# Development of polyester composite as water-soluble support material for 3D printer

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## Abstract

The study was carried out to develop a 3D-printing support material which has water solubility, moisture resistance, high Tg, and high toughness. For this purpose, polyester resins having functional groups were prepared and their properties were determined. By controlling structure of the polymer, the polyester showed both solubility in neutral water at 70 $^oC$ and high moisture resistance. Furthermore, the Tg of the polymer was above 100 $^oC$, which is higher than the chamber temperature of 3D printers using ABS, so the polymer is suitable as a support material in 3D printing of ABS.

However, the polyester was too brittle for the production of tough, flexible filaments that are needed for 3D printing. Compounding the polyester with elastomer and compatibilizer was investigated to improve toughness of the polyester. Using a batch mixer / twin screw extruder, three components were mixed. The cross sections of the composites were observed by SEM. Submicron domains of dispersed elastomer were observed in the polymer matrix. The toughness of the composite was high enough to produce filaments with sufficient flexibility for 3D printing. Filaments of the composite were made by single screw extruder.

3D printing of model material (ABS) and the water-soluble support material was examined. The support material showed good solubility in neutral water at 70 $^oC$ after printing and it was easy to remove from ABS.

## Introduction

Recently, 3D printing technology[1] has been a topic of much attention. There are different 3D printing methods (material extrusion, ink jet material deposition, stereolithography, selective laser sintering etc.). Among these methods, extrusion of thermoplastic is widely used due to its cost effectivity. The technology is called Fused Deposition Modeling (FDM) or Fused Filament Fabrication (FFF). (Fused deposition modeling and FDM are trademarked by Stratasys.) FDM uses two materials: a model material and a support material. As a model material, ABS is used most commonly for industrial or personal 3D printers. For industrial 3D printers, acrylic copolymer[2,3,4] is used as support material for ABS. After printing, the acrylic copolymer support material is removed by dissolving in hot alkaline solution (such as aqueous sodium hydroxide). However, hot alkaline solution requires extreme caution in handling. Thus water-soluble support materials have been developed to bring health and environmental advantages. Although polyvinylalchohol (PVA) is used as water-soluble material, PVA is highly hydrophilic and has low moisture resistant. PVA absorbs moisture in the air which generates foam when it is heated. PVA foam impedes precise 3D printing. In addition, support material for FDM printing requires high heat resistance (high Tg) because the printing chamber of the printer is heated to suppress warping of the material. For ABS, the printing chamber is heated to near 90 $^oC$. Moreover, materials for FDM printing must be in the form of filaments for proper feeding into FDM printer, and toughness of the filament material is required for winding the filaments on spools.

The purpose of this study is to develop a support material with water solubility, moisture resistance, high Tg, and high toughness.

## Experiment

### *Materials*

ABS filament was used as a model material ABS. ABS was purchased from MakerBot Industries, LLC. (True red ABS). PVA filament for 3D printer was purchased from KenBill Inc.

The Elastomer and the compatibilizer used (Elastomer A and Compatibilizer A) were commercially products.

### *Polymerization of water-soluble polyester*

Polyester monomers and catalyst were heated to 230 $^oC$ for 6 hours in 3-L flask under $N_2$ atmosphere. Then the flask was heated to 265 $^oC$ and the mixture was stirred under vacuum condition. Yellowish clear polymer was obtained after the reaction. Scale-up productions of the polymer were carried out in a 100-L batch reactor in same process.

### *Measurement of molecular weight of polyesters*

The weight average molecular weight (WAMw) was measured by gel permeation chromatography (GPC) (HLC-8320 GPC, Tosoh). DMF containing 0.01 M LiBr was used as eluent. Monodisperse fractions of polystyrene were used as standard samples.

### *DSC measurement*

Differential scanning calorimetry (DSC) measurements were performed with DSC 7020 (Hitachi Hitech Science). Samples of the polymers (4-6 mg) were heated from 30 $^oC$ to 230 $^oC$ at 10 $^oC$ / min and cooled to 30 $^oC$ rapidly to erase thermal history. Then the samples were heated from 30 $^oC$ to 230 $^oC$ at 10 $^oC$ / min again. Tg's of the samples were measured by this process.

### *Solubility of the polyester in water*

The polymer was crushed into powder by electric coffee mill. 0.25 g of the polymer powder were dispersed in ion-exchange water (5.0 g) for 10 min at 70 $^oC$. Then the sample was filtered using filter paper. The cake on the paper was dried and weighed (A g). The solubility of the samples were calculated by the following equation.

$$\text{Solubility in water (\%)} = 100 \cdot (0.25 - A) / 0.25$$

### *Moisture absorption*

2.00 g of the polymer powder was vacuum-dried at 80 $^oC$ for 3 hours. Then the sample was put in the chamber of 25 $^oC$ / 98Rh%

 

for 24 hour. After that, the weight of the sample was measured (B g). Amount of moisture absorption was calculated by the following equation.

$$\text{Moisture absorption (\%)} = 100 \cdot (B - 2.00) / 2.00$$

### Kneading of the materials

Water-soluble polyester, Elastomer A and Compatibilizer A were melt-kneaded at 230 °C in a batch mixer (Labo Plastomill, Toyo Seiki Co.Ltd.). Then the polymer composite was ground in a coffee mill.

Scale-up productions of the composites were produced by mixing twin screw extruder (TEM-41SS, Toshiba Machine Co., Ltd.) at 230 °C. After melt-mixing, the composites were cut into pellet form.

### Filament production of support material

The polymer filaments were produced by capillary rheometer (Capillograph 1D, Toyo Seiki Ltd.). The polymer composites were extruded in a capillary rheometer with 2.0 mm diameter die at 210 °C. Polymer filaments with diameter: 1.7 mm were extruded from the die and were drawn manually.

The toughness of the filament was evaluated by bending test. The filament with high toughness could be bent at 180 ° while the filament with low toughness broke and could not be bent (Figure 1).

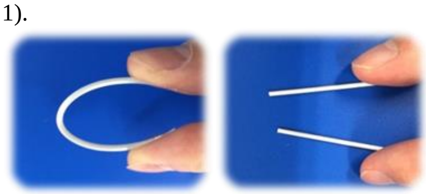

***Figure 1**. Bending test of the filaments (Left: Filament with high toughness.)*

Scale-up productions of the filaments were produced by single screw extruder (Uniplus Corporation). Pellets of polymer composites were put in the extruder at 210 °C. The composites were extruded and the polymer filaments (diameter: 1.7 mm) were wound on the spools (Figure 2).

***Figure 2**. Spool of support material filament*

### Solubility test of the filaments

500 mL of ion-exchange water was stirred by magnetic stirrer at 300 rpm and heated to 70 °C. Then the filament of the composite (10 cm length) was put into the water (Figure 3). The time was measured until the filament dissolved and snapped in water.

### SEM observations

The composites were pressed into 0.4 mm thick sheets at 230 °C and cooled to 15 °C rapidly. The sheets were put into liquid nitrogen and were kept for a minute. Then the samples were bent and broken in liquid nitrogen to make cross sections. The samples were put into ethyl acetate to dissolve elastomer. After an hour, the sample sheets were taken out of ethyl acetate and dried at 60 °C for an hour in a vacuum dryer. The cross sections of the samples were observed by SEM (VE-8800, Keyence Corporation).

***Figure 3**. The solubility test of the filaments*

### 3D printing test and solubility test

3D printing tests of the polymer composite were evaluated by using MakerBot Replicator 2X (MakerBot Industries, LLC., Figure 4). For the evaluation, scale-up filament was used. MakerBot Replicator 2X is desktop 3D printer with dual extrusion nozzle. For 3D printing test, we designed "the cube" (Figure 5). The red part of the cube is the model material (ABS) and the white part is the support material. Support material is filled in the cube without cavity. The filament produced by single extruder was used as the support material. Nozzle temperature for ABS was 230 °C and nozzle temperature for the water-soluble polyester was 250 °C. After 3D printing, the solubility tests of the composites were examined. 500 mL of ion-exchange water was stirred by magnetic stirrer at 500 rpm and heated to 70 °C. The printed model was suspended in the water using a wire basket and the support materials were dissolved (Figure 6).


***Figure 4.** MakerBot Replicator 2X*

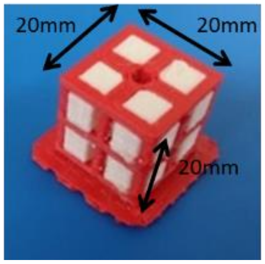


***Figure 5.*** *3D model of "The cube" (Red material: ABS, White material: Support material)*

***Figure 6.*** *Solubility test of 3D printed model*

## Results and Discussion

### *Properties of water-soluble polyester*

Table 1 shows properties of water-soluble polyesters and commercial support materials. Polyester A showed high solubility in 70 $^{o}$C water and low moisture absorption.

Polyester B had higher molecular weight than Polyester A and it showed low solubility. Its low solubility was caused by its high molecular weight and high molecular entanglement. Polyester C had lower molecular weight and showed high solubility in water, although it showed high moisture absorption. It contains more hydrophilic end groups than Polyester A and showed higher hydrophilicity. PVA showed high moisture absorption. As a result, polyester A had both high solubility and high moisture resistance. Polyester A was selected as a candidate of base polymer for water-soluble support material.

**Table 1. Properties of Polyesters and commercial materials**

| Polymer | Poly-ester A | Poly-ester B | Poly-ester C | PVA |
|---|---|---|---|---|
| Tg ($^{o}$C) | 110 | 105 | 106 | 85 |
| WAMw | 19000 | 41000 | 8500 | - |
| Solubility in 70 $^{o}$C water (%) | 98 | 28 | 99 | 99 |
| Moisture Absorption (%) | 5 | 3 | 13 | 35 |

### *Producing polymer composites*

In general, the materials used for FDM-type 3D printing must be in filament form, .so it is necessary to process the support material into filaments. Polyester A was a brittle polymer and was difficult to process into filament. Elastomer and compatibilizer were added to the polyester to improve toughness. Table 2 shows the compositions and properties of polymer composites produced by a batch mixer.

Polyester A, Elastomer A and Compatibilizer A were melt-kneaded and the composites were processed to filament shape by a capillary rheometer. The toughness of the filaments were evaluated by bending test. The filaments with low toughness broke and could not be bent.

The toughness of Composite A was not high enough, so the toughness of the filament was improved by adding elastomer and compatibilizer (Composite B). Excess of elastomer reduced filament toughness (Composite C). The filaments of the composites were used for solubility tests. The solutions after solubility test were cloudy since the elastomer and the compatibilizer were not water-soluble polymer. They were dispersed as minute particles in the water. The filament of Composite C showed low solubility because of its high content of elastomer.

**Table 2. The Composition of composites**

| | Unit | Com-posite A | Com-posite B | Com-posite C |
|---|---|---|---|---|
| Polyester A | PHR * | 100 | 100 | 100 |
| Elastomer A | PHR * | 12.5 | 12.5 | 30 |
| Compatibilizer A | PHR * | 0 | 5 | 5 |
| Bending test | Y/N | N | Y | N |
| Solubility time of filament | min | 3.5 | 3.8 | >15 |

** PHR: per hundred resin*

### *SEM observations*

The cross sections of the composites were observed by SEM and the elastomer domain sizes were compared. Figure 7-9 shows the cross sections of the composites. The elastomer is soluble in ethyl acetate, although the polyester and compatibilizer are not soluble in ethyl acetate. The samples were observed after elastomer was removed in ethyl acetate. Circular domains in the matrix are dissolved elastomer domains.

In Composite A, elastomer domains are less than 5.6 μm. There were some coarse particles. Elastomer domains in composite B were less than 3.0 μm. In Composite B, elastomer domains were smaller than those in Composite A and they dispersed uniformly.

High toughness of Composite B was achieved by fine dispersion of elastomer. As the content of elastomer increases, the diameter of the dispersed elastomer became much larger (Composite C).

Water-soluble polyester and the elastomer were not compatible. The compatibilizer interacts with end functional groups of the polyester during the mixing process. The compatibilizer improves dispersion of elastomer. However, at high elastomer content, elastomer aggregated.

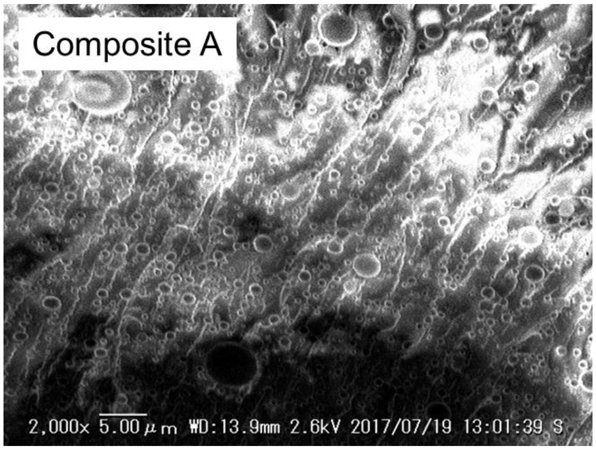


***Figure 7**. Cross section of the composite A*

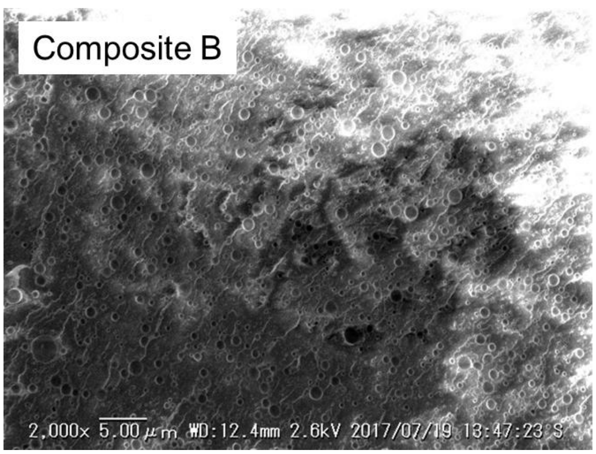


***Figure 8**. Cross section of the composite B*

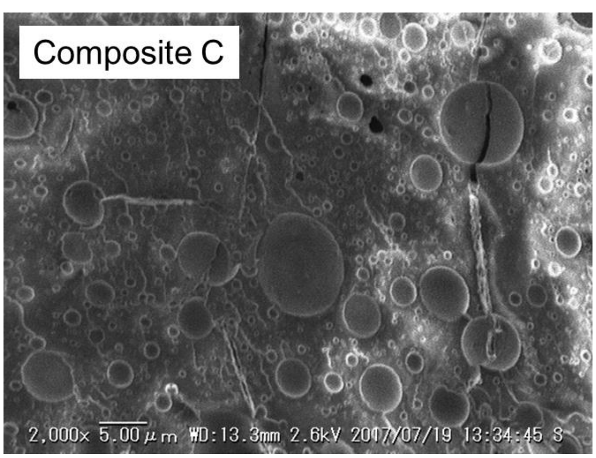


***Figure 9**. Cross section of the composite C*

## 3D Printing tests of the materials and solubility tests of the printed models

The scale-up production of Composite B was carried out by twin screw extruder and the its filament was produced by single screw extruder. 3D printing of Composite B was examined by using the filament.

Nozzle temperatures of ABS and composite B were set at 230 $^{o}$C and 250 $^{o}$C. The models of "the cube" was printed well. The printed model of ABS and composite B was submerged in 70 $^{o}$C water. Figure 10 shows the results of solubility tests of the printed model. Water could not flow through inside the cube before support material dissolved. Most of Composite B dissolved in 60 min. Composite B showed high solubility and it looks promising for water-soluble support material.

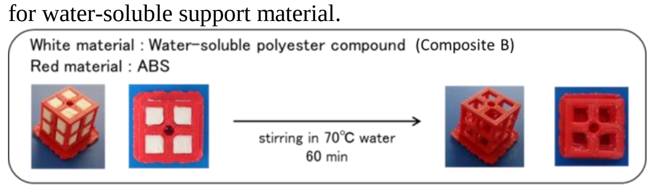


*Figure 10. The results of dissolution tests of Composite B*

## Conclusion

The study was carried out to develop a support material for 3D printer with water solubility, moisture resistance, high Tg, and high toughness. For this purpose, water-soluble polyester resins were prepared and their properties were determined. By controlling molecular weight, the polyester with high Tg, high moisture resistance and high water-solubility was successfully developed. The water-soluble polyester, elastomer and compatibilizer were mixed to improve the toughness of filaments of water-soluble polyester. The structure of the composite was investigated by SEM. Elastomer domains in the matrix were submicron-size and dispersed uniformly. The toughness of the composite was high enough to allow filament filament production. Using the filament of the composite, 3D printing of ABS and the support material were examined. The support material showed good solubility in neutral water at 70 $^{o}$C after printing. It shows high water-solubility and looks promising as a water-soluble support material.

## References

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## Author Biography

Tomoya Tsuboi obtained a masters degree in engineering at Kyoto University in Japan in 2008. He finished his Ph.D. within the group of Prof. Itoh (Kyoto Institute of Technology) in 2013 with a focus on polymer crystallization and modifying physical properties of polymer. He continued his work at Kao Corporation in Japan. The topics include polymer synthesis and physical properties of polymers.