Unsaturated polyesters based on bis(2-hydroxyethyl)terephthalate

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A series of unsaturated polyesters based on bis(2-hydroxyethyl)terephthalate, ethylene glycol, propylene glycol, diethylene glycol, maleic anhydride and styrene were prepared. Properties of these castings were investigated and compared with those analogues based on dimethyl terephthalate or polyester oligomers formed by depolymerization of poly(ethylene terephthalate). It is found that properties of castings based on bis(2-hydroxyethyl)terephthalate are superior to those based on polyester oligomer. When compared with those based on dimethyl phthalate, the castings have higher hardness and heat distortion temperature, but lower tensile strength and elongation; other properties are very similar.

Keywords Unsaturated polyester; bis(2-hydroxyethyl) terephthalate; polyester oligomer; dimethyl terephthalate; waste polyester

INTRODUCTION

Poly(ethylene terephthalate) is one of three main synthetic fibres. Recently, application of waste polyester has attracted attention. Except for its use as a filler, depolymerization has been studied in the presence of a variety of catalysts and glycols to obtain dimethyl terephthalate (DMT) or oligomeric polyester[1-15]. Furthermore, a few patents reported that the oligomeric polyester, thus formed, was able to prepare unsaturated polyester[16-18]. In this work, the utilization of bis(2-hydroxyethyl)terephthalate (BHET) is considered, and a systematic study is done on the unsaturated polyester based on bis(2-hydroxyethyl)terephthalate, ethylene glycol (EG), propylene glycol (PG), maleic anhydride (MA) and styrene. In addition, analogous resins based on dimethyl terephthalate or polyester oligomer by depolymerization of polyethylene terephthalate (PET) were also investigated. The purpose is to develop the application of bis(2-hydroxyethyl)terephthalate in FRP industry.

EXPERIMENTAL

Dimethyl terephthalate, maleic anhydride, ethylene glycol, propylene glycol, styrene and manganese acetate were reagent grade and used without further purification. A fibre grade poly(ethylene terephthalate) was obtained from Oriental Chemical Fiber Corporation.

Unsaturated polyester based on polyester oligomers was prepared as follows. Poly(ethylene terephthalate) fibre (192 g), ethylene glycol (66 g, 1.07 mol) and propylene glycol (81 g, 1.07 mol) were heated under reflux in the presence of manganese acetate (1.7 g) at 190°–200°C for 4 h, and at 210°C for 1 h. The temperature of the reaction system was then allowed to drop to 100°C, and maleic anhydride (196 g, 2 mol) added. The temperature was raised again, and the condensation reaction was continued at 170–210°C for 4 h, and at 220°C until the acid number of 35 ± 2 was reached. The temperature of the entire contents of the reactor was allowed to drop, then diluted with styrene monomer (334 g) containing hydroquinone (0.12 g) as an inhibitor.

Bis(2-hydroxyethyl)terephthalate was prepared by transesterification of dimethyl terephthalate (1164 g, 6 mol) with ethylene glycol (2232 g, 36 mol) in the presence of manganese acetate (3.4 g) at 140°–180°C for 6 h, then poured into cold distilled water. The crude product was purified by recrystallization four times from distilled water. The material, thus prepared, had a melting point of 109°C (d.s.c.); literature[19] m.p. is 109°–110°C. The ^{1}H n.m.r. spectrum of this material indicated it to be BHET.

Unsaturated polyester based on BHET was prepared by a one-step fusion process. For example, BHET (254 g, 1 mol), maleic anhydride (196 g, 2 mol) and propylene glycol (80 g, 1.05 mol) were added to the reactor, and the condensation was carried out at 190°–200°C for 4 h, and at 220°C until an acid number of 35 ± 2 was obtained.

Unsaturated polyester based on DMT was prepared by a two-step fusion process. Thus, DMT (194 g, 1 mol), ethylene glycol (130 g, 2.10 mol) and propylene glycol (80 g, 1.05 mol) were heated under reflux at 140°–180°C for 6 h in the presence of manganese acetate (2 g), then allowed to drop to 100°C. Maleic anhydride (196 g, 2 mol) was added to reactor, and the condensation reaction was continued at 170°–200°C for 4 h and then at 220°C until an acid number of 35 ± 2 was obtained.

All the unsaturated polyesters prepared in this study contained 40% styrene monomer and 150 ppm hydroquinone.

A Waters Associates Model ALC/GPC 244 liquid chromatograph equipped with a Model 6000A solvent delivery system, a U6K closed loop injector, a Model 660 solvent programmer, two Model 6000A pumps, and a Model 440 dual channel u.v. detector at 254 nm were used. The tests of oligomers were performed using Waters Associates μ-Bondapak C-18 (30 cm × 3.9 mm i.d.) column. The gradient eluting system consisted of 20% methanol and 80% water programmed to 80% methanol at a 1.0 ml min^{-1} flowrate over a 90 min scan. A sample (0.0162 g) was dissolved in 10 ml dioxane, and a 2.0 μl

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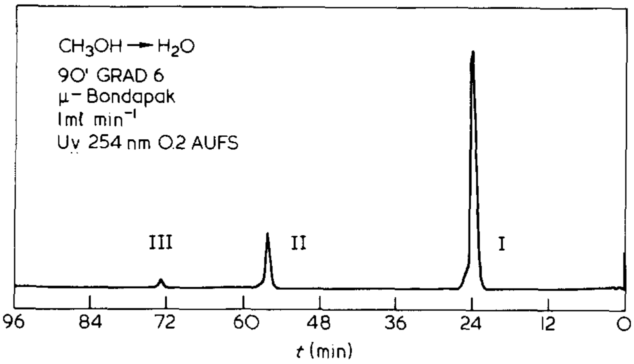


Figure 1 L.c. chromatogram of polyester oligomers

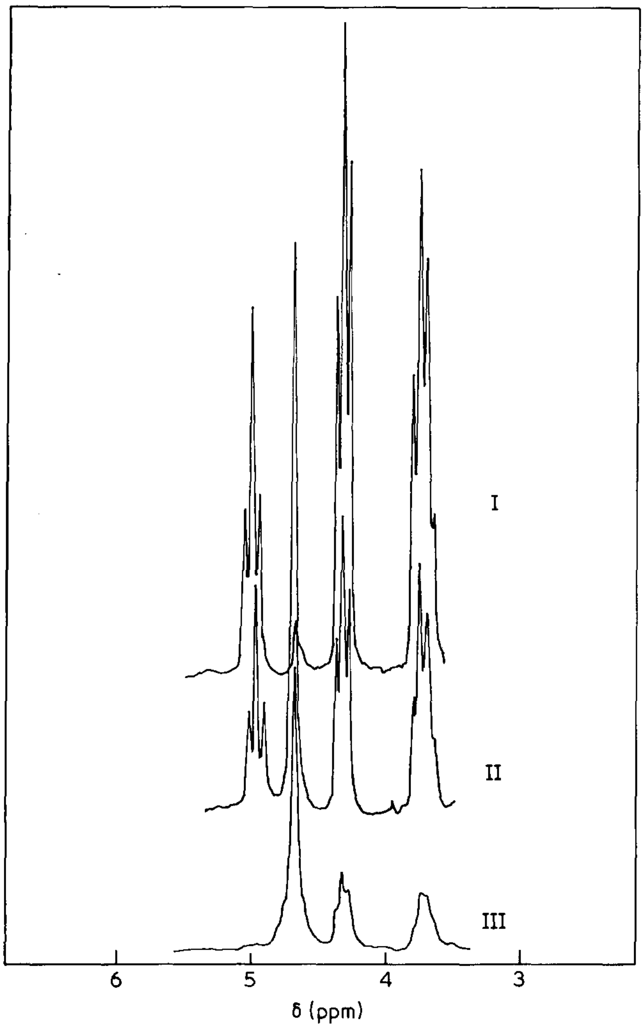


Figure 2 ^{1}H n.m.r. spectra of polyester oligomers

injection was made. Solvent, methanol and water were distilled just prior to l.c. analysis. The molecular weight distribution of the resultant unsaturated polyesters were performed with Waters 1000, 500, 100 Å μ-styragel columns. Tetrahydrofuran was the carrier solvent, and the detector was the Waters differential refractometer; 1.0 mg of sample was injected each time; a flow rate of 1 ml min^{-1} was used.

D.s.c. analyses were carried out with a Perkin-Elmer DSC-2 calorimeter at a heating rate of 10°C min^{-1}.

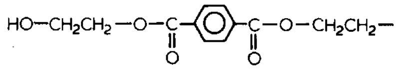
^{1}H n.m.r. spectra were recorded by a FX 100 FT n.m.r. spectrometer (100 MHz, Japan Electron Optics Laboratory). The concentrations of the sample solution were higher than 5% w/v in DMSO-d$_6$.

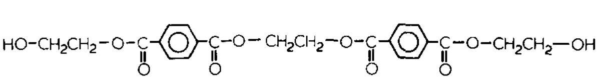
The resultant unsaturated polyesters for casting were mixed with 0.2 phr cobalt naphthenate, then with 1 phr methyl ethyl ketone peroxide, and cured at room temperature. The post-curing condition was 1 h at 80°C, then 1 h at 100°C, and finally 4 h at 120°C.

Tests were carried out according to the following specifications: heat distortion temperature, ASTM D648; tensile testing, ASTM D638; flexural testing, ASTM D790; and impact testing, ASTM D256.

RESULTS AND DISCUSSION

In this study, BHET was prepared by transesterification of DMT with ethylene glycol. Two moles of ethylene glycol are theoretically required for each mole of DMT. However, when the stoichiometric 2:1 ratio was employed, the monomeric yield is very low, and the remaining products are higher molecular weight condensation. Reverse phase liquid chromatography (l.c.) on a low-polarity, bonded-phase C-18 packing with a highly polar mobile phase was used for separation of the products. The separation is based on the relative solubility and distribution of solutes between the mobile and stationary phase with components of highest polarity tending to elute earliest. Thus, monomer comes first, then dimer and finally trimer. *Figure 1* shows a good reverse phase l.c. separation using a CH_3OH/H_2O gradient. The ration of I/II/III is 79.3/16.7/4.0, when the stoichiometric ratio of I/II/III is 79.3/16.7/4.0, when the stoichiometric were collected individually. Melting points measured by d.s.c. are 109° (I), 169° (II) and 198°C (III) respectively (literature[19] m.p.: monomer, 109°–110°C; dimer, 168°–170°C; trimer, 200°–202°C). The ^{1}H n.m.r. spectra of these components are shown in *Figure 2*. They indicate that these components have the following structure respectively.


(I)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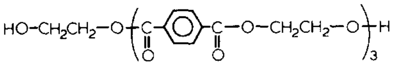
(III)

Figure 3 is the reverse phase liquid chromatogram of the sample obtained by depolymerization of PET in the

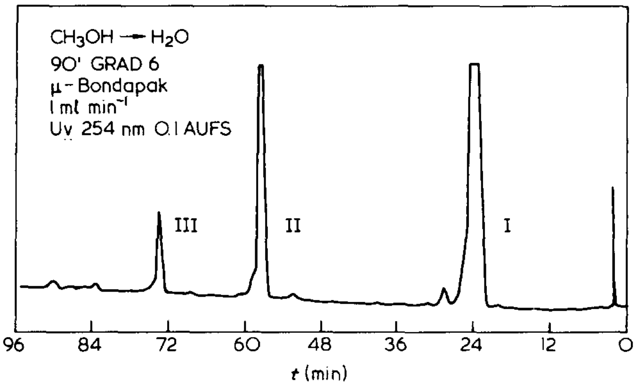

Figure 3 L.c. chromatogram of polyester oligomers by depolymerization of PET

Table 1 Effect of glycol composition on properties of unsaturated polyester casting

	BH-3	BH3A	BH-4	BH-4A	Error
Composition					
BHET/MA (mol%)	25/75	25/75	20/80	20/80	
EG/PG (mol%)	50/50	67/33	40/60	67/33	
Degree of unsaturation (%)	75	75	80	80	
Property					
Barcol hardness	38	42	39	44	±2
HDT,* 264 psi (°C)	133	131	131	134	±2
Unnotched Izod (ft-lb/in)	1.28	0.89	0.83	0.67	±0.05
Tensile strength (x 10^2 kg cm^{-2})	4.1	1.9	2.0	1.4	±0.2
Tensile modulus (x 10^4 kg cm^{-2})	3.7	3.5	3.6	3.3	±0.1
Flexural strength (x 10^3 kg cm^{-2})	0.7	0.6	0.7	0.4	±0.1
Flexural modulus (x 10^4 kg cm^{-2})	3.6	3.6	3.7	3.4	±0.1
Elongation (%)	0.8	0.6	0.6	0.4	±0.2

* *HDT*: heat distortion temperature

Table 2 Effect of degree of unsaturation on properties of unsaturated polyester casting

	BH-2		BH-3A	BH-4A		Error
Composition						
BHET/MA (mol%)	33/67		25/75	20/80		
EG/PG (mol%)	67/33		67/33	67/33		
Degree of unsaturation (%)	67		75	80		
Property						
Barcol hardness	37	(23)*	42	44	(32)*	±2
HDT, 264 psi (°C)	129	(106)	131	134	(126)	±2
Unnotched Izod (ft-lb/in)	1.16	(1.26)	0.89	0.67	(1.59)	±0.05
Tensile strength (x 10^2 kg cm^{-2})	4.2	(5.8)	1.9	1.4	(4.2)	±0.2
Tensile modulus (x 10^4 kg cm^{-2})	3.5		3.5	3.3		±0.1
Flexural strength (x 10^3 kg cm^{-2})	1.1	(0.9)	0.6	0.4	(0.7)	±0.1
Flexural modulus (x 10^4 kg cm^{-2})	3.6	(3.1)	3.6	3.4	(3.0)	±0.1
Elongation (%)	1.3	(2.3)	0.6	0.4	(1.4)	±0.2

* In parentheses, PG is substituted by diethylene glycol

presence of glycol. It indicates that in addition to monomer, dimer and trimer, the products, thus formed, contain higher molecular weight oligomers and a small amount of several unidentified components.

In our previous tests, it was found that unsaturated polyester based on BHET, maleic anhydride and ethylene glycol was not compatible with styrene monomer. Therefore, propylene glycol was used to substitute part of ethylene glycol. Properties of castings based on BHET, EG, PG and MA are given in *Tables 1* and *2*. *Table 1* shows that, at a fixed degree of unsaturation, the higher the molar ratio of EG in the glycol mixture, the higher the Barcol hardness, but the lower the impact strength, tensile property, flexural property and elongation. Obviously, the composition of glycol is a very important factor on the properties of castings. In *Table 2*, the mole per cent of EG/PG is fixed at 67/33. It shows that Barcol hardness and heat distortion temperature (*HDT*) increase with decrease of mole per cent of BHET in BHET/MA mixture, that is, with the increase of degree of unsaturation, but impact strength, tensile strength, flexural strength and elongation show an inverse effect. In general, Barcol hardness and *HDT* are a strong function of degree of unsaturation[20], this is in good agreement with the results. Owing to the limitation of compatibility between resin and styrene monomer, as mentioned before, castings show the maximum value of tensile, flexural, impact strength and elongation at about 60–67 mol% unsaturation. On the other hand, if the ethylene glycol is substituted by a long-chain glycol, such as diethylene glycol or dipropylene glycol, it will impart flexibility to the polymer chain (this effect has been shown in parentheses of *Table 2*) and this resin has been shown to improve the compatibility of resin with the styrene monomer.

The resultant unsaturated polyester based on BHET or DMT has number average molecular weight $\bar{M}_n \simeq 1600$ and dispersity $\bar{M}_w/\bar{M}_n = 2.8$, while that based on polyester oligomers has $\bar{M}_n \simeq 1800$ and $\bar{M}_w/\bar{M}_n = 3.1$. Obviously, the presence of the much higher molecular weight condensates results larger $\bar{M}_n$ and dispersity.

The comparison of properties of castings based on different sources of saturated dibasic acid is shown in *Table 3*. Casting based on BHET has the highest Barcol hardness and *HDT*. Because the casting based on *DMT* contains higher molecular weight dimer and trimer which increase the flexibility of the polymer chain, it shows lower Barcol hardness and *HDT*, but higher tensile strength and elongation, and other properties are very similar. However, the castings based on polyester oligomers by depolymerization of PET have some much higher molecular weight condensates, the properties are relatively poor.

Table 3 Effect of saturated dibasic acid on properties of unsaturated polyester casting

	DM	BH-2	PET	Error
Composition				
Saturated dibasic acid	DMT	BHET	polyester oligomer	
Saturated dibasic acid/MA (mol%)	33/67	33/67	33/67	
EG/PG (mol%)	67/33	67/33	67/33	
Property				
Barcol hardness	35	37	33	±2
HDT, 264 psi (°C)	124	129	118	±2
Unnotched Izod (ft-lb/in)	1.18	1.16	0.86	±0.05
Tensile strength (x 10^2 kg cm^{-2})	5.4	4.2	3.3	±0.2
Tensile modulus (x 10^4 kg cm^{-2})	3.6	3.5	3.3	±0.1
Flexural strength (x 10^3 kg cm^{-2})	1.1	1.1	0.7	±0.1
Flexural modulus (x 10^4 kg cm^{-2})	3.8	3.6	3.5	±0.1
Elongation (%)	1.7	1.3	0.8	±0.2

CONCLUSION

A series of styrenated unsaturated polyesters based on BHET have been prepared. The resultant resin shows poor miscibility in styrene, when ethylene glycol is the only diol in the system. The substitution of some ethylene glycol by propylene glycol has improved the miscibility. The use of diethylene glycol gives much better improvement still.

Owing to the inherently bonded ethylene glycol in BHET molecule and the miscibility in styrene, the ratios of BHET/MA and EG/PG have been limited to some range. The maximum properties, such as tensile, flexural, impact strength and elongation are obtained at about 60–67 mol% unsaturation. Castings of unsaturated polyesters based on BHET have the highest Barcol hardness and *HDT*, when compared with those based on DMT and polyester oligomers.

This study will solve the problem of the overcapacity of production in the polyester fibre industry and create a new application of BHET in the FRP industry.

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