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Chemical Recycling of Unsaturated Polyester Resin and Its Composites via Selective Cleavage of ester Bond

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An efficient strategy has been developed for chemical recycling of unsaturated polyester resin (UPR) and its glass fibre reinforced polymer composites (GFRP) by selectively cleaving C-O bonds using $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system. AlCl_3 promotes acyl exchange reaction between CH_3COOH and UPR. This process facilitates recovery of valuable oligomers and monomers from UPR, and glass fibres from GFRP.

The recovery of valuable units from end-of-life polymeric materials has become an important issue in view of sustainable chemistry and environmental protection.¹ Unsaturated polyester resin (UPR) and its composites, for example, glass fibre reinforced unsaturated polyester resin composites (GFRP), have been widely applied in the aeronautical, automotive, construction industries, new energy and transport fields.² With the large number applications of UPR and its composites, the waste UPR and composites including off-cuts during manufacture, unused prepreg and end-of-life components have caused a great trouble on the environment.³ Developing an effective recycling method for waste UPR and its composites becomes an urgent issue that needs to be addressed. However, as a thermoset resin, UPR and its composites are thermal and chemical stable because of their strengthful three-dimensional network structure.⁴ At the beginning, landfill and incineration were adopted to deal with thermosetting resin and their composites.^{5, 6} However, simple treatment of the scrap thermosetting resins and composites would cause a great waste of valuable materials. Current recycling strategies for UPR and its composites mainly includes mechanical, thermal and chemical methods.⁷ Mechanical recycling technique involves grinding process

to comminute the scrap material for reuse as fillers or partial reinforcement in new composite material. This method consumes a large amount of mechanical energy, and the length of recovered GF is drastically declined which limits the reuse of recovered GF.^{8, 9} In the thermal process, high temperatures are demanding to decompose the scrap material. However, small molecules would inevitably produce in this process, most of which are toxic gases.¹⁰⁻¹²

Compared to mechanical and thermal methods, chemical recycling is more promising because it can obtain glass fibre, monomers and their derivatives from end-of-life thermoset resin and its composites. Major efforts in chemical recycling strategy are concentrated on the depolymerisation of the resin matrix for liberation of glass fibres by solvolysis, including hydrolysis (using water),¹³ alcoholysis (using alcohols), aminolysis (using ammonia) and acid digestion (using acid). During the solvolysis process, either sub- or supercritical conditions with high temperature and high pressure are normally required to gain fast dissolution and high efficiency.^{14, 15} For example, supercritical water was reported as the solvent to degrade epoxy resin or UPR;¹⁶⁻²⁰ numerous studies demonstrated that the decomposition of epoxy resin or UPR can be achieved in supercritical alcohols.²¹⁻²⁵ In the examples of acid digestion of resin, atmospheric conditions were normally applied but the separation was troublesome.^{26, 27} In addition to solvolysis, the degradation of UPR was reported by using strong oxidants such as hydrogen peroxide²⁸⁻³⁰ and ionic liquid.³¹⁻³³ However, high temperature, long reaction times, strong corrosive solvent (e.g., nitric acid), or rigorous conditions (e.g., supercritical fluid) are usually required to cleave the chemical bonds of UPR. More importantly, such cleavage of chemical bonds is non-selective, which inevitably produces small toxic molecules, introduces a complex distribution of products and causes a serious damage in the strength of GF.

Ideally, it is desirable to decompose UPR and to recycle GF by selective cleavage of specific bonds of resin. The complexity in products and emission of toxic gases in such case would be minimized. Noticeably, UPR is mainly built up by C-C, C-H and C-O bonds (as shown in scheme 1). The exact name of the selected UPR

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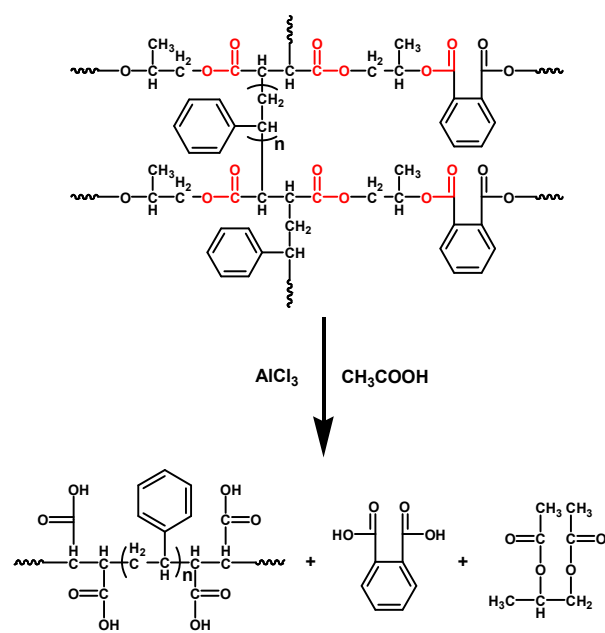
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(scheme 1) is poly-maleic anhydride-phthalic anhydride-1,2-propylene glycol cross-linked with styrene (PMPPS) which is a convenient and versatile resin for general purpose. The selective cleavage of C-O bond could not only facilitate recycling of GF, but also favor the retaining of valuable carbon skeleton of resin and other chemicals. Herein, we report using $\text{AlCl}_3/\text{CH}_3\text{COOH}$ as the degradation system to recycle thermoset resins and their composites under mild conditions (180 °C, 1-3 atm).

The synthesis process of PMPPS is shown in SI Scheme 1 in ESI. The major functional groups of PMPPS are ester bonds and benzene ring. As benzene ring is very stable because of the aromatic structure, ester bonds would be cleaved in the decomposition process of the PMPPS. To selectively break C-O bond, a Lewis acid is essential due to the existence of isolated electron pairs in O atom. Thus, AlCl_3 was selected as the Lewis acid catalyst for the cleavage of C-O bond in PMPPS, and this paper focuses on understanding the origin of the high efficiency of $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system for decomposing PMPPS and its composites. In particular, the contributions of AlCl_3 and CH_3COOH to the degradation reaction were explored, from which the reaction mechanism was proposed.



Scheme 1. Degradation mechanism of PMPPS in $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system.

It has been demonstrated in our previous work that the incompletely coordinated zinc ions in concentrated ZnCl_2 aqueous solution enable the cleavage of C-O and C-N bonds in organic polymers.^{34, 35} Moreover, as ester bonds can hydrolyze in water, water may be an effective solvent for decomposing PMPPS. Accordingly, we investigated the degradation of PMPPS in metal chloride aqueous solutions (SI Table 1 in ESI, entries 1-5). PET was also chosen because it is also built up by C-C and C-O bonds (SI table 1 in ESI, entries 6-12). ZnCl_2 and AlCl_3 are effective in the cleavage

of C-O bonds, and PET decomposed completely in these solutions. Surprisingly, PMPPS was stable in these solutions, and no swelling of PMPPS was observed in the degradation process. This indicates that the metal ions in the solutions could not enter the matrix of PMPPS. Hence, the swelling of PMPPS in solvent is vital for the following degradation. In other words, the solvent molecules should enter the body of PMPPS readily to transfer active centres (the metal ions). The swelling behaviours of PMPPS were carried out in various inorganic and organic solvents. The swelling effect of water was the worst and the weight increase ratio of PMPPS in water is about 1.5% and the swelling effect of alcohol is relatively low (Figure 1). On the contrary, PMPPS swells the best in tetrahydrofuran (THF) and its weight increase reaches more than 30%, followed by that of acetic acid (about 25%). THF are unable to provide the terminal groups to complete the cleavage of ester bonds in PMPPS, and it is more expensive than acetic acid. Taking these into account, acetic acid was chosen as solvent.

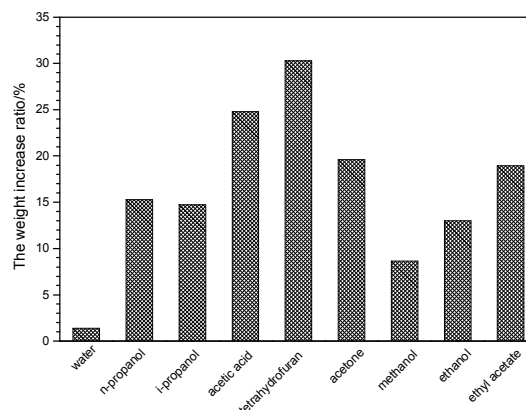


Figure 1. Swelling of PMPPS in various solvents. Reaction condition: 180 °C, 6 h.

The degradation of PMPPS was performed in acetic acid with various metal salts as the catalyst (Table 1). AlCl_3 and FeCl_3 show superior ability for decomposing PMPPS compared with other counterparts. PMPPS swelled and decomposed completely in $\text{AlCl}_3/\text{CH}_3\text{COOH}$ and $\text{FeCl}_3/\text{CH}_3\text{COOH}$ solutions. In contrast, MgCl_2 and CuCl_2 have little catalytic effect for breaking C-O bond of PMPPS. The solubility of AlCl_3 in acetic acid is less than 0.14 wt% at room temperature, but it increases with improving temperatures and the added 10 wt% AlCl_3 dissolves entirely at reaction temperature (180 °C). Interestingly, after the degradation, the majority of Al was deposited from the solution when the reactor was cooled down to room temperature. This process facilitated the separation of products from the reaction system. However, this process was not observed for $\text{FeCl}_3/\text{CH}_3\text{COOH}$ system as the solubility of FeCl_3 can reaches more than 20 wt% in acetic acid at room temperature, bringing troubles in product separation. Hence, $\text{AlCl}_3/\text{CH}_3\text{COOH}$ was chosen as the catalytic system.

The effect of anions on the catalytic behaviours of Al ions was explored. $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}(\text{CH}_3\text{COO})_3$ have no catalytic effect, while

$\text{Al}(\text{NO}_3)_3$ shows much lower efficiency towards the degradation of PMPPS than AlCl_3 . As active centers, the distribution of metal ions in resin plays a crucial role for the degradation reaction. The mass transfer behaviours of metal ions were investigated with acetic acid as solvent. As the swelling of PMPPS was nearly complete at 3 hours (SI Figure 1 in ESI), the reaction time in the mass transfer experiments was fixed at 3 hours. The ICP results indicate that the metal cations in all metal chlorides including AlCl_3 , ZnCl_2 , MgCl_2 , FeCl_3 and CuCl_2 can enter the PMPPS body (Table 2, entries 1-5), whereas it is troublesome for $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}(\text{CH}_3\text{COO})_3$ to enter the interior of resin (Table 2, entries 1, 6-8). This result indicates that the incapability of $\text{Al}(\text{CH}_3\text{COO})_3$ and $\text{Al}_2(\text{SO}_4)_3$ for decomposing PMPPS is caused by the steric hindrance of CH_3COO^- and SO_4^{2-} . The radii of SO_4^{2-} and CH_3COO^- are larger than that of Cl^- . As a result, it would be highly problematic for Al^{3+} ions to enter the matrix of PMPPS when the paring anions are SO_4^{2-} or CH_3COO^- .

Table 1. The degradation of PMPPS in various catalyst systems. ^[a]

Entry	Catalyst	R_d ^[b]
1	AlCl_3	100
2	ZnCl_2	71.34
3	MgCl_2	5.99
4	FeCl_3	100
5	CuCl_2	6.29
6	$\text{Al}_2(\text{SO}_4)_3$	swollen
7	$\text{Al}(\text{NO}_3)_3$	29.43
8	$\text{Al}(\text{CH}_3\text{COO})_3$	swollen

[a] reaction condition: acetic acid as solvent; the weight ratio of catalyst: 10 wt%; temperature: 180 °C; time: 12 h. [b] R_d : degradation ratio.

Table 2. The distribution of cation in PMPPS on different reaction condition by ICP. ^[a]

Entry	Catalyst	Content of cation/wt%
1	AlCl_3	0.20
2	ZnCl_2	0.71
3	MgCl_2	0.12
4	FeCl_2	0.74
5	CuCl_2	0.13
6	$\text{Al}_2(\text{SO}_4)_3$	0.0017
7	$\text{Al}(\text{NO}_3)_3$	0.10
8	$\text{Al}(\text{CH}_3\text{COO})_3$	0.0001

[a] reaction condition: acetic acid as solvent, 10 wt%, 180 °C, 3 h.

The degradation process of PMPPS in $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system was also investigated by FT-IR (Figure 2). For original PMPPS, the peaks appeared at 1600 cm^{-1} , 1581 cm^{-1} , 1493 cm^{-1} and 1453 cm^{-1} are assigned to the C=C stretching vibration in benzene ring, while the peaks at 1728 cm^{-1} and 1286 cm^{-1} are characteristic absorptions of C=O and C-O stretching vibrations in ester bonds. The IR spectroscopy of swollen PMPPS is similar to original PMPPS, indicating that during the swelling process, $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system has no effect on the cleavage of ester bond (see SI Figure 2 in ESI).

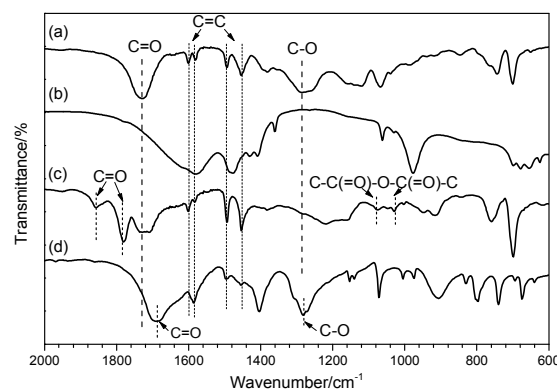


Figure 2. FT-IR spectra of PMPPS and its degradation products: (a) PMPPS, (b) product 1, (c) product 2, (d) product 3.

After the degradation, the degradation products in the reaction mixture were collected and weighted (see SI Figure 3 and SI Table 2 in ESI), and their compositions were analyzed by FT-IR (Figure 2), ICP (Table 3), gel permeation chromatography (GPC) (SI Table 3 in ESI) and NMR (Figure 3, SI Figure 4 and SI Figure 5 in ESI). As indicated by ICP, product 1 is the Al catalyst. In the IR spectroscopy of product 1, the peaks at 1579 cm^{-1} and 1477 cm^{-1} are the characteristic peaks of $\text{Al}(\text{CH}_3\text{COO})_3$. The NMR spectroscopy of product 1 has two peaks, one around 179 ppm belongs to C=O, and the other at 25 ppm is assigned to CH_3 . Thereby, the main component of product 1 is $\text{Al}(\text{CH}_3\text{COO})_3$. This result indicates that AlCl_3 changed into $\text{Al}(\text{CH}_3\text{COO})_3$ after the degradation. Product 2 is organic compound, as implied by ICP. In the IR spectroscopy, peaks that are assigned to benzene ring and ester bond existed in product 2; additionally, there exists peaks for C=O (1780 cm^{-1} and 1856 cm^{-1}) and C-C(=O)-O-C(=O)-C (948 cm^{-1} and 915 cm^{-1}) stretching vibrations in cyclic anhydride. The existence of C=O (at 172 ppm), benzene ring (at 128 ppm), 1,2-propylene glycol (at 68 ppm) and maleic anhydride (at 42 ppm) in product 2 are also ascertained by NMR. Besides, the number-average molecular weight of product 2, as indicated by GPC, is 12891 $\text{g}\cdot\text{mol}^{-1}$ and its polydispersity is 1.79 (SI Table 3 in ESI). These results indicate that the main components of product 2 are polyaddition products of maleic anhydride and styrene. Further degradation of product 2 was also carried out in $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system at 180 °C for 12 h. FT-IR Results show that

no ester bond was found, and only anhydride (1784 cm^{-1}) and carboxyl (1713 cm^{-1}) existed (SI Figure 6 in ESI). For product 3, the C=O stretching vibration in aryl conjugate acid appears at 1686 cm^{-1} , while the peak at 1281 cm^{-1} is assigned to C-O stretching vibration. In the NMR graph of product 3, besides the C=O bond structure (at 172 ppm), benzene ring of phthalic acid was observed (at 132 ppm) as the value of chemical shift moves to low-field due to the effect of carbonyl group. Hence, product 3 is mainly phthalic acid. Therefore, it is verified that the $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system enables the selective cleavage of C-O bond in ester group of in PMPPS, leaving the carbon skeleton intact (see scheme 1). The weight of recycled polyaddition products of maleic anhydride and styrene (product 2), and phthalic acid (product 3) accounts for 91.93 wt% of original PMPPS, indicating the high recovery yield of the $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system (see SI Figure 3 and SI Table 2 in ESI).

Table 3. Elemental analysis of PMPPS and degradation products.

sample	Carbon content /wt%	Hydrogen content /wt%	Oxygen content /wt%	Aluminium content /wt%
PMPPS	68.53	6.09	25.38	0.00
product 1	19.19	4.83	33.57	14.14
product 2	73.77	6.62	16.40	0.05
product 3	38.96	4.80	36.87	3.95

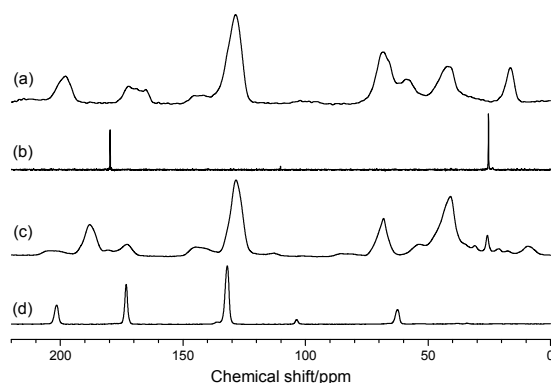
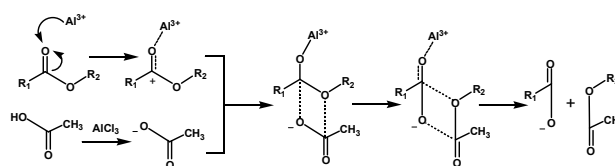


Figure 3. Solid state ^{13}C -NMR graphs of PMPPS and its degradation products: (a) PMPPS, (b) product 1, (c) product 2, (d) product 3.

The compositions of degradation products are illustrated in scheme 1 based on the above characterizations. Specifically, part of the C-O bond in ester group of PMPPS were cleaved by $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system, leading to the formation of polyaddition products of maleic anhydride and styrene, phthalic acid and 1,2-propylene glycol diacetate. It is noticed that although 1,2-propylene glycol diacetate was detected by GC, its content in the degradation products was trace (see SI Figure 7(a) in ESI). This unexpected low

concentration of 1,2-propylene glycol diacetate may be due to that 1,2-propylene glycol diacetate is not stable in the degradation system. To validate this hypothesis, 1,2-propylene glycol diacetate was added into the 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system. The GC signal for 1,2-propylene glycol diacetate decreased drastically after reacting at 180°C for 2 hours (see SI Figure 7(b) and 7(c) in ESI). As the reaction time in the degradation reactions is 12 hours, the majority of the formed 1,2-propylene glycol diacetate transformed. This accounts for the observed low concentration of 1,2-propylene glycol diacetate.



Scheme 2. The possible reaction mechanism for decomposing PMPPS in $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system.

It can be deduced from the distributions of degradation products that acyl exchange reaction occurred between PMPPS and acetic acid, that is, an acidolysis of the polyester bonds of PMPPS by carboxyl group of solvent molecule. This process led to the formation of phthalic acid and 1,2-propylene glycol diacetate. But for acyl exchange reaction, while there are many examples using enzyme catalysts^{36, 37}, the studies using metal ions catalyst systems are, to date, not reported. IR characterization was explored to understand the role of AlCl_3 in the degradation reaction (SI Figure 8 and SI Figure 9 in ESI). No shifts in the peak positions of C(=O)-O bond was observed for acetic acid after adding AlCl_3 (SI Figure 8 in ESI). Ethyl acetate was chosen as the model molecule for PMPPS because it also has ester bond. Interestingly, the peak of C=O in ester group of ethyl acetate appears at 1744 cm^{-1} , while it appears at 1698 cm^{-1} with the presence of AlCl_3 (SI Figure 9). This red shift indicates clearly the catalytic effect of AlCl_3 on C=O bond. In particular, the active Al ions coordinate with oxygen atoms of C=O bonds, leading to weakness in the strength of C(=O)-O bonds. The NMR results are consistent with FT-IR (SI Figure 10, 11, 12 and 13 in ESI). The addition of AlCl_3 directly leads to the decrease of signals of carbonyl and methylene of ethyl acetate (SI Figure 12). Moreover, different mole ratio of aluminum chloride and ethyl acetate were investigated using NMR spectra (SI Figure 14 and 15). The changes of the signals of methyl connected with carbonyl and methylene connected with oxygen are obvious, which indicate that the Al ion attack the ester bond (SI Figure 15). In addition, we noticed that the signal of H of carboxyl in acetic acid disappeared when AlCl_3 was added, as indicated by the ^1H -NMR spectrum (SI Figure 11). This result indicates that the addition of Al ions promotes the dissociation of acetic acid. The formed CH_3COO^- ions would be more active than acetic acid molecules towards acyl exchange reaction. Combined with the above results, the possible reaction mechanism for decomposing PMPPS is illustrated in Scheme 2. Al ion attacks oxygen atom of C=O in ester group of PMPPS, leading to the formation of carbenium ion; the acyl exchange reaction takes

place between acetate ions and ester bond of PMPPS, resulting in the cleavage of C-O bonds of PMPPS. To verify this hypothesis, ethyl butyrate was chosen as the model for PMPPS, and the reaction was performed in 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system at 180 °C. As expected, ethyl acetate was produced with the diminishing of ethyl butyrate (SI Figure 16 and SI Table 4 in ESI). The formation of ethyl acetate ascertains the above hypothesis, that is, Al ions catalyze the acyl exchange reaction between acetate ions and ester bond of PMPPS. Therefore, the high efficiency of $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system for decomposing PMPPS originates from not only the catalytic effect of AlCl_3 , but also the participation of acetic acid in the reaction.

The effects of AlCl_3 concentration and conditions on the degradation behaviors of PMPPS were investigated (Table 4, entries 1-5). The PMPPS decomposed completely in 12 h with the AlCl_3 concentration no less than 10%. The degradation behaviors of PMPPS in 7 wt% and 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system were further investigated at 180 °C. The results are as shown in SI Figure 17, SI Table 5 and SI Table 6 in the supporting information. The results clearly show that the degradation of PMPPS in 7 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ delayed about 5 hours compared with 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$. The rational reason can be explained by the variation in the mass transfer rates of Al ions. It needs a period of time for enough Al ions in CH_3COOH to enter the matrix of UPR and decompose UPR. More time would be needed for 7 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ to reach required Al concentration to decompose PMPPS, in comparison with 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$. The aluminum contents in residual UPR in 7 wt% and 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ systems were detected during the degradation process. As shown in SI Table 5 and SI Table 6, it took 12 hours for the aluminum content in residual UPR to reach 0.3095 wt% in 7 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system, whereas it needed 6 hours for 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system to reach similar Al content. The PMPPS can decompose into monomers and their derivatives completely in 10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ when the reaction temperature increases to 180 °C (Table 4, entries 1 and 6-8). The decomposition time has a significant effect on the degradation process of PMPPS because the mass transfer, that is the diffusion of active centers (catalyst) into the matrix of PMPPS, is a dynamic-controlled process. It took 9 hours to degrade PMPPS completely. Thus, 12 h was selected to guarantee the complete degradation of PMPPS (Table 4, 9-12).

Table 4. The degradation of PMPPS in different conditions.^[a]

Entry	Percentage/wt%	Temp./°C	Time/h	$R_d^{[b]}$
1	10	180	12	100
2	7	180	12	9.92
3	5	180	12	swollen
4	3	180	12	swollen
5	1	180	12	swollen
6	10	190	12	100
7	10	170	12	5.11

8	10	160	12	swollen
9	10	180	9	100
10	10	180	8	63.94
11	10	180	7	23.44
12	10	180	6	1.27

[a] AlCl_3 as catalyst. [b] R_d : degradation ratio.

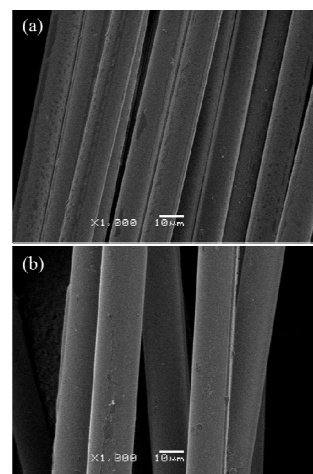


Figure 4. SEM graphs of: (a) Virgin GF, (b) Recycled GF from GFRP.

The degradation of GFRP was carried out in the same condition with that of PMPPS (10 wt% $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system, 180 °C, 9 h). Glass fiber (GF) was recycled from GFRP (SI Figure 18 in ESI). SEM results demonstrated that the recovered GFs were as clean and smooth as virgin GFs (Figure 4). The monofilament tensile strength of virgin glass fiber is 1783 MPa, while that of recycled glass fiber is 1719 MPa. The tensile strengths of the recovered GFs maintained more than 96% of original one (SI Figure 19 in ESI). These results indicate the effectiveness of $\text{AlCl}_3/\text{CH}_3\text{COOH}$ degradation system on recycling valuable GFs from their composites.

Conclusions

We reported a green and effective method for decomposing UPR and its composites waste (GFRP) by $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system. $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system enables the selective cleavage of C-O bond in ester chains of UPR, leaving the carbon skeleton intact. This process facilitates not only the recovery of valuable carbon skeleton of UPR and other chemicals, but also favors recycling of GF from GFRP. More than 91 wt% of monomers and oligomers can be recycled from UPR.

In the degradation process, AlCl_3 interacts with C=O bond in ester chain of UPR, leading to the formation of carbenium ions. This process promotes acyl exchange reaction between acetic acid and

ester bond of UPR. Therefore, the high efficiency of $\text{AlCl}_3/\text{CH}_3\text{COOH}$ system for decomposing UPR originates from not only the catalytic effect of AlCl_3 , but also the participation of acetic acid in the reaction.

Notes and references

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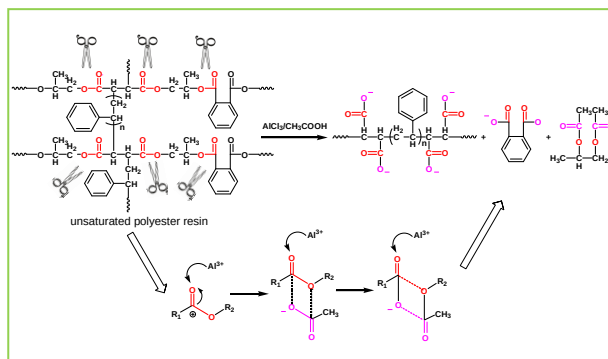
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- 1 A. Conroy, S. Halliwell and T. Reynolds, *Composites Part A.*, 2006, **37**, 1216-1222.
- 2 D. Perrin, L. Clerc, E. Leroy, J. M. Lopez-Cuesta and A. Bergeret, *Waste Manage.*, 2008, **28**, 541-548.
- 3 A. C. Meira Castro, J. P. Carvalho, M. C. S. Ribeiro, J. P. Meixedo, F. J. G. Silva, A. Fiúza and M. L. Dinis, *J. Clean. Prod.*, 2014, **66**, 420-430.
- 4 M. Malik, V. Choudhary and I. K. Varma, *J. Macromol. Sci., Polym. Rev.*, 2000, **40**, 139-165.
- 5 R. A. Witik, R. Teuscher, V. Michaud, C. Ludwig and J.-A. E. Månson, *Composites Part A.*, 2013, **49**, 89-99.
- 6 J. Shi, L. Bao, R. Kobayashi, J. Kato and K. Kemmochi, *Compos. Sci. Technol.*, 2012, **72**, 1298-1303.
- 7 G. Oliveux, L. O. Dandy and G. A. Leeke, *Prog. Mater. Sci.*, 2015, **72**, 61-99.
- 8 K. Hamad, M. Kaseem and F. Deri, *Polym. Degrad. Stab.*, 2013, **98**, 2801-2812.
- 9 D. García, I. Vegas and I. Cacho, *Constr. Build. Mater.*, 2014, **64**, 293-300.
- 10 S. J. Pickering, *Composites Part A.*, 2006, **37**, 1206-1215.
- 11 A. M. Cunliffe and P. T. Williams, *Fuel*, 2003, **82**, 2223-2230.
- 12 A. M. Cunliffe, N. Jones and P. T. Williams, *J. Anal. Appl. Pyrolysis.*, 2003, **70**, 315-338.
- 13 H. Oka, S. Yamago, J. Yoshida and O. Kajimoto, *Angew. Chem. Int. Ed.*, 2002, **41**, 623-625.
- 14 M. Goto, *J. Supercrit. Fluids.*, 2009, **47**, 500-507.
- 15 C. Morin, A. Loppinet-Serani, F. Cansell and C. Aymonier, *J. Supercrit. Fluids.*, 2012, **66**, 232-240.
- 16 K. Li and Z. Xu, *Environ. Sci. Technol.*, 2015, **49**, 1761-1767.
- 17 M. Prinçaud, C. Aymonier, A. Loppinet-Serani, N. Perry and G. Sonnemann, *ACS Sustainable Chem. Eng.*, 2014, **2**, 1498-1502.
- 18 Y. Bai, Z. Wang and L. Feng, *Mater. Des.*, 2010, **31**, 999-1002.
- 19 R. Piñero-Hernanz, C. Dodds, J. Hyde, J. García-Serna, M. Poliakov, E. Lester, M. J. Cocero, S. Kingman, S. Pickering and K. H. Wong, *Composites Part A.*, 2008, **39**, 454-461.
- 20 G. Oliveux, J.-L. Bailleul and E. L. G. L. Salle, *Composites Part A.*, 2012, **43**, 1809-1818.
- 21 A. Kamimura, K. Kaiso, S. Suzuki, Y. Oishi, Y. Ohara, T. Sugimoto, K. Kashiwagi and M. Yoshimoto, *Green Chem.*, 2011, **13**, 2055.
- 22 A. Kamimura, K. Ikeda, S. Suzuki, K. Kato, Y. Akinari, T. Sugimoto, K. Kashiwagi, K. Kaiso, H. Matsumoto and M. Yoshimoto, *ChemSusChem*, 2014, **7**, 2473-2477.
- 23 A. Kamimura, Y. Oishi, K. Kaiso, T. Sugimoto and K. Kashiwagi, *ChemSusChem*, 2008, **1**, 82-84.
- 24 G. Jiang, S. Pickering, E. Lester, T. Turner, K. Wong and N. Warrior, *Compos. Sci. Technol.*, 2009, **69**, 192-198.
- 25 I. Okajima, M. Hiramatsu, Y. Shimamura, T. Awaya and T. Sako, *J. Supercrit. Fluids.*, 2014, **91**, 68-76.
- 26 W. Dang, M. Kubouchi, S. Yamamoto, H. Sembokuya and K. Tsuda, *Polym.*, 2002, **43**, 2953-2958.
- 27 W. Dang, M. Kubouchi, H. Sembokuya and K. Tsuda, *Polym.*, 2005, **46**, 1905-1912.
- 28 J. Li, P.-L. Xu, Y.-K. Zhu, J.-P. Ding, L.-X. Xue and Y.-Z. Wang, *Green Chem.*, 2012, **14**, 3260.
- 29 P. Xu, J. Li and J. Ding, *Compos. Sci. Technol.*, 2013, **82**, 54-59.
- 30 J. Durner, M. Stojanovic, E. Urcan, W. Spahl, U. Haertel, R. Hickel and F. X. Reichl, *Dent. mater.*, 2011, **27**, 573-580.
- 31 A. Kamimura, S. Yamamoto and K. Yamada, *ChemSusChem*, 2011, **4**, 644-649.
- 32 Q. Wang, Y. Geng, X. Lu and S. Zhang, *ACS Sustainable Chem. Eng.*, 2015, **3**, 340-348.
- 33 A. M. Al-Sabagh, F. Z. Yehia, A.-M. M. F. Eissa, M. E. Moustafa, G. Eshaq, A.-R. M. Rabie and A. E. ElMetwally, *Ind. Eng. Chem. Res.*, 2014, **53**, 18443-18451.
- 34 T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou and Y. Zhu, *Chem. Commun.*, 2012, **48**, 5494-5496.
- 35 T. Deng, Y. Liu, X. Cui, Y. Yang, S. Jia, Y. Wang, C. Lu, D. Li, R. Cai and X. Hou, *Green Chem.*, 2015, **17**, 2141-2145.
- 36 R. A. Hess, A. C. Hengge and W. W. Cleland, *J. Am. Chem. Soc.*, 1998, **120**, 2703-2709.
- 37 S. Yamada, T. Sugaki and K. Matsuzaki, *J. Org. Chem.*, 1996, **61**, 5932-5938.

Graphical abstract

Chemical Recycling of Unsaturated Polyester Resin and Its Composites via Selective Cleavage of ester Bond

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Unsaturated polyester resin (UPR) is recycled by $\text{AlCl}_3/\text{CH}_3\text{COOH}$ degradation system via selectively cleaving ester bond.