Synthesis of Thermosetting Polymers from the By-Products of Coal Conversion Processes

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Synopsis

The use of coal conversion by-products as raw materials in the synthesis of thermosetting polyesters has been investigated. Heavy tar residues were oxidized by gaseous oxygen in an alkaline medium, yielding a complex mixture of benzenecarboxylic acids and smaller amounts of aliphatic carboxylic acids. The mixture was polymerized by condensation with tetraethylene glycol "bottoms," a by-product of the synthesis of ethylene glycol. The resultant polyesters were cured by reacting them with epoxy resins in the presence of basic catalysts. Molded sheets and laminates were fabricated and tested. Tensile strength was found to increase with increasing curing time and with increasing concentration of epoxy crosslinking agent. Glass-reinforced composites fabricated by the autoclave process showed an increase in flexural and shear strength with decreasing autoclave pressure.

INTRODUCTION

Coal gasification and liquefaction processes have been studied in recent years as alternate sources of energy. These processes have a number of by-products, the most important of which are the heavy tars and chars. If these residues could be converted to commercially useful chemicals, then the overall economics of coal conversion processes would be improved and the monumental problem of disposing of these materials, many of which are thought to be carcinogenic, would be eliminated.

The feasibility of converting these by-products into potentially useful raw materials was the subject of a study recently conducted in our laboratories. Specifically, we investigated the oxidation of selected by-products using gaseous oxygen in an alkaline medium.[1] The oxidation yielded a complex mixture of benzenecarboxylic acids and smaller amounts of aliphatic carboxylic acids, materials potentially useful for the synthesis of condensation polymers. This work parallels studies that have been performed with coal.[2] Montgomery and co-workers[3] suggested a number of possible uses for the products obtained in a similar oxidation of coal. This paper deals with the synthesis and evaluation of epoxy-modified polyester resins from the tar-derived carboxylic acid mixture.

EXPERIMENTAL

Materials

COED (Char Oil Energy Department Project) Western Kentucky filtered oil was obtained from the FMC Corporation, Princeton, N.J. Tetraethylene glycol (TEG) "bottoms" was obtained from the Dow Chemical Company and used

0021-8995/79/0024-2323$01.00

without purification. DER 331, an epoxy resin based on epichlorohydrin, and DEH 52, an aminofunctional catalyst, were also obtained from the Dow Chemical Company.

Oxidation

Oxidation was carried out in a 2-liter Parr Series 4500 pressure vessel constructed of stainless steel and equipped with an adjustable-speed motor for variable stirring (maximum speed 1400 rpm). A suspension of 20.0 g Western Kentucky filtered oil in an aqueous sodium carbonate solution (80.0 g sodium carbonate dissolved in 1.0 liter distilled water) was placed in the reactor and vigorously agitated until thoroughly mixed. Heating was then begun. When a temperature of 270°C was reached, the pressure of the system was adjusted to a value equal to the vapor pressure plus the desired oxygen pressure (1400 psi). Oxygen was introduced into the reactor at a rate of 2.0 l./min. The reactor was equipped with internal coils for cooling, and the reaction temperature was maintained at ±5°C. Pressure in the reactor was also kept constant by discharging reaction gases using check valves before and after the reactor. Oxygen flow to the reactor and discharge of gases from the reactor were stopped after 45 min and the vessel was cooled to room temperature. The gases that were present in the headspace were discharged, and the reaction mixture was removed from the bomb for analysis.

Isolation of Oxidation Products

The reaction mixture was filtered to remove any material suspended in solution. The filtrate was diluted to exactly 1.5 liter. The reaction mixture was then acidified with sulfuric acid to a pH of 1.0. An aliquot (25 ml) was set aside for the benzenecarboxylic acid analysis.

The filtrate was saturated with sodium sulfate at 25°C and extracted with a volume of methyl ethyl ketone equal to 75% of the volume of the total filtrate. The extract was dried with magnesium sulfate and the solvent removed by a rotary evaporator. The resultant brown syrupy material was dried under vacuum at 100°C, yielding a brown solid. This material is referred to as the organic extract.

Typical Polyesterification Procedure

The desired ratio of organic extract and TEG bottoms was placed in a 250-ml Erlenmeyer flask equipped with nitrogen inlet and outlet. The flask was then gradually heated in an oil bath to 150°C over a period of 2 hr.

The viscosity of the reaction mixture increased gradually, while the water produced as a by-product of polyesterification was allowed to distill. The reaction mixture was further heated at 150–170°C until a highly viscous, slowly pourable resin was obtained. The polyester resin was then evaluated for curing characteristics, moldability, and laminating properties.

Polyester Curing and Molding

The casting and curing proceeded as follows. The polyester resin was first weighed on a glass plate, then mixed with epoxy DER 331 (10%, or 20 wt %). The mixture was heated sufficiently to obtain a good flow and thoroughly mixed with a spatula. After cooling, DEH 52 catalyst (28% with respect to the epoxy) was added. Again, the mixture was heated and thoroughly mixed. It was spread into the heated mold while still hot and flowing, at the same time removing air bubbles trapped in the resin. The mold was then placed in an air-circulating oven for 5 hr at 150°C and for an additional 4–8 hr at 200°C. Microtensile specimens were prepared from molded sheets in accordance with ASTM D1708-59T.

Fabrication of Composites by the Autoclave Process

The autoclave process involves the application of variable temperature and pressure on the composite lay-up. The binder resin—a mixture of polyester resin, epoxy DER 331, and DEH 52 catalyst—was prepared in the same manner as the plastic moldings. The mixture was spread over a 4×5 in. glass cloth (S-120) on a hot plate heated to 100°C. The coated glass layers were stacked on an aluminum support plate to form a 12-ply laminate. The edges of the laminate were trimmed and a corprene boundary dam was placed around the laminate. In a typical setup for vacuum bagging, one-ply TX 1040 separator cloth, one-ply bleeder cloth, one-ply perforated Teflon film, one-ply 181 vent cloth, and an aluminum pressure plate were placed on the laminate. This setup was then placed on the heating platen and covered with the second vent cloth, which extended over the perforated area of the vacuum intake. Press-Tite high-temperature rubber sealant was placed around this cloth. A sheet of Mylar laid over the sealant served as the vacuum bag. The thermocouple and the vacuum line were then connected, and the autoclave was sealed and pressurized.

Pressures of 15, 30, and 90 psi were utilized. After 5 hr of pressure in the autoclave at 150°C and overnight cooling with the pressure and vacuum still applied, the laminate was removed and placed in an air-circulating oven to postcure at 200°C. At the completion of the postcuring time, the composite was removed from the oven and samples were cut for flexural and shear strength tests.

Composite Testing

Flexural and shear strength were determined according to ASTM D732-46. The tests were conducted with a punch-type apparatus set on a compression load cell (full-scale ranges of 5, 10, 20, 50, 100, and 200 lb) attached to an Instron tester.

Specific gravity was obtained by weighing the sample in air (w_a) and in water (w_w). The weight in air was divided by the difference in weight obtained in air and water:

$$\text{specific gravity (g/cc)} = \frac{w_a}{w_a - w_w}$$

The resin content of the laminate was obtained by pyrolysis. The percentage resin content was determined from the difference in weight of the initial sample (w_i) and the pyrolyzed sample (w_p) divided by the initial weight:

$$\% \text{ resin content} = \frac{w_i - w_p}{w_i} \times 100$$

The percentage fiber volume was obtained from the difference in density of the composite (d_c) and the resin (d_r) divided by the difference in density of the glass fiber (d_f) and the resin (d_r):

$$\% \text{ fiber volume} = \frac{d_c - d_r}{d_f - d_r} \times 100$$

The density of glass fiber was 2.54; of the resin, 1.32.

ANALYSES

Carbon Dioxide Determination

The carbon dioxide produced in the reaction was swept from the reactor by the oxygen supply at a rate of 2.0 l./min. The gas stream was first passed through two gas absorption bottles containing Dririte to remove moisture and then into two bottles containing ascarite. The carbon dioxide present in the sample was determined using the ascarite weight difference before and after the collection.

Benzenecarboxylic Acid Analysis

A 2.0-ml aliquot of the acidified reaction mixture was placed in a small crystallizing dish and evaporated to dryness. The solid material obtained was esterified with an ethereal solution of diazomethane.[4] An internal standard (methyl m-toluate) was added at this point. The solution was filtered and the filtrate evaporated under reduced pressure at room temperature to a volume of ~1 ml. The mixture of methyl esters was analyzed using a Varian Series 2440 dual-column programmed-temperature gas chromatograph equipped with a dual hydrogen flame-ionization detector. A 7 ft × 1/8 in. O.D. stainless steel column packed with 3% OV-1 on 60–80 mesh AW-DMCS Chromosorb G was used. Helium at a flow rate of 30 ml/min was used as the carrier gas. All runs were programmed 90–250°C at a rate of 6°C/min. Each of the 12 benzenecarboxylic acids was identified by comparison with the mass spectra and gas chromatograms of corresponding authentic compounds. To carry out the quantitative analysis, flame ionization detector response factors for each of the acids were determined relative to methyl toluate as an internal standard.

A sample of the organic extract was esterified with an ethereal solution of diazomethane and was analyzed by combined gas chromatography–mass spectrometry using a Varian MAT 311A mass spectrometer and Spectro System 100C data system. The GC (Varian model 2740) was interfaced to the MS through a two-stage Biemann–Watson separator.

The carboxyl group concentration of the organic extracts was determined by potentiometric titration.

Polyester End Group Analysis

The method for carboxyl group analysis was based on direct titration with sodium hydroxide in pyridine solution. The method for hydroxyl group analysis was based on a quantitative acetylation[5] followed by hydrolysis of the excess acetic anhydride and titration of the acetic acid, plus any carboxyl groups present in the polymer. If the carboxyl group concentration in the polymer is known (from an independent titration), the hydroxyl group concentration can be calculated. The procedure employed was the following:

A 1.0-g polyester sample was dissolved in 25 ml of a mixture of acetic anhydride–pyridine containing 23% acetic anhydride by volume. After refluxing for 1 hr, 5 ml water was added and the mixture was heated for another 5 min to allow hydrolysis of the excess acetic anhydride. After washing with 25 ml methanol, the mixture was cooled and titrated potentiometrically with $0.5N$ NaOH solution. A blank was then run on a mixture of the same volumes of acetic anhydride, pyridine, and water as above, with methanol added prior to titration. Another titration was then carried out under identical conditions on a sample of polymer in pyridine without acetic anhydride. Based on the values obtained, the carboxyl and hydroxyl groups present in the polyester could be determined by simple stoichiometric calculations.

RESULTS AND DISCUSSION

Oxidation of Coal Conversion Process By-products

The acid mixture used in this study was derived from COED Western Kentucky filtered oil, a heavy black tar by-product of the pyrolysis of coal. The ultimate analysis of COED Western Kentucky filtered oil is presented in Table I. This by-product was oxidized with oxygen in an 8% aqueous sodium carbonate solution at a temperature of 270°C and a total pressure of 1400 psi. The carbonate-to-feed ratio was 4.

The products obtained in the oxidation, given in Table II, included a reaction residue, carbon dioxide, and the organic extract. The reaction residue, which was found suspended in solution at the end of the reaction, consisted of base insolubles derived from the ash present in the feed. Only trace amounts of the reaction residue were typically found.

The carbon dioxide was continuously swept from the reactor by the oxygen supply, while the pressure was maintained by a system of check valves before and after the reactor. A total of 69.5% of the carbon in the tar was converted to carbon dioxide (Table III).

TABLE I
Ultimate Analysis of COED Western Kentucky Filtered Oil

	%
Carbon	82.28
Hydrogen	7.22
Nitrogen	0.84
Sulfur	1.33
Ash	0.20
Oxygen	8.13

TABLE II
Product Analysis of the Oxygen Oxidation of COED Western Kentucky Filtered Oil in Aqueous
Sodium Carbonate

Products	g/100 g Feed
Reaction residue	trace
Carbon dioxide	209.7
Organic extract	35.2
Benzenecarboxylic acids in the organic extract	23.5

The organic extract is a complex mixture of organic acids obtained by extracting the acidified reaction mixture. This experiment yielded 35.2 g organic extract, that is, 21.6% of the carbon in the original feed was converted to the organic extract (Table III). A portion of the organic extract was methylated using an ethereal solution of diazomethane and the resulting mixture of esters was analyzed using vapor phase chromatography. The major components of the organic extract were the benzenecarboxylic acids (66.8%), whose composition is given in Table IV. Only eight of the possible unsubstituted benzenecarboxylic acids were found in measureable quantities in the reaction mixture. Higher acids in the benzenecarboxylic mixture, i.e., the benzenetetra-, penta-, and hexacarboxylic acids, constituted 52.4%.

A number of other compounds were identified when the organic extracts were esterified with an ethereal solution of diazomethane and analyzed by gas chromatography–mass spectrometry, namely, aliphatic dicarboxylic acids in methylated aromatic carboxylic acids (Table V). Only traces of the aliphatic dicarboxylic acids were found in the organic extract. It is most likely that the partition

TABLE III
Carbon Material Balance: Oxygen Oxidation of COED Western Kentucky Filtered Oil

Product	% Carbon in feed
Carbon dioxide	69.5
Organic extract	21.6
Total	91.1

TABLE IV
Analysis of Benzenecarboxylic Acid Mixture

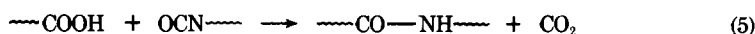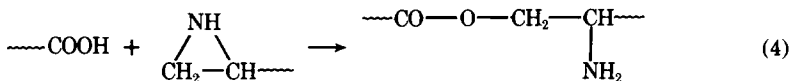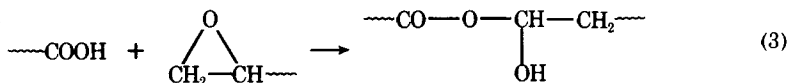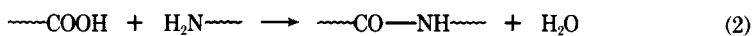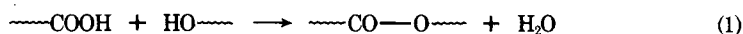| Benzenecarboxylic acids	Wt % of Total
Benzoic acid	—
1,2-Benzenedicarboxylic acid (o-phthalic)	11.6
1,3-Benzenedicarboxylic acid (m-phthalic)	—
1,4-Benzenedicarboxylic acid (p-phthalic)—	
1,2,3-Benzenetricarboxylic acid (hemimellitic)	14.9
1,2,4-Benzenetricarboxylic acid (trimellitic)	21.0
1,3,5-Benzenetricarboxylic acid (trimesic)	—
1,2,3,4-Benzenetetracarboxylic acid (prehnitic)	15.5
1,2,3,5-Benzenetetracarboxylic acid (pyromellitic)	7.4
1,2,3,5-Benzenetetracarboxylic acid (mellophanic)	6.2
Benzenepentacarboxylic acid	16.2
Benzenehexacarboxylic acid	6.8

TABLE V
Compounds Identified in the Methylated Organic Extract

Methyl ester
Succinic acid
Toluenedicarboxylic acid (3 isomers)
Xylenedicarboxylic acid
Toluenetricarboxylic acid (3 isomers)
Naphthalenedicarboxylic acid
Toluenetetracarboxylic acid (2 isomers)
Toluenepentacarboxylic acid
Xylenetricarboxylic acid
Methylhydroxybenzenetricarboxylic acid
Naphthalenetricarboxylic acid
Naphthalenetetracarboxylic acid
Naphthalenepentacarboxylic acid
Methylanthracenetetracarboxylic acid

coefficient for methyl ethyl ketone and an aqueous acid solution does not favor the extraction of the aliphatic dicarboxylic acids from the acidified reaction mixture. An analysis of the acidified reaction mixture indicated that a significant quantity of oxalic acid (4.2 g/100 g feed) was formed during oxidation.

Polymerization of the Organic Extract

Several possible reactions can be identified for the synthesis of polymeric materials from the organic extract. Because of the high average carboxyl functionality of this material, the synthesis of thermosetting, crosslinkable resins was undertaken. A number of possible condensation reactions involving carboxyl groups may be utilized:

$$\text{---COOH} + \text{HO---} \longrightarrow \text{---CO---O---} + H_2O \tag{1}$$

$$\text{---COOH} + H_2N\text{---} \longrightarrow \text{---CO---NH---} + H_2O \tag{2}$$

$$\text{---COOH} + \overset{O}{\underset{CH_2-CH\text{---}}{\triangle}} \longrightarrow \text{---CO---O---}\underset{OH}{\overset{}{CH}}\text{---}CH_2\text{---} \tag{3}$$

$$\text{---COOH} + \overset{NH}{\underset{CH_2-CH\text{---}}{\triangle}} \longrightarrow \text{---CO---O---}CH_2\text{---}\underset{NH_2}{\overset{}{CH}}\text{---} \tag{4}$$

$$\text{---COOH} + OCN\text{---} \longrightarrow \text{---CO---NH---} + CO_2 \tag{5}$$

Reaction (1), polyesterification by reaction with hydroxy-functional compounds, has been investigated. Several polyester compositions were prepared by condensing the organic extract with various glycols. Among the various glycols investigated, tetraethylene glycol "bottoms" was found to be a promising coreactant for polyesterification. This is a by-product of the synthesis of ethylene glycol, consisting mainly of tetra- and pentaethylene glycol as well as other

glycols having a wide molecular weight range. It is a promising coreactant be-
cause of its low cost and its ability to flexibilize the polymerization product by
acting as an "internal" plasticizer.

Polyesters were prepared by using weight ratios of organic extract to TEG
"bottoms" of 1:0.3, 1:0.5, 1:1, 1:1.5, and 1:2. Polyesterfication reactions were
conducted under various reaction conditions. Some typical polyester compo-
sitions are shown in Table VI. The type of product obtained and its degree of
polymerization depends upon the organic extract to TEG "bottoms" ratio em-
ployed, the reaction temperature and time, and whether the reaction is conducted
at atmospheric or reduced pressure. Polymers synthesized at weight ratios of
organic extract to TEG "bottoms" of 1:2 and 1:1.5 were highly viscous liquids;
at a ratio of 1:1, the polymer was semisolid; at lower TEG contents, solid polymers
were obtained. Solid polymers were generally infusible and not suitable for
mixing with epoxies, even at elevated temperatures.

The formation of water as a by-product of polycondensation does not present
a problem in the synthesis of the polyester. For the final curing step, however,
it is desirable to utilize a crosslinking reaction generating minimum amounts
of volatile by-products. The curing reaction was performed using epoxide-
functional compounds capable of reacting with residual functional groups present
in the polyester. The use of epoxy resins in the presence of basic catalysts was
found to be a suitable curing process. The polyesters exhibited excellent com-
patibility with the epoxies and good shelf life.

The polyesters obtained from the organic extract and TEG "bottoms" were
combined with epoxy resin DER 331. The curing reaction was catalyzed by
adding DEH 52. Typical curing experiments and tensile properties of the
products obtained are shown in Table VII. All the materials tested exhibited
high elongation but relatively low tensile strength. Tensile strength increases
with increasing curing time and with increasing concentration of epoxy cross-
linking agent. Elongation is not substantially affected by an increase in curing
time when the epoxy concentration is 10%. At 20% epoxy concentration, an
increase in curing time causes a decrease in elongation (Table VII).

The feasibility of using the organic extract/TEG "bottoms" polyesters in
glass-reinforced composite structures was investigated. The binder resin em-
ployed was polyester #4 of Table VI cured with epoxy DER 331 (20 wt %) and

TABLE VI
Synthesis of Organic Extract/TEG "Bottoms" Polyester

Sample no.	Organic extract [COOH], meq/g	Organic extract/ TEG "Bottoms," wt ratio	Polymerization conditions			Polyester end-groups		
			Time, hr	Temp., °C	Pressure, mm Hg	[COOH], meq/g	[OH], meq/g	Yield, %
1	12.7	1:2	4 4	150 150	760 0.4	1.75	3.8	88
2	12.7	1:1.5	4 4	150 150	760 0.4	2.00	3.05	86
3	12.7	1:2	5 18	105 150	760 760	1.40	2.65	91
4	13.1	1:2	44 2	150 170	760 760	0.62	1.75	90
5	13.1	1:1.5	8	150	760	1.85	1.42	91

TABLE VII
Tensile Properties of Epoxy-Cured Polyesters

Polyesterification conditions[a]		DER 331/DEH 52	Curing Conditions		Tensile strength,	Elongation,
Time, hr	Temp., °C	wt %	Time, hr	Temp., °C	psi	%
18	150	10/2.8	5 4	150 200	420	41
18	150	10/2.8	5 8	150 200	524	42
18	150	20/5.6	5 4	150 200	413	51
18	150	20/5.6	5 8	150 200	619	46
44 2	150 170	10/2.8	5 4	150 200	243	36
44 2	150 170	10/2.8	5 8	150 200	412	39
44 2	150 170	20/5.6	5 4	150 200	422	45
44 2	150 170	20/5.6	5 8	150 200	883	34

[a] Polyesterification reactions were conducted at atmospheric pressure under nitrogen flow at a ratio organic extract/TEG "bottoms" = 1:2 wt. The organic extract employed had a carboxyl group content of 13.1 meq/g.

DEH 52 catalyst (28 wt % with respect to the epoxy). The laminated structures obtained were tested for flexural strength, interlaminar shear strength, resin content, and density of the cured products. The results obtained show that the autoclave pressure has a pronounced effect on both flexural and shear strength of the resulting laminates (Table VIII).

CONCLUSIONS

The feasibility of synthesizing potentially useful polymers by using coal conversion by-products as raw materials has been demonstrated. Thermosetting polymers have been prepared by polyesterifying the carboxylic acid mixture obtained by the oxidation of a heavy tar. This application appears to offer a definite potential for the utilization of large volumes of by-products from coal gasification and liquefaction processes. In order to achieve the greatest cost advantage, this study has dealt with the utilization of the carboxylic acid mixture as a whole, without separation of specific components or fractions. The relatively

TABLE VIII
Properties of Glass-Reinforced Polyester Composites

Autoclave pressure, psi	Flexural strength, psi	Shear strength, psi	Specific gravity, g/cc	Fiber volume, %	Resin content, %
15	37,200	3,675	1.95	51.4	21.2
30	7,250	1,607	1.92	49.9	22.8
90	too low to be measured	too low to be measured	2.03	58.1	18.5

low tensile strength of the polymers obtained can be ascribed to the broad distribution of carboxylic acids present in the crude oxidation mixture. A pH fractionation of the crude oxidation mixture could be employed to provide fractions having controlled acid functionality.[6] It is conceivable that these fractions will allow the synthesis of polymers with improved mechanical properties owing to a more controlled composition and distribution of molecular weights.

References

1. W. C. Eisenberg and I. J. Solomon, *Fuel,* **56,** 181 (1977).

2. H. H. Lowry, Ed., *Chemistry of Coal Utilization,* Wiley, New York, 1963, p. 377.

3. R. S. Montgomery and R. McMurtrie, *Fuel,* **35,** 49 (1956).

4. K. Blair and G. King, *Handbook of Derivatives for Chromatography,* Heyden, London, 1977, p. 192.

5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry,* Wiley-Interscience, New York, 1968, p. 155.

6. R. S. Montgomery and P. J. Sienknecht, *Ind. Eng. Chem.,* **47,** 1274 (1955).