM, Silva FG, Meixedo JP, Alvim MR. Experimental study on polyester based concretes filled with glass fibre reinforced plastic recyclates – A contribution to composite materials sustainability. *ICCE19* 2011:961-2.
- [8] Pickering SJ, Kelly RM, Kennerley JR, Rudd CD, Fenwick NJ. A fluidised-bed process for the recovery of glass fibres from scrap thermoset composites. *Composites Science and Technology* 2000; 60:509-23.
- [9] Grause G, Mochizuki T, Kameda T, Yoshioka T. Recovery of glass fibers from glass fiber reinforced plastics by pyrolysis. *J Mater Cycles Waste Manag* 2013; 15: 122–8.
- [10] Torres A, DeMarco I, Caballero BM, Laresgoiti MF, Chomo'n MJ. Recycling of the Solid Residue Obtained from the Pyrolysis of Fiberglass Polyester Sheet Molding Compound. *Advances in Polymer Technology* 2009; 28(2):141–9.
- [11] Shima H, Takahashi H, Mizuguchi J. Recovery of Glass Fibers from Fiber Reinforced Plastics. *Materials Transaction* 2011; 52(6):1327-9.
- [12] Iwaya T, Tokuno S, Sasaki M, Goto M, Shibata K. Recycling of fiber reinforced plastics using depolymerization by solvothermal reaction with catalyst. *J Mater Sci*

- 2008; 43: 2452–6.
- [13] Kubota S, Ito O. Feedstock Recyclibility of Cured Unsaturated Polyester Waste Using Glycol. The 1st International Symposium on Feedstock Recycling of Plastics in Sendai 1999:247-50.
- [14] Yoon KH, DiBenedetto AT, Huang SJ. Recycling of unsaturated polyester resin using propylene glycol. *Polymer* 1997; 38(9):2281-5.
- [15] Kubota S, Mori H, Maeda K. Chemical Recycling of Unsaturated Polyester Wastes by Decomposition in Glycol. *Network Polymer* 2003; 24(1):22-9 (in Japanese)
- [16] Vallee M, Tersac G, Destais-Orvoen N, Durand G. Chemical Recycling of Class A Surface Quality Sheet-Molding. *Ind Eng Chem Res* 2004; 43: 6317-24.
- [17] Perrin D, Guillermain C, Bergeret A, Lopez-Cuesta JM, Tersac Gilles. SMC composites waste management as reinforcing fillers in polypropylene by combination of mechanical and chemical recycling processes. *J Mater Sci* 2006; 41: 3593–602.
- [18] Kamimura A, Yamada K, Kuratoni T, Taguchi Y, Tomonaga F. Effective depolymerization waste FRPs by treatment with DMAP and supercritical alcohol. *Chem Lett* 2006; 35:586-7.
- [19] Kamimura A, Konno E, Yamamoto S, Watanabe T, Yamada K, Tomonaga F. Formation of recycled plastics from depolymerized monomers derived from waste fiber-reinforced plastics. *J Mater Cycles Waste Manag* 2009;11:38–41.
- [20] Kamimura A, Konno E, Yamamoto S, Watanabe T, Yamada K, Tomonaga F. Improved method for the formation of recycled resins from depolymerized products of waste fiber-reinforced plastics: simple and effective purification of recovered monomers by washing with water. *J Mater Cycles Waste Manag* 2009;11:133–7.
- [21] Yamada K, Tomonaga F, Kamimura A. Improved preparation of recycled polymers in chemical recycling of fiber reinforced plastics and molding of test product using recycled polymers. *J Mater Cycles Waste Manag* 2010;12:271–4.
- [22] Kamimura A, Kaiso K, Sugimoto T, Kashiwagi K, Watanabe T, Yamada K, Tomonaga F. Supercritical Lower Alcohols as a Useful Media for Depolymerization. ISSF in Arcachon, France 2009:C32-CO54.
- [23] Shi J, Bao L, Kobayashi R, Kato J, Kemmochi K. Reusing recycled fibers in high-value fiber-reinforced polymer composites-Improving bending strength by surface cleaning. *Composites Science and Technology* 2012 ; 72:1298–303.
- [24] Kao CC, Ghita O, Evans KE, Oliveux G. Mechanical Characterisation of glass fibres recycled from thermosetting composites using water-based solvolysis

- process. 18th International Conference on Composite Materials 2011: T8-1-IF0572.
- [25] Sugeta T, Nagaoka S, Otake K, Sako T. Decomposition of fiber reinforced plastics using fluid at high temperature and pressure. *Kobunshi Ronbunshu* 2001; 58(10):557-63 (in Japanese)
- [26] Oliveux G, Bailleul JL, Salle ELGL. Chemical recycling of glass fibre reinforced composites using subcritical water. *Composites: Part A* 2012;43:1809–18.
- [27] Oliveux G, Bailleul JL, Salle ELGL, Lefèvre N, Biotteau G. Recycling of glass fibre reinforced composites using subcritical hydrolysis: Reaction mechanisms and kinetics, influence of the chemical structure of the resin. *Polymer Degradation and Stability* 2013;98:785-800.
- [28] Suyama K, Kubota M, Shirai M, Yoshida H. Degradation of crosslinked unsaturated polyesters in sub-critical water. *Polymer Degradation and Stability* 2007 ; 92: 317-22.
- [29] Suyama K, Kubota M, Shirai M, Yoshida H. Chemical recycling of networked polystyrene derivatives using subcritical water in the presence of an aminoalcohol. *Polymer Degradation and Stability* 2010; 95:1588-92
- [30] Nakagawa T, Urabe T, Maekawa T, Hidaka M, Seto K, Miyazaki T, Fukiage M, et. al. Development of FRP material recycling technology through critical water decomposition. Proceeding of Study Results Reporting Meeting 2002 of Joint Research and Development for Environment Protection Technology (Commissioned by the Ministry of Economy Trade and Industry) 2003; 85-90 (in Japanese)
- [31] Tester JW, Holgate HR, Armellini FJ, Webley PA, Killulea WR, Hong GT, Barner HE. Oxidation of hazardous organic wastes in supercritical water. *ACS Symp Ser* 1993; 518,:35-76
- [32] Kusumoto Chemicals Ltd. Home page, Technical information, “Acting and category for pigment moistening and dispersing agent .”
<http://www.kusumoto.co.jp/pdf/tecnews/ganryo.pdf> (in Japanese)
- [33] Seiko PMC Corporation Home page, Products information/
Paper Making Chemicals/Surface Sizing Agent
http://www.seikopmc.co.jp/english/products/paper/ss_se.html
- [34] Akiyama S, Izawa S, Development and application of polymer alloy. *CMC Publishing Co.,Ltd*, 1997:14 (in Japanese)
- [35] Nishi T, Izawa S, Akiyama S. *Polymer ABC Handbook*. The society of polymer science, Japan, NTS Publishing Co., Ltd. 2001:366-9, 640 (in Japanese)
- [36] Sanada T, Moritomi S, Utsumi S. Morphology control of polymer alloy by reactive

- processing and morphology evaluation. Sumitomo Chemical R&D report 2003-Part II, 2003:43-54 (in Japanese)
- [37] Akiyama S, Essential Polymer Alloy 2012:72-8 (in Japanese)
- [38] Yazaki F, Foresight of reactive processing. Kobunshi, 45-7,1996:462-5 (in Japanese)
- [39] Idemitsu Kosan Co., Ltd. Hopmpage, Syndiotactic polystyrene (SPS)
<http://www.idemitsu.co.jp/ipc/products/sps/> (in Japanese)
- [40] JP4723296, "Two axes stretched polyester film and film capacitor used the film,"
Filed on 7/1/2005 (in Japanese)
- [41] JP4778683, "Two axis oriented film and film capacitor used the film,"
Filed on 1/29/2004 (in Japanese)
- [42] Sumoto I, Plastic material seminar 11 Styrol resin, 1970 ; 2 (in Japanese)
- [43] Adschiri T, Sato O, Machida K, Saito N, Arai K. Recovery of Terephthalic Acid by Decomposition of PET in Supercritical Water. Kagakukogaku Ronbunshu 1997:23-4:505-11(in Japanese)
- [44] Chen CC and White JL, Compatibilizing agents in polymer blends: Interfacial tension, phase morphology, and mechanical properties, Polymer Engineering and Science, 1993:33-14;923-30
- [45] Paul S, Kale DD. Blends of Acrylonitrile–Butadiene–Styrene/Waste Poly(ethylene terephthalate) Compatibilized by Styrene Maleic Anhydride. Journal of Applied Polymer Science 2001:80(13);2593-9
- [46] Basu D and Banerjee A. Determination of optimum compatibilizer (SMA) concentration for PBT/ABS (70/30) blend using tensile strength data. Journal of Applied Polymer Science 1997:64(8);1485-7
- [47] Ju MY and Chang FC. Polymer blends of PET–PS compatibilized by SMA and epoxy dual compatibilizers. Journal of Applied Polymer Science 1999:73(10); 2029-40
- [48] Ju MY and Chang FC. Compatibilization of PET/PS blends through SMA and PMPI dual compatibilizers. Polymer 2000:41(5);1719-30
- [49] Kawai M. Breakthrough of film capacitor. Nikkei Electronics, Sept. 2012;57-62 (in Japanese)
- [50] Takeoka H. Small film capacitor for hybrid electric vehicles (HEV) with high withstand voltage. Panasonic Technical Journal 2011:57(3);51-5 (in Japanese)
- [51] Mitsubishi Electric Coporation, Home Page, Factroy Automation Systems,
<http://www.mitsubishielectric.co.jp/fa/products/drv/clutch/case/appli/> (in Japanese)
- [52] Nippon Shokubai Co., Ltd., Home Page ,Epocros, rps,

<https://www.shokubai.co.jp/ja/products/functionality/epocros-rps.html>

- [53] Morris KF and Johnson Jr. CS. Diffusion-Ordered Two-Dimensional Nuclear Resonance Spectroscopy. J Am Chem Soc 1992; 114: 3139-41
- [54] Morris KF and Johnson Jr. CS. Resolution of Discrete and Continuous Molecular Size Distributions by Means of Diffusion-Ordered 2D NMR Spectroscopy. J Am Chem Soc 1994; 115: 4291-9
- [55] Wu D, Chen A, and Johnson Jr. C.S., An Improved Diffusion-Ordered Spectroscopy Experiment Incorporating Biopolar-Gradient Pulses, J Magn Reson A 1995; 115: 260-4
- [56] Nakagoshi M. New evolvment for DOSY analysi. JOEL News 2006; 38: 10-3 (in Japanese)
- [57] Swaitala-Zeliazkow M. Thermal degradation of copolymers of styrene with dicarboxylic acids - I. alternating styrene-maleic acid copolymer. Polymer Degradation and Stability 2001; 74: 579-584
- [58] Swaitala-Zeliazkow M. Thermal degradation of copolymers of styrene with dicarboxylic acids - II. Copolymers obtained by radical copolymerization of styrene with maleic acid or fumaric acid. Polymer Degradation and Stability 2006; 91:1233-9

Research achievements

Papers

- P1) Nakagawa T, Urabe T, Hidaka M, Maekawa T, Okumoto S, et al. FRP Recycling Technology Using Subcritical Water Hydrolysis. *Network Polymer* 2006; 27(2); 88-95. (in Japanese)
- P2) Nakagawa T, Urabe T, Hidaka M, Miyazaki T, Hidaka M, Oka K, et al. FRP Recycling Technology Using Subcritical Water Hydrolysis. *Reinforced Plastics* 2006; 52(10):478-84. (in Japanese)
- P3) Yoshimura T, Nakagawa T, Urabe T, Maekawa T, and Itoh T. Upgrade Recycling Technology of FRP Sub-Critical Water Hydrolysis to Low Profile Additive. *Network Polymer* 2007; 28(3):27-34. (in Japanese)
- P3) Nakagawa T. FRP recycling technology using sub-critical water hydrolysis, *JEC Composites* 2008; 40:56-9.
- P4) Nakagawa T, Itoh T, Hidaka M, Urabe T, and Yoshimura T. Enhanced and Horizontal Recycling Technology of FRP Using Sub-critical Water. *Network Polymer* 2008; 29(3):158-65. (in Japanese)
- P5) Nomaguchi K and Nakagawa T. FRP Recycling in EU, NA and Pacific Rim Area -Challenging Development in Chemical Recycling by Subcritical Water Process-. *Review of Automobile Engineering* 2009; 20(1):3-10
- P6) Shimokage T, Okumoto T, Hidaka M, and Nakagawa T. Influence of Compounding Styrene on the Hardening Structures of Unsaturated Polyester Resins. *Network Polymer* 2009; 30(1):10-5. (in Japanese)
- P7) Nakagawa T, Matsugi S, Hirota S, Miyazaki T, Shibata K, et al. Enhanced and Horizontal Recycling Technology of FRP Using Sub-critical Water. *Network Polymer* 2009; 30(2):83-90. (in Japanese)
- P8) Nakagawa T. Enhanced Recycling of FRP Using Subcritical Water. *Koubunshi* 2010; 59:162-3. (in Japanese)
- P9) Nakagawa T, Hirota S, Yabunouchi N, Shibata K, Yasuda Y, et al. Enhanced and Horizontal Recycling Technology of FRP Using Sub-critical Water (3). *Network Polymer* 2011; 32(1):26-34. (in Japanese)
- P10) Nakagawa T and Goto M. Recycling Thermosetting Polyester Resin into Functional Polymer Using Subcritical Water. *Polymer Degradation and Stability* 2015; accepted.
- P11) Nakagawa T and Goto M. Recycling thermosetting polyester resin into aqueous agents using subcritical water reaction. *Engineering Journal* 2015; In review.

International Conferences

- I1) Nakagawa T, Urabe T, Miyazaki T, Hidaka M, Oka K, et al. FRP Recycling Technology Using Subcritical Water Hydrolysis. International Symposium on Supercritical Fluid, Kyoto (Japan), Nov. 5-8 (2006): OC-2-08
- I2) Nakagawa T, Matsugi S, Hirota S, Miyazaki T, Yano H, et al. Enhanced and Horizontal Recycling of FRP Using Subcritical Water. International Symposium on Supercritical Fluid, Arcachon (France), May 18-20 (2009): C26
- I3) Nakagawa T. Enhanced Recycling of FRP Using Subcritical Water. Super Green, Sendai(Japan), Oct. 15-17 (2009): O3-306
- I4) Nakagawa T and Goto M. Recycling Thermosetting Polyester Resin Into Functional Polymer Using Subcritical Water. The 10th International Conference on Separation Science and Technology, Nara (Japan), Oct.30-Nov.1 (2014): FP-24
- I5) Nakagawa T and Goto M. Recycling of Thermosetting Polyester Resin Using Subcritical Water. The 2nd International Seminar on Fundamental & Application Of Chemical Engineering, Bali (Indonesia), Nov.12-13 (2014):F04

Papers covering the contents in this thesis

2. Subcritical hydrolysis of thermosetting polyester resin
 - 2.1. Fundamental verification
P1, P2, P3, and P5
 - 2.2. Functional mechanism of alkali catalyst and optimization of reaction conditions and catalysts
P4 and P10
 - 2.3. Evaluation of subcritical hydrolysis process for various FRPs
None. Published by only proceeding of domestic conferences.
3. Application of styrene-fumaric acid copolymer (SFC)
 - 3.2. Low profile additive (LPA)
P7, P8, and P9
 - 3.3 Aqueous agent
P11
 - 3.4 Compatibilizing agent for polymer alloy
Not published.