

Feedstock Recyclibility of Cured Unsaturated Polyesters Waste Using Glycol

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We have studied the recycling of waste with unsaturated polyester resins for the making of buttons. The resin waste was ground and decomposed with glycol together with acid, base and ester exchange catalysts. The decomposition rate of the basic catalyst was larger than that of acid and ester exchange catalysts. When they were treated with ethylene glycol and NaOH catalyst for 2.0 hrs at 290 °C, 84.6% of them were degraded and the molecular weight of the decomposition product showed $\overline{M}_w=198$ and $\overline{M}_w/\overline{M}_n=1.04$. A phthalic glycol ester was produced by decomposing them at 200°C. The destruction of crosslinking of styrene-fumarate copolymer was observed at 230°C. The same phenomenon was found at the decomposition of styrene/maleic anhydride(75/25) copolymer with glycol, too. The unsaturated polyester($\overline{M}_n=1,508$) was synthesized by the decomposition product. The flexural strength of recycled resin was 132.2Mpa(the commercial one:92.1MPa)

Introduction

For recycling of the waste of glass-fiber reinforced plastics of which the matrix consists of unsaturated polyester resin(UP), the following methods have been studied: mechanical recycling in such a manner in which the waste is finely ground for reuse as a filler [1] and feedstock recycling in which the waste is thermally decomposed at 500°C in a water vapor atmosphere [2] or hydrolyzed at 260°C in the butanone/water system [3] into chemical constituents for reuse.

We have studied feedstock recycling in which the unsaturated polyester resin waste for the production of buttons and FRP waste are subjected to glycolysis to obtain chemical components for reuse.

Experimentals

The sample of UP resin waste was taken from a bulk of scrap produced during the punching-out step in the production of shirt buttons. The scrap was ground by use of a Horai Co. Type U-140 granulator in the form of fine powder which was then filtered through a 300 μ m mesh screen. Ethylene glycol, propylene glycol and diethylene glycol were used for glycolysis, whereby sodium methylate, sodium ethylate, sodium hydroxide, methane sulfonic acid and zinc acetate etc. were used as the catalysts. The degree of decomposition was determined by weighing of the insoluble residual resin. Decomposition reaction was performed in a glass flask in atmosphere and in a TVS-N2 type portable reactor (Taiatsu Corporation) under pressure. Decomposition products were measured for their molecular weight with the use of a Waters GPC 150CV at 40°C using THF as the solvent, whereby an Ultrastyrigel Linear, 10⁴Å, 500Å was used as the column and five polystyrene molecular weight standards from 580 to 21,900 were also employed.

Results and Discussion

From the results of glycolysis with ethylene glycol of UP resin waste with the use of various catalysts, the use of the acid and ester exchange catalysts are suggested to result in slower glycolysis than the use of an alkali catalyst. The use of sodium hydroxide was also found to be effective regarding glycolysis. The glycolysis with propylene glycol proceeded slower than that with ethylene glycol.

In Table 1 and Fig. 1 are given the effects of reaction temperatures on decomposition.

Table 1 Glycolysis of Unsaturated Polyester Resin Waste

No	Resin waste (g)	Catalyst (g)	Glycol (g)	Temp. (°C)	Time (hrs)	Decomposition percent	Total decomposition percent	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	100	NaOH 1.0	ethylene glycol 120	200	24	51.9	51.9	467 250 292	1.04 1.01 1.11
2	residue of 51.9% decomposition 50	NaOH 0.5	ethylene glycol 80	200	27	4.3	54.0		
3	residue of 54.0% decomposition 40	NaOH,2 EtONa,2	diethylene glycol 250	245	8.5	98.2	99.2	147	1.02

It is seen from Table 1 that Run No.1 at 200°C gave a glycolysis by 51.9%. Run No.2 treated the residual resin of Run No.1 further at 200°C, and gave a glycolysis as low as only 4.3%. Run No.3, i.e., decomposition with diethylene glycol at 245°C, gave a decomposition of the resin waste by 99.2%.

Fig.1 shows that, in glycolysis with ethylene glycol at 200°C, decomposition reached 56.8% after 7hrs, 56.9% after 14hrs and 57.0% after 45hrs, suggesting no further production of decomposition. On the contrary, at a reaction temperature of 230°C resulted in decomposition by 67.0% after 23hrs and by 78.3% after 67hrs. From these results, it can be concluded that decomposition needs a reaction temperature higher than 230°C to attain complete decomposition of UP resin waste.

In Table 2 is given the analytical result of the decomposition product obtained by the glycolysis Run No. 1 in Table 1. Table 2 shows that the compound obtained by glycolysis at 200°C, i.e., Run No. 1 was mainly a phthalic acid ethylene glycol ester. Based on this finding and the IR spectrum, the residual resin of Run No. 1 was a styrene fumarate copolymer, i.e., the portion crosslinked by styrene. These residual resins were found insoluble in such solvents as tetrahydrofuran and acetone, indicating that they had crosslinked structures.

Styrene/maleic anhydride(75/25) copolymers that are model of the styrene crosslinking part can be decomposed using this decomposition treatment. Based on these results, the UP resin waste is concluded to be decomposed at the position of ester bond by glycolysis at 200°C to leave a styrene-fumarate copolymer which was then decomposed at the position of the styrene crosslinking bond by further decomposition at temperatures higher than 230°C.

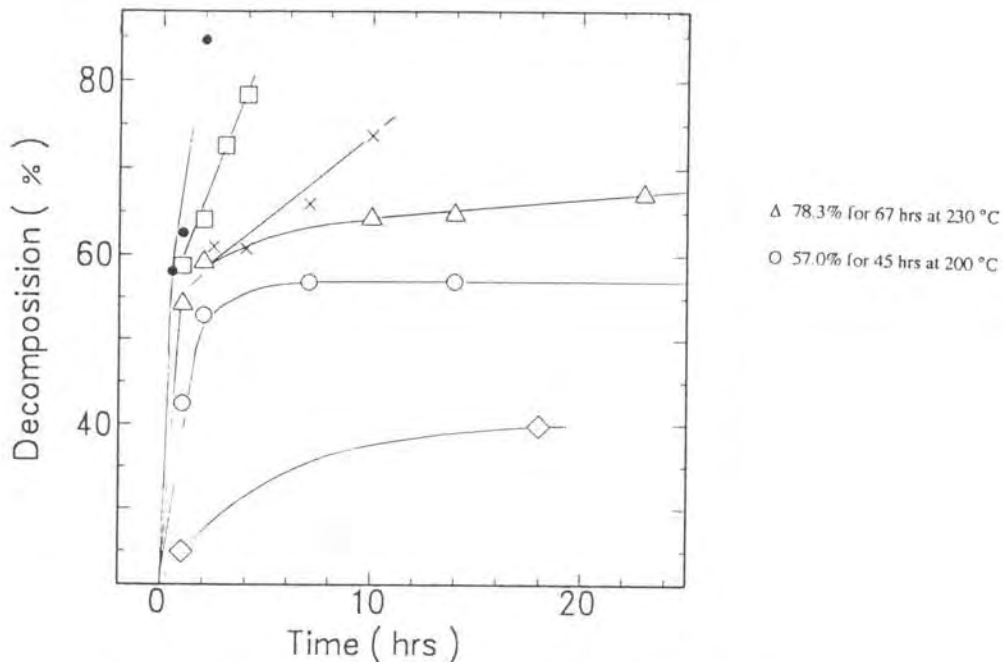


Fig.1 Decomposition of unsaturated polyester resin waste with ethylene glycol

• 290 °C □ 270 °C × 250 °C
 △ 230 °C ○ 200 °C ◇ 150 °C

Table 2 Decomposition products of Procedure No.1

ethylene glycol	45.2 wt%
diethylene glycol	0.9
propylene glycol	3.1
dipropylene glycol	4.9
EG(PA-EG) _n	45.9 ^{a)}
a) EG-PA-EG (mainly)	Mw =254
EG-PA-EG-PA-EG	Mw =446
EG: ethylene glycol	
PA: phthalate	

Decomposition at 290°C for 0.5hrs produced such decomposition products that showed peaks at ca. 390,260 and 200 in the molecular weight distribution curve which those for 1hr and 2hrs produced peaks at ca.200 that each showed no peak at ca. 390 with a smaller peak at ca. 260. The values for \bar{M}_w of the decomposition products obtained by decomposition with ethylene glycol, decreased with an increase in the reaction temperature and time of decomposition.

From the Arrhenus plot of the values for the decomposition reaction rate is obtained from the curves in Fig.1 at decompositions higher than 60%, apparent activation energy of decomposition of the crosslinking bond at temperatures ranging from 230 to 290°C was estimated 176 KJ/mol; 42kcal mol.. The activation energy of thermal decomposition (320 to 370°C) of FRP under a nitrogen atmosphere is reportedly 179kJ/mol. [4] .

The resynthesized UP showed $\bar{M}_n = 1,508$ and $\bar{M}_w/\bar{M}_n = 2.02$ (commercial UP : $\bar{M}_n = 1,646$ and $\bar{M}_w/\bar{M}_n = 3.26$). This resynthesized UP was added to styrene to the amount of 40% and subjected to cast molding: bending strength of the recycled resin was found to be 132.2 MPa and bending modulus of elasticity 6.84 GPa (the commercial resin: bending strength 92.1 MPa and bending modulus of elasticity 3.68 GPa).

A sample of waste of tank grade FRP plate was pulverized and subjected to decomposition. When subjected to decomposition with ethylene glycol at 290°C for 7hrs, FRP waste was decomposed by 64.7% with only glass fiber remaining. The decomposition product showed two peaks in the molecular weight distribution curve, i.e., at $\bar{M}_n = 243$ and 131.

Conclusion

When treated with glycols, i.e., ethylene glycol, at temperatures higher than 230°C, UP resin waste was found to decompose not only at the ester bond, but also at the styrene crosslinking bond (i.e., styrene-fumarate copolymer). The decomposition product was used as the glycol component in the production of resynthesized UP according to chemical recycling and proved to be useful.

References

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