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Synthesis and applications of unsaturated polyester resins based on PET waste

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Abstract−Three types of unsaturated polyester resins were synthesized from the glycolysis of polyethylene terephthalate (PET) plastic waste, considering environment, cost and properties for their applications. These synthesized unsaturated polyester resins could be used for various construction processes and materials such as no dig pipelining (NDR-1), pultrusion (PLR-1) and polymer concrete (PCR-1). PET was taken from common soft-drink bottles, and ethylene glycol (EG), diethylene glycol (DEG) and MPdiol glycol mixtures were used for the depolymerization at molar ratios. The glycolyzed PET 1st products (oligomers) were reacted with maleic anhydride, phthalic anhydride and dicyclopentadiene (DCPD) (especially for polymer concrete) to form unsaturated polyester resins with mixed styrene. The lab scale (1-5 kg) and pilot plant scale-up tests (200 kg) were experimented to evaluate the processing characteristics, viscosity, acid number and curing behaviors. The main properties such as hardness, flexural strength, tensile strength, heat distortion temperature, elongation, and chemical resistance were determined based on the various uses of the three resins. Furthermore, the applicability and the properties of these developed resins were verified through many real application tests.

Key words: PET Waste, Glycolysis, Unsaturated Polyester Resins, Construction Material

INTRODUCTION

Unsaturated polyester resins based on PET recycling have not been used widely yet due to their poor properties, long operating times and non-uniform products even though their cost is low. Colored PET wastes also have limited their recycle. Many companies producing unsaturated polyester resins have made an effort to decrease raw materials because of the high oil cost. Customers, however, still want low cost resins with high performance.

Polyethylene terephthalate (PET) is a thermoplastic polyester with excellent thermal and mechanical properties that is widely used in many countries as an ecological and consumer-friendly material for video and audio tapes, X-ray films, food packing, drinking bottles and jars. The demand for PET and the wastes of PET have been increasing year by year. PET recycling technologies have become well known in industry and represent one of the most successful and widespread examples of polymer recycling. There are two methods for PET recycling. One method is physical recycling to produce PET flakes and to re-use it with resin PET. The other is chemical recycling by depolymerization of PET wastes. Many researches report considerable PET waste recycle by various methods for several applications. Among the different recycling techniques, the acceptable one, following the principles of sustainable development, is chemical recycling, mainly because it leads to the formation of the raw materials from which the polymer is made, as well as of the secondary value-added products [1].

The chemical recycling method of polymers is generally based on breaking the ester bonds by using some reagents. The processes of chemical degradation of waste PET are divided as follows: (i) methanolysis, (ii) glycolysis, (iii) hydrolysis, (iv) ammonolysis, (v) aminolysis, (vi) other processes [2]. Methanolysis involves converting PET into dimethyl terephthalate (DMT) and ethylene glycol (EG), which are raw materials needed for the production of this polymer. The reaction condition for methanolysis is 2-4 MPa and 180-280 °C [3-6]. Glycolysis is chemical recycling with ethylene glycol, diethylene glycol, propylethylene glycol, depropylene glycol, butanediol, and triethelene glycol [7,8]. The temperature range of the glycolysis process operation is 180-250 °C [2]. In the ammonolysis process, anhydrous ammonia reacts with PET producing the TPA amide. Reaction conditions are: temperature range 120-180 °C, pressure 2 MPa and time 1-7 hours [9]. Among previous chemical recycling methods, a recent growing interest has been applied for the production of specialized products such as unsaturated polyester resins, polyurethane and polymer concrete using glycolysis due to consumer needs and cost [10].

The purpose of this research is to develop a new method of producing unsaturated polyester resins from the recycling unsaturated oligomers. The resins are used as various construction materials such as pultrusion, polymer concrete and especially no-dig pipelining. The colored PET can be also recycled with this method. In order to fulfill this goal, synthesis and reaction conditions were studied by lab scale experiments. A pilot plant scale-up was also done to find design specifications. The final mechanical properties of the resins were compared with commercial products to verify good properties of the developed resins.

EXPERIMENTAL

1. Materials

PET flakes were obtained from post-consumer clear bottles and the bottles were cut with a maximum size of 10 mm. The colors of

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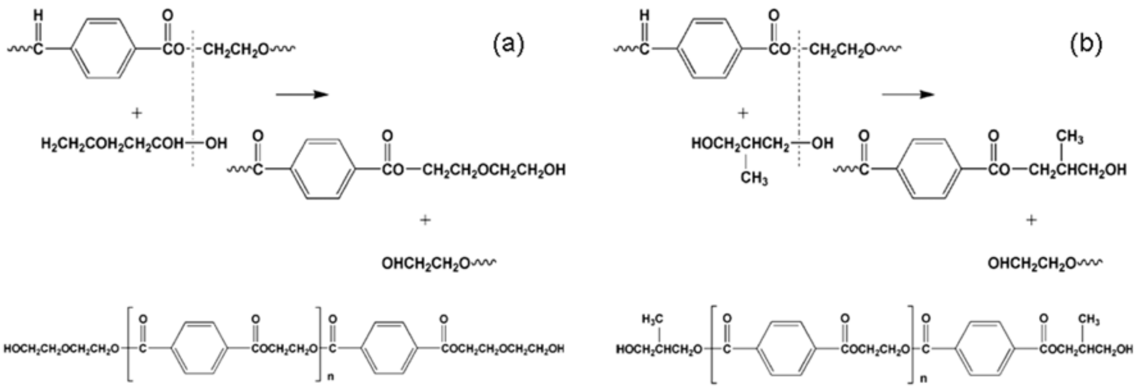
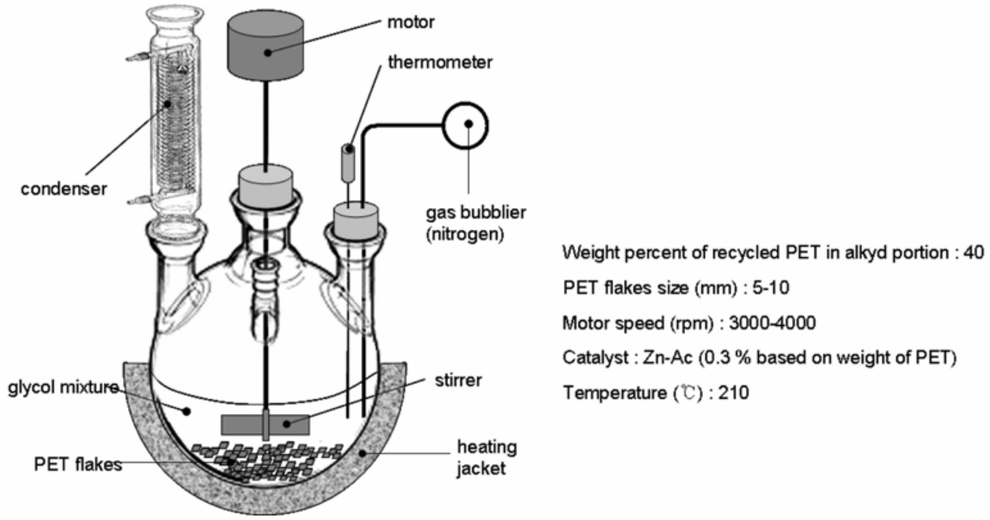


Fig. 1. The glycolysis reactions of PET ((a) DEG and (b) MPDiol).



Weight percent of recycled PET in alkyd portion : 40
PET flakes size (mm) : 5-10
Motor speed (rpm) : 3000-4000
Catalyst : Zn-Ac (0.3 % based on weight of PET)
Temperature (℃) : 210

Fig. 2. PET glycolysis reactor.

PET flakes were three: transparent, blue and green. The clear flakes were used for pultrusion and polymer concrete, the others for no-digging pipe lining. Ethylene glycol (EG), diethylene glycol (DEG) and MPdiol glycol mixtures were used for the depolymerization at molar ratios. Maleic anhydride, phthalic anhydride and dicyclopentadiene (DCPD) [11] (especially for polymer concrete) were reacted with the glycolyzed PET oligomer in the second reaction. After reacting, unsaturated polyester resins were mixed with styrene monomer by 35-45 weight percent in resin. The initiator for curing reaction of synthesized unsaturated polyester resins was benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKPO).

2. Glycolysis of PET

The glycolysis of PET with diethylene glycol (DEG) and MPDiol glycol proceeds according to the following reaction. The glycolysis consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of its molecular weight. When glycols are used for the depolymerization of PET, the oligomers obtained have two hydroxyl end groups, i.e., oligoester diols are formed.

In the glycolysis of PET, PET waste flakes were charged into the reactor together with ethylene glycol (EG), diethylene glycol (DEG) and MPDiol glycol in case of the resins for the production of polymer concrete and no-digging pipe lining, and diethylene glycol (DEG) were omitted in case of resins for pultrusion. The weight ratio of PET/glycol was 250/142, 250/153 and 250/200 for polymer concrete, pultrusion and no-digging pipe lining, respectively. 0.3% Zinc acetate, based on weight of PET, was used as a transesterification catalyst. The glycolysis reactions were carried out at 210 °C for 5 hours in a round-bottom flask equipped with a reflex system, gas bubblier, contact thermometer, mechanical stirrer and temperature and timer controller system in nitrogen atmosphere. After reacting, the flask was cooled below 100 °C at room temperature. Fig. 2 shows a reactor and other equipment for PET glycolysis.

3. Synthesis of Unsaturated Polyester Resins

Unsaturated polyester resins are complex polymers resulting from a cross-linking reaction of liquid unsaturated polyester with vinyl type monomers, most often styrene monomer such as in Fig. 3. The unsaturated polyester is formed from the condensation reaction of an unsaturated dibasic acid or anhydride, a saturated dibasic acid or anhydride, and a polyfunctional alcohol [12]. Fig. 4 shows the condensation reaction that an oligomer produced from PET glycolysis is reacted with maleic anhydride and phthalic anhydride.

Unsaturated polyester resins can be produced by a fusion or a solvent process. In the fusion process, an inert gas (typically nitrogen) is used to remove water that is generated during the produc-

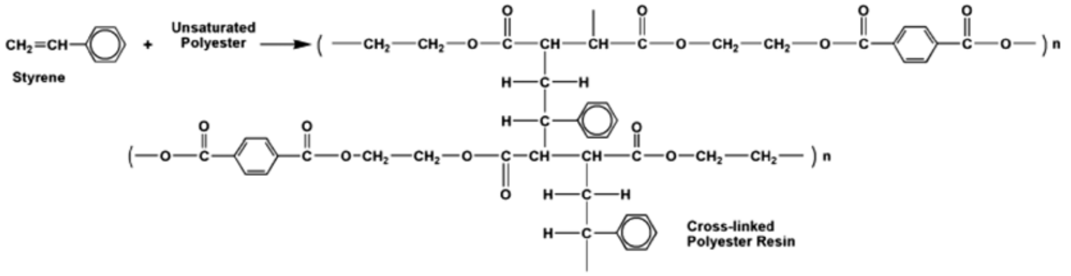


Fig. 3. The cross-linking reaction of unsaturated polyester with styrene monomer.

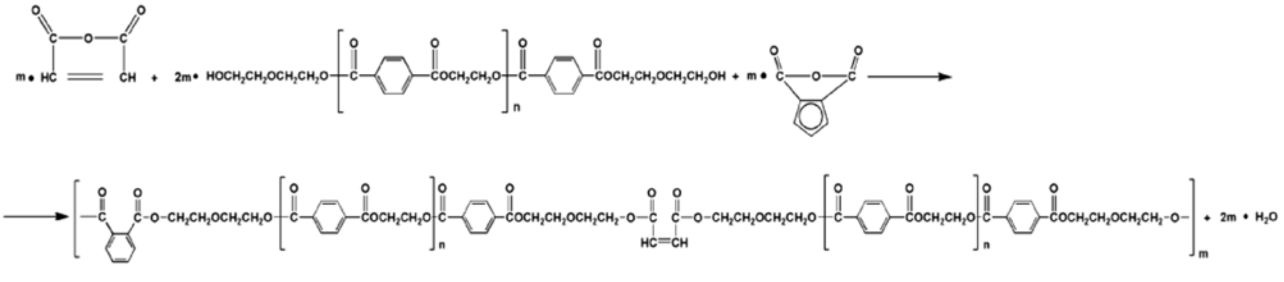


Fig. 4. The reaction for unsaturated polyester from an oligomer of PET glycolysis.

tion process. The solvent process uses azeotropic distillation. Both of these are batch processes. This study adopted the fusion process. The fusion process consists of the reacting (polyesterification) and thinning stage. Three types were synthesized in this study: the first is for no-dig pipelining resins (NDR-1), the second is for pultrusion process (PLR-1), and the last is for polymer concrete resin (PCR-1).

In the case of NDR-1, maleic anhydride was added to oligomer produced from PET glycolysis with equivalent ratio equal to the oligomer. Highest temperature was 200 °C. Hydroquinone (HQ-S) and PTBC (p-tetra-butylcatechol) were used for reaction inhibitors. After reaction, synthesized resin was thinned with 33-37 wt% styrene monomer and hydrophilic fumed silica (Aerosil). Ethylene glycol was used for the dispersing agent.

PLR-1 was synthesized by using maleic anhydride (0.67 equivalent ratios) and phthalic anhydride (0.33 equivalent ratios) with PET glycolysis oligomer (1.00 equivalent ratios). The mixture was heated to 200 °C held for 4-6 hours, and water (by-product) was continuously removed by using a condenser by bubbling the inert gas through the mixture. Hydroquinone (HQ-S) and PTBC (p-tetra-butylcatechol) also were used for reaction inhibitor. The amount of cross linking monomer (styrene monomer) was 38-42 wt%.

For PCR-1, maleic anhydride (1.00 equivalent ratios) was reacted with oligomer (0.92 equivalent ratios). The mixture was heated to 150 °C (maleic anhydride was solved perfectly at this temperature) and cooled to 120 °C and then dicycropentadiene (DCPD) (0.80 equivalent ratios) was added by a dropping bottle for 1-2 hours during the exothermic reaction. After dropping, the reactant was heated again to 190 °C and held to 3-5 hours. Styrene monomer was used as thinner. Hydroquinone (HQ-S) and PTBC (p-tetra-butylcatechol) were also used for reaction inhibitors. Low profile agent and wax for surface were added to resins after the thinning process.

4. Operation of Pilot Plant

The pilot plant is based on lab scale experiments and 200 kg resins can be produced through one batch processing. Fig. 5 shows the schematic process of the pilot plant. The pilot plant consists of two kettles (reaction kettle and thinning kettle), two types of condenser (vertical condenser and total reflux condenser), heating jacket, stirrer, outside cooling coil, vent, gas injector (Nitrogen or air), pressure gauge, dropping panel, filter, control box and pipes between the reaction kettle and the thinning kettle.

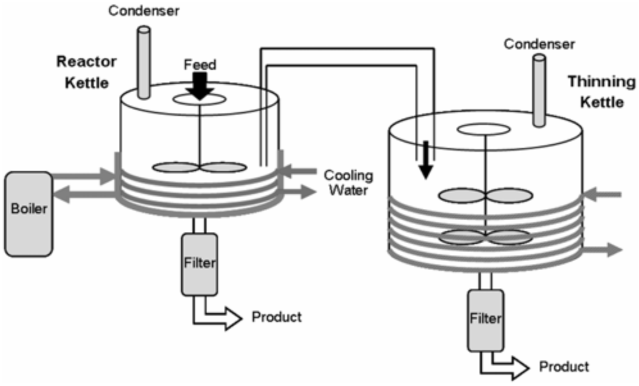


Fig. 5. Schematic of the pilot plant.

The glycolysis of PET waste and the estrification of unsaturated polyester anhydride were reacted in the reaction kettle. After reaction, the temperatures were cooled from the top temperature (200-210 °C) to below 160 °C, and then the reactants were transferred through the pipes by the pressure drop to thinning kettle which was already filled with styrene monomers. The major points of the transfer process were to control the temperature of the thinning kettle below 60 °C due to the volatility of the styrene monomer. The specifications of the resins were determined when the temperatures were below 40 °C by using a cooling water coil and then the products were packed through the filter (10-100 μ).

5. No Dig Pipelining, Pultrusion and Polymer Concrete Processes

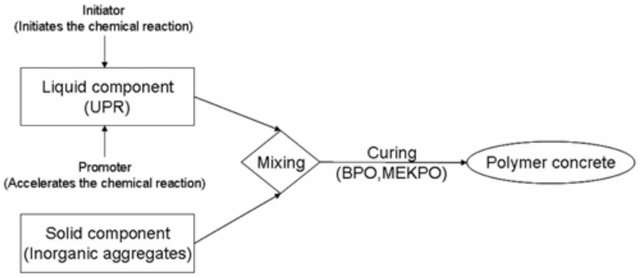


Fig. 6. Polymer concrete production process.

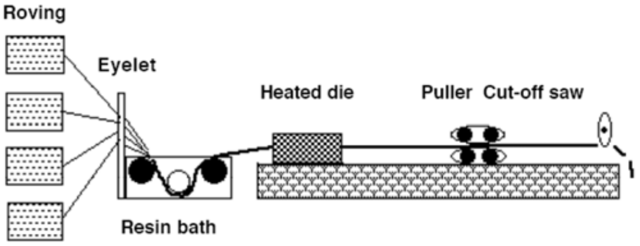


Fig. 7. Schematic diagram of a pultrusion machine.

Polymer concrete (PC) is made of inorganic aggregates bonded together by a resin binder. PC is a relatively new high-performance material that has been commercialized since the 1960s [13,14]. The material is strong, durable and cures fast. One common binder used in PC is unsaturated polyester due to its relatively low cost and good properties compared with other resin binders. The major shortcoming of PC, however, is the relatively high cost of the material compared with cement-based materials. Most of the PC cost comes from the resin component; the cost of the filler component is comparatively negligible. A resent survey ranked lower cost resins as the most important need for PC. PC is commonly produced under a process such as Fig. 6.

Pultrusion is a continuous process of producing high strength and quality composite materials such as fishing rods, electric wires, aircraft structures and bridge structures. A bundle of fiber roving is passed through a wet resin bath, squeezed into a desired shape, passed through a heated die, and cured into a final composite. Fig. 7 is a schematic diagram of a pultrusion machine. Heat transfer, pressure, properties and experimental works for curing and shrinkage in the pultrusion process have been studied since the 1990s. The cost of production in pultrusion is relatively high compared with other materials such as steel. It is necessary to decrease the cost of the composite based on unsaturated polyester resins [15].

No dig pipe lining is a simple method of repairing inside PVC or cement pipes without digging and replacing the pipes. The lining process is to pressure the wetted felt with resins and dispersing agent mixture into the pipe and then to cure the felt inside the pipe with steam [16]. The strength of the no dig technique is to reduce the construction time and is relatively harmless to workers, motorists, and the environment. The unsaturated polyester resin is one of the most suitable curing binders. Fig. 8 shows real pictures of no dig pipe lining test using NDR-1.

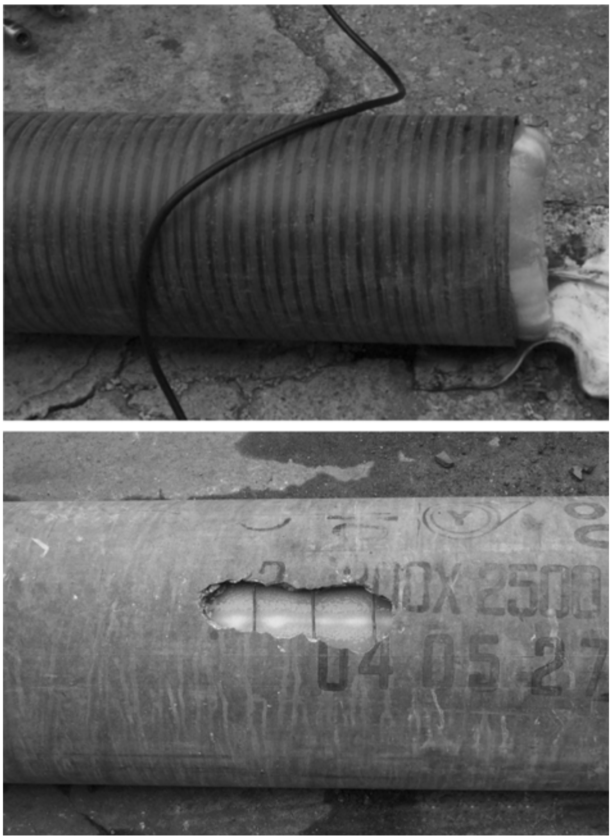


Fig. 8. Pictures of no dig pipe lining with UP resin based on green PET recycle.

RESULTS AND DISCUSSION

1. Specification of Unsaturated Polyester Resins

The properties of three synthesized resins in this experiment were as follows:

Table 1 represents basic properties of three synthesized resins. NDR-1 is a thixotropic resin for cured-in-place-pipe applications and therefore has high viscosity. The color of the resin is green since the oligomer comes from colored PET wastes. The others have yellow transparent color (3 max., GARDNER) and low viscosity.

2. Curing of the Unsaturated Resins

2-1. NDR-1

Table 1. Properties of the synthesized resins

Name of resin	Appearance	Viscosity (Poise, 25 °C)	Specific gravity	Acid number (KOH ml/g)	Non-volatiles content (%)
NDR-1	Slight green	25-30	1.07-1.12	12-20	64-66
PLR-1	Slight yellow	3-6	1.08-1.13	22-28	59-61
PCR-1	Slight yellow	3-6	1.10-1.15	25-30	60-62

In the case of NDR-1, peroxide-amine was used in order to cure the resins at high temperature (above 80 ºC). Benzoyl peroxide (BPO), t-butyl perbenzoate (TBPB, Trigonox C) and bis(4-t-butyl cyclohexyl) peroxydicar-bonate (Percadox 16 N) were used according to different temperature conditions. (Percadox and Trigonox are registered trademarks of Akzo Chemicals.) The crosslinking was studied by the SPI (Society of the Plastic Industry) standard method. The method is based on changes in electrical conductivity with temperature. A test tube containing polyester dissolved in styrene and initiators is placed in a water bath at 82.2 ºC. A thermo-detector coupled with a plotter is placed in the middle of the test tube to measure the changes in the temperature of the resin. The gel time is defined as the time for the heat of reaction to rise from 65 to 90 ºC. The maximum curing time is defined as the time for the heat of reaction to rise from 65 ºC to the maximum temperature. These initiators have to be contained in the resins before working (curing in pipe), so the shelf life test detects the important checkpoints.

SPI gel time (82.2 ºC, BPO 1%): 8-10 min
SPI maximum cure time: 10-12 min
SPI peak exothermic temperature: 220-230 ºC

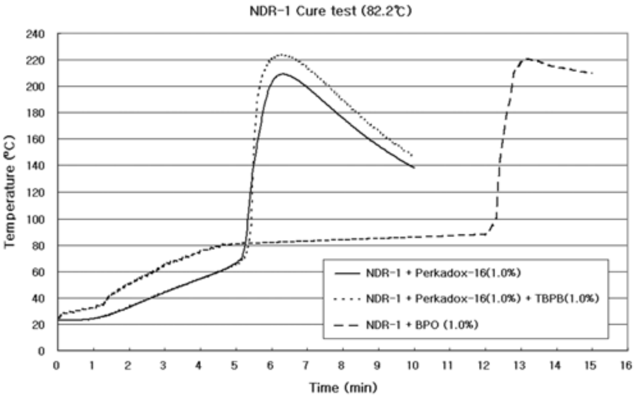


Fig. 9. SPI cure graph of the NDR-1 resin.

Table 2. Shelf life test of the NDR-1 resin

	BPO	Percadox 16 N	Trigonox C	Shelf life (hrs)
NDR-1	1.0%	-	-	340
	-	1.0%	1.0%	50
	-	1.0%	0.5%	50
	-	0.5%	1.0%	100

Based on Fig. 9 and Table 2, the results for the operating time in the lining process and shelf life were suitable compared with other curing conditions. The guarantee of enough operating time is one of most important factors in the no dig lining process.

2-2. PLR-1

Crosslinking tests of the PLR-1 resin were checked with SPI standard method by using BPO initiator. Gel time and curing time of the PLR-1 resin were shorter than that of the NDR-1 resin because most pultrusion processes produce products speedily. The resin for pultrusion process usually is cured with mixing low profile agents (5-10 wt%). It is important not to change the gel time, the curing time and the maximum temperature under the low profile mixing conditions. In this experiment, four kinds of low profile agents (LP) were used, that is LP1(NPG-IPA-AA), LP2 (MPdiol-TPA-AA), LP3 (PMMA in SM) and LP4 (blank). The reaction processes of these low profile agents are not presented in this paper due to the related company status.

Based on Table 3, data for SPI gel time and maximum curing time were similar with all low profile agents. For peak exothermic

Table 4. Gel time of the PCR-1 resin according to initiators and inhibitors

PCR-1	
Initiator/Inhibitor	Gel time (25 ºC)
MEKPO 1%	10 min 30 sec
8% Co-Oct 2,500 ppm DMA 200 ppm	3 min 15 sec
8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm	7 min 25 sec
8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 20 ppm	11 min 15 sec
8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 50 pm	15 min 50 sec

Table 3. SPI gel time of the PLR-1 resin according to low profile agents

	Low profile agent	SPI gel time	SPI max. cure time	SPI peak exothermic temperature (ºC)
PLR-1	None	3 min 40 sec	6 min 20 sec	196
	LP1 (5%)	3 min 44 sec	6 min 10 sec	200
	LP1 (10%)	3 min 45 sec	6 min 20 sec	196
	LP2 (5%)	3 min 42 sec	6 min 10 sec	196
	LP2 (10%)	3 min 50 sec	6 min 25 sec	193
	LP 3 (5%)	3 min 47 sec	6 min 13 sec	200
	LP3 (10%)	3 min 50 sec	6 min 25 sec	202
	LP4 (5%)	3 min 33 sec	6 min 10 sec	201
	LP4 (10%)	3 min 36 sec	6 min 18 sec	197

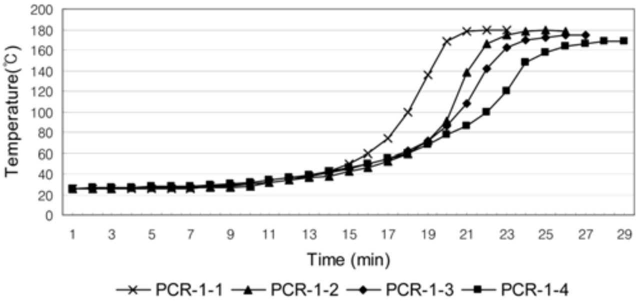


Fig. 10. Cure characterization graph of the PCR-1 resins. (PCR-1-1: MEKPO 1%, PCR-1-2: 8% Co-Oct 2,500 ppm, DMA 200 ppm, P-TBC 50 ppm, PCR-1-3: 8% Co-Oct 2,500 ppm, DMA 200 ppm, P-TBC 50 ppm, HQ-S 20 ppm, PCR-1-4: 8% Co-Oct 2,500 ppm, DMA 200 ppm, P-TBC 50 ppm, HQ-S 50 ppm)

temperature, LP2 (10%) had the lowest temperature. Too high a peak exothermic temperature may cause a crack or bending in the pultrusion process.

2-3. PCR-1

The PCR-1 resin is a promoted resin containing 5% copper naphthenate (5% Cu-Naph) (20 ppm/total resin). In order to cure the PCR-1 resin at ambient temperature (25 °C), 8% cobalt-octate, dimethylamine (DMA) and methyl ethyl ketone peroxide (MEKPO) were used. Hydroquinone (HQ-S) and PTBC (p-tetra-butylcatechol) were used as inhibitors to extend the curing time. The polymer concrete resin is usually used with a glass fiber mat and used by mixing filler ($CaCO_3$). In the case of glass fiber mat, the resin containing initiators is dispersed to the glass fiber mat (usually 10 pieces) with a roller. Therefore, mat life time (cure time on the surface of glass fiber mat, MLT) and barcol hardness time (the starting time to be able to check barcol hardness of the surface of glass fiber mat, BCT) have to be checked. The gel time, maximum cure time and peak exothermic temperature are necessary to check for the mixture of the resin and filler ($CaCO_3$).

For results, PCR-1-1 had too short time until gel time to peak exothermic temperature and PCR-1-2 reached gelation state in a very short time. In the case of PCR-1-4, peak exothermic temperature was too low and BCT took a long time. PCR-1-3 had the most suitable conditions for the polymer concrete process.

3. Mechanical and Chemical Properties of the Resins

The main advantage of the resins recycling PET wastes is the relatively low cost of materials compared to different unsaturated polyester resins. If the resins based on recycled PET wastes, however, have lower physical and chemical properties than the current resins, these would be limited to the low cost production fields. The resins using the production of no-dig pipe lining, pultrusion process and polymer concrete must have good properties such as flexural and tensile strength, hardness, lower distortion, low contraction rate, chemical resistance, corrosion resistance and so on. Physical properties are among the most important to use the unsaturated polyester resins and need to be determined [17].

The resins (400 g) were cured with 1% Benzoyl peroxide (BPO),

Table 5. MLT and BCT of the glass fiber mat dispersing the PCL-1 resin

PCR-1 resin (300 g) Glass fiber mat (10 pieces)		MEKPO 1%	8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm	8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 20 ppm	8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 50 ppm
PCR-1	MLT	13.5 min	13 min	13.5 min	14 min
	BCT	25 min	20 min	25 min	30 min

Table 6. GT, MCT and PET of the mixture the PCR-1 resin and $CaCO_3$

PCR-1 resin (100 g) $CaCO_3$ (300 g)		8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm	8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 20 ppm	8% Co-Oct 2,500 ppm DMA 200 ppm P-TBC 50 ppm HQ-S 50 ppm
PCR-1	GT	10 min 30 sec	12 min	12 min
	MCT	60 min	60 min	60 min
	PET	44 °C	44 °C	42 °C

Table 7. Physical properties of the NDR-1, PLR-1 and PCR-1 resins

Property	Unit	NDR-1	PLR-1	PCR-1	Method
Barcol hardness	-	47	48	48	ASTM D 2583
Heat distortion temperature		106	112	113	ASTM D 648
Flexural strength	kgf/mm^2	18.57	17.91	20.22	ASTM D 790
Flexural modulus	kgf/mm^2	485.89	462.40	481.7	ASTM D 790
Tensile strength	kgf/mm^2	9.33	8.87	9.67	ASTM D 638
Elongation	%	3.84	3.47	3.11	ASTM D 638

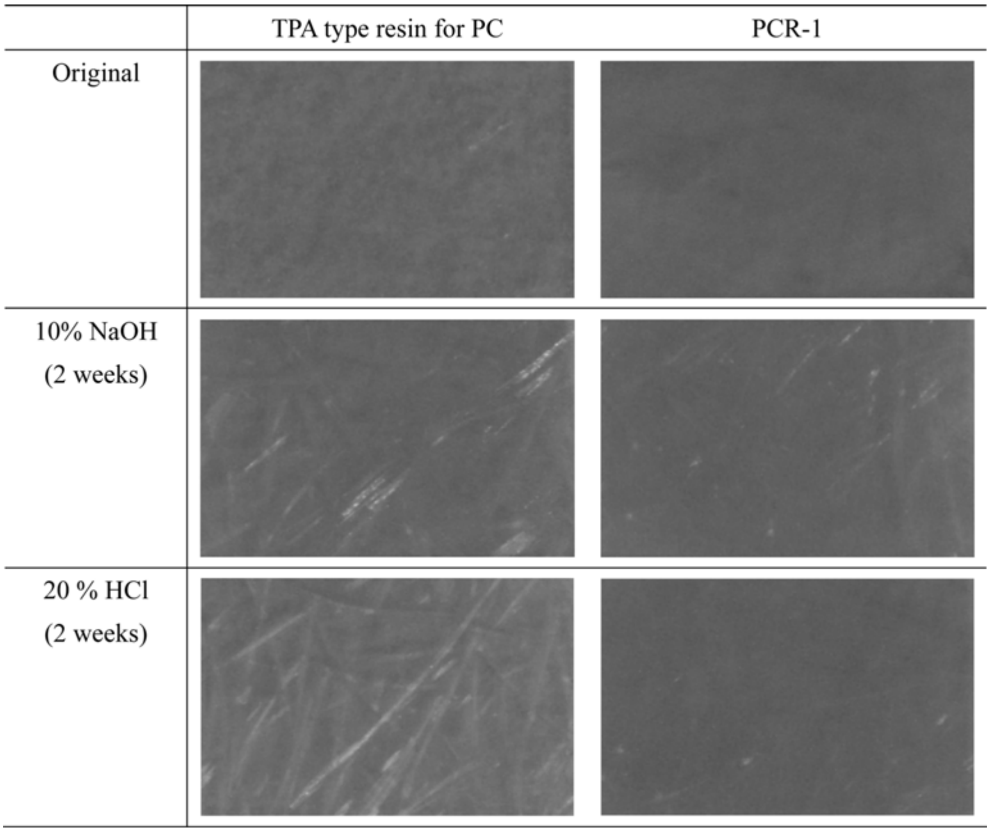


Fig. 11. Chemical resistance test for 10% NaOH and 20% HCL of the PCR-1 resins.

and procured for 8 hours at 55 °C, and then held for 1 hour at 80 °C, followed by postcure for 2 hours at 110 °C. The size of the resin casting for physical test was 300 mm×300 mm×3 mm (t). The physical properties of the thermosetting polymers were determined by using ASTM test methods. Tensile strength, modulus, and elongation are determined by ASTM D 638, Type 1, and flexural strength and flexural modulus using ASTM D 790. Heat distortion temperature is determined by using ASTM D 648, and ASTM D 2583 is used for barcol hardness.

Oven cure system: Resin (400 g)
+BPO (1%), 55 °C×8 h+80 °C×1 h+110 °C×2 h

In the case of the PCR-1 resin, it must have good chemical resistance and durability as well as strength due to its main application for floors. The chemical resistance tests were determined. 10% NaOH and 20% HCl solutions were used as reagents for the test, and the testing materials were made through the resins (300 g) containing initiators which were dispersed to a glass fiber mat (usually 10 pieces) by using a roller. Test solutions of the reagents were filled in a glass beaker and then the testing materials were soaked for 2 weeks in these beakers. After 2 weeks, the surfaces of the tested materials were checked by digital camera. From the results in Fig. 11, the PCR-1 resins had better chemical resistance for 10% NaOH and 20% HCl than the current TPA (terephptalate) type resins because less of the glass fibers were shown over the surface of PCR-1 than the others.

CONCLUSIONS

Three types of resins (NDR-1, PLR-1 and PCR-1) based on recycled PET wastes were formulated in order to use for no dig pipe lining, pultrusion and polymer concrete in this study instead of TPA and IPA, both materials which are currently used as a raw material. The production costs of these resins were 20-25% less than raw material costs. The processing conditions of synthesizing these resins were experimented through a lab scale and a pilot plant. Basic specifications, curing characterizations and physical and chemical properties were determined according to these applications.

The NDR-1 resin for no dig pipe lining was formulated from colored PET wastes and had thixotropic condition, medium viscosity, long shelf life-time, corrosion resistance, water resistance and high physical properties. The PLR-1 resin for pultrusion had low viscosity, short curing time, crack resistance and high mechanical properties. The PCL-1 resin for polymer concrete had low viscosity, high physical properties and higher chemical resistance than the reference TPA type resin. This paper described the synthesis of three new resins using PET glycolysis with less raw material cost and good properties.

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