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Disposal of Thermoreactive Epoxy Resin-Based Polymers by Thermal Solvolysis in Coal Tar Medium Accompanied by Chemical Raw Materials Receipt

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Abstract

Thermal solvolysis of thermoreactive polymers in coal tar medium was examined at 360–420 °C. The cured epoxy diane resin ED-20 and industrial samples of polymer binder based thereon that is part of polymeric composite materials were used as polymers. The composition of liquid products of solvolysis was determined using GC-MS. It was found that coal tar had an effect on the yield and composition of decomposition products of thermoreactive polymers during thermal solvolysis. Characteristics of coal tar were determined after treatment of polymers therein.

Keywords: thermal solvolysis, thermoreactive polymers, coal tar

INTRODUCTION

Epoxy resin refers to a type of thermoreactive resins that may yield various materials and is widely used as components of adhesives, paints, in potting and impregnating compounds. Cured epoxy resins have high adhesion, mechanical strength, thermal, and electrical insulation properties, owing to which they are used in electrotechnical and radioelectronic industries, aerospace branch, ship building and mechanical engineering [1, 2]. This is one of the best types of binders to produce polymer composite materials (PCM) that are in demand in the sports industry, machine building, electrical and electronic devices, automotive, aviation and space industries [3].

The growing volumes of production of products based on epoxy resins require the development of methods of their disposal with the return for the practical use of the initial chemical compounds and expensive fillers, carbon and quartz fibers made of PCM [4–6]. New disposal methods are required not only in economic terms, but also to ensure environmental safety.

With the purpose of producing commercial chemical compounds during disposal of spent

polymeric products, techniques of pyrolysis and thermal polymer decomposition in solvents, and thermal solvolysis are widely used [6–8].

Pyrolysis, thermal degradation of organic compounds at elevated temperatures in the absence of oxygen leads to the formation of gaseous products, condensable organic substances, and carbon residue of pyrolysis. The use of this method to produce chemical raw materials from waste thermoreactive polymers is inefficient, since the yield of organic compounds is low, and the main product is the carbon residue.

The advantages of thermal solvolysis of epoxy resin materials include lower process temperatures, high yields of phenolic products and the ability to minimize the yield of carbon residue. Hydrogen-donor solvents and pre- and supercritical liquids are most effective in this respect [8–13]. However, to carry out solvolysis of epoxy polymers in hydrogen-donor solvents, such as tetralin and dihydroanthracene [11–13], or in pre- and supercritical liquids, expensive equipment, able to work under high pressure conditions, is required. Organic solvents are also notable for a high cost. These factors constrain the wide use of the above disposal methods.

We propose to use coal tar as a solvent during thermal solvolysis of thermoreactive polymers based on epoxide resins. An opportunity to use it for polycarbonate disposal at atmospheric pressure has been earlier demonstrated [14, 15]. Its main structural component, as in case of epoxy diane resins, is bisphenol A. Patent [16] declared the prospects of its use as a solvent during disposal of wastes containing thermoreactive polymers.

The present work purpose is the exploration of disposal of cured epoxy resins based on bisphenol A and products based thereon *via* thermal solvolysis in coal tar medium.

EXPERIMENTAL

The work used the cured epoxy resin and industrial samples of the hardened polymer epoxy binder that is part of PCM composition. Industrial coal tar was a solvent during thermal solvolysis. Its characteristics, such as softening temperature according to the "Ring and rod" (T_r) of 68 °C; the mass fraction of substances: insoluble in toluene (α) 27.3 %, in quinoline (α_1) 5.2 %; volatile matter yield (V^r) of 60.8 % at 850 °C.

To produce the cured resin, there was used ED-20 epoxy diane resin (epoxy number of 19.2 according to GOST 10587–84). Curing was carried out by adding 10 mass % of polyethylene polyamine (PEPA) and ageing at room temperature for 24 h. Industrial samples of epoxide binder were obtained at OKB Innovator JSC enterprise (Ekaterinburg).

For test samples, there were assigned the following code numbers: P (coal tar), S (initial epoxy resin), SP (epoxy resin, cured PEPA), SV (epoxy binder).

Thermal solvolysis of thermoreactive polymers in fluxed coal tar was carried out in a metal reactor under isothermal conditions at 360–420 °C and atmospheric pressure. A mixture of coal tar and a polymer was loaded into the reactor. Mixtures with different polymer contents and thermal treatment conditions were indicated as P-S(SP, SV)-*X*-*Y*-*Z* (*X* is polymer content in the mixture, mass %; *Y* is solvolysis temperature, °C; *Z* is the isothermal ageing time, min). After coal tar fluxing and reactor temperature reaching to 130–160 °C, mixing was begun using a propeller stirrer. Liquid products released from the reactor and the residue in the reactor were weighed. The amount of gaseous products along with probable losses was determined according to the difference in load mass and the sum of masses of distillate products and the residue in the reactor.

For comparison purpose, there were carried out experiments on thermal decomposition of polymers with the lack of coal tar at 380 °C: a sample was loaded into a porcelain crucible, which was located inside a metal reactor; a thermocouple was placed in a polymer layer.

To identify liquid products of decomposition, there was used Agilent GC 7890A MSD 5975C inert XL EI/CI spectrometer (GC-MSD) with a quadrupole MS detector (USA) in electron ionization mode (70 eV), an HP5-MS quartz capillary column (polydimethylsiloxane, 5 % of phenyl groups), 30 m length, 0.25 mm in diameter, film thickness of 0.25 μm. The initial temperature of the column of 40 °C (3 min ageing), heating with a rate of 10 °C/min to 290 °C (30 min exposure). The temperature of the evaporator is 250 °C, of the transition chamber is 280 °C, of the MS source is 230 °C,

of quadrupole is 250 °C; helium is gas-carrier; flow division is 1 : 50; the flow rate through the column is 1.0 mL/min. The registration of chromatograms was carried out according to for the full ion current while scanning in the 20–1000 Da mass range. The identification was performed with the assistance of NIST05 mass spectral library and on the ground of analysis of individual substances.

To measure contents of reaction products, analysis of reaction mixtures was carried out using Shimadzu GC 2010 gas chromatograph (Japan) with a flame ionization detector (GC-FID), a GsBP-5MS quartz capillary column (polymethylsiloxane, 5 % of phenyl groups) 30 m long, 0.25 mm diameter, and 0.25 μm film thickness. The initial temperature of the column is 40 °C (ageing is 3 min), then, heating at a rate of 10 °C/min to 280 °C (exposure of 20 min). Evaporator temperature is 250 °C, detector – 300 °C, nitrogen is gas-carrier, the partition of 1 : 30, the flow through the column is 1.0 mL/min. The calculations were performed according to the method of internal normalization of peak squares.

The initial coal tar and residues in the reactor after polymer solvolysis were analysed according to GOST 10200–83 (Electrode coal tar. Technical conditions).

RESULTS AND DISCUSSION

Mass balance and composition of liquid products of solvolysis

Thermal treatment of polymers was carried out in coal tar medium and without it; for comparison, the initial epoxy resin ED-20 was also subjected to heat treatment. Table 1 gives mass balance data of the experiments.

During thermal treatment of the initial resin, the main product is the carbon residue. Its yield at 380 °C is 50 % per the loaded resin (experiment 1). The output of liquid products is 43.7 %. Under conditions of thermal solvolysis of epoxy resin in the coal tar medium at 380 °C (experiment 2), the yield of liquid products reached 66.4 %. Increasing process temperature to 420 °C leads to the fact that liquid products of resin decomposition contain components evaporated from coal tar, therefore their output in experiment 3 exceeds 100 %.

There was obtained 38 % of the carbon residue and the output of liquid products was 42.0 % per the loaded resin during thermal destruction of the cured SP resin (experiment 4, 380 °C). The yield increased to 80 % in case of thermal solvolysis in coal tar medium (experiment 5).

During SV solvolysis in the same environment at 380 °C (experiment 6), liquid products yield is 73.0 %, and it reaches 87 % with temperature increase to 400 °C. Liquid products of thermal solvolysis of epoxy resins contain phenol and *p*-isopropylphenol; bisphenol A is not detected. Figure 1 gives the data on the yields of individual phenols per loaded polymer.

In thermal solvolysis of epoxy resins and epoxy binder in coal tar medium, the yield of phenol increases by 23–25 %, and that of *n*-isopropylphenol – by 87 % for noncured and in 2.7 times for cured resin.

In [12], when using Fe_2O_3 catalyst and tetralin as solvent at 440 °C, 42.8 % of phenolic products (16.7 % of phenol and 24.3 % of *n*-isopropylphenol)

TABLE 1

Mass balance data of thermal treatment of polymers and its mixtures with coal tar

No. of experiment	Sample	Load mass, g			Product yield		
		Coal tar	Resin	Total	Residue, g	Liquid products, g/mass %*	Gases, g
1	S-100-380-60	–	39.8	39.8	19.8	17.4/43.7	2.6
2	P-S-17-380-60	68.5	13.7	82.2	72.1	9.1/66.4	1.0
3	P-S-17-420-60	50.0	10.2	60.2	47.8	10.8/105.8	1.6
4	SP-100-380-60	–	5.0	5.0	1.9	2.6/42.0	0.5
5	P-SP-17-380-60	40.0	8.0	48.0	40.4	6.4/80.0	1.2
6	P-SP-12-380-60	50.0	6.6	56.6	50.6	4.8/73.0	1.2
7	P-SP-12-400-60	67.0	8.8	75.8	66.8	7.6/87.0	1.4
8	P-SP-25-360-120	44.8	14.8	59.6	49.3	9.1/61.0	1.2

*Per loaded polymer.

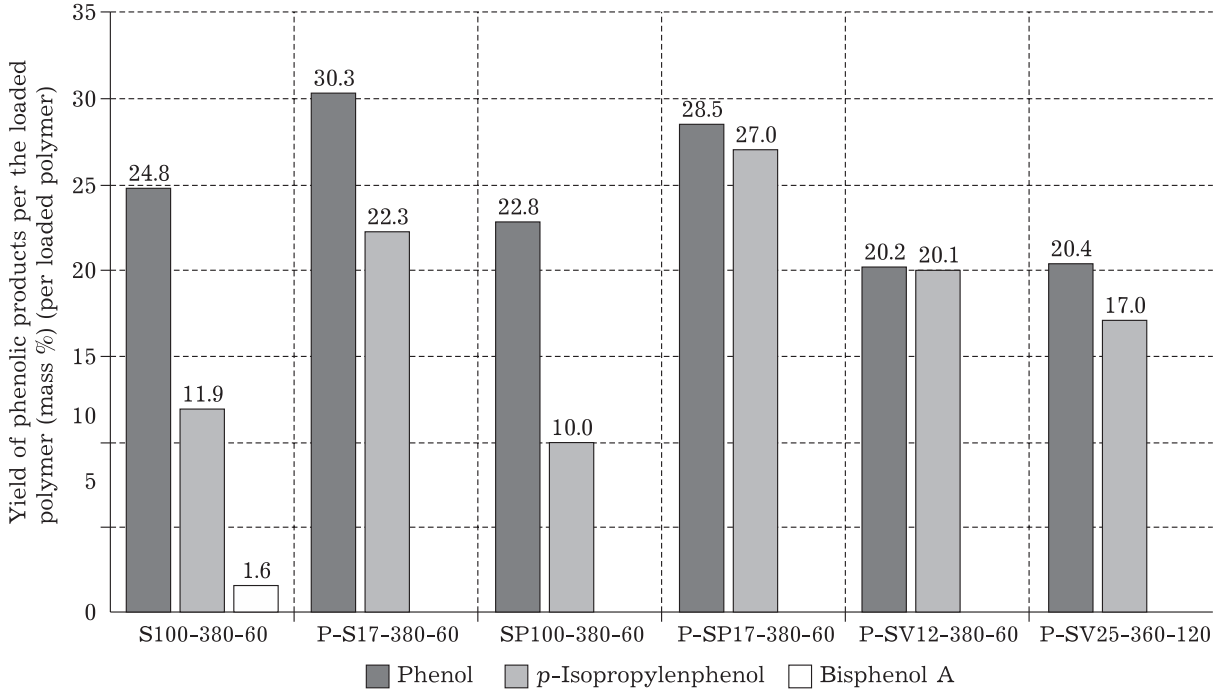

Fig. 1. Yields of phenolic products of thermal solvolysis of polymers in coal tar medium and without it.

is generated from epoxy resin based on bisphenol A. Experiments at the same temperature but without catalysts and using decalin yield significantly less phenolic products, *i.e.* 14.4 % including 4.7 % of phenol и 5.0 % isopropylphenol.

Phenolic species obtained during solvolysis of polymers may be used in the production of phenolic resins [17].

As with the use of tetralin and decalin, the formation of phenolic products is due to hydrogen transfer from coal tar to radical products of thermal degradation of resin [11–13]. The basis of coal tar is polycyclic aromatic hydrocarbons [18, 19], during hydrogen transfer from which intra- and intermolecular dehydrogenation polycondensation reactions occur in coal tar. They are similar to processes that take place during the thermal treatment of other polymers in coal tar [16, 20, 21]. Figure 2 gives a schematic diagram of reactions occurring during epoxy resin solvolysis in coal tar medium.

Examination of solvolysis residues

Resulting from dehydrogenation polycondensation reactions initiated by hydrogen transfer, coal tar composition changes. Table 2 gives characteristics of residues obtained during thermal solvolysis of polymers in coal tar medium. For comparison, also provided herein are the data for coal tar treated at 400 °C.

Samples of residues of mixtures of the polymer with coal tar after thermal solvolysis are characterised by high softening point. There is a high content of insoluble substances in quinoline and low volatile matter yield compared to the coal tar sample treated at 400 °C.

According to mass balance data, a minor part of polymer decomposition products may remain in the reactor with solvolysis temperatures of 380–420 °C. Therefore the residues of thermal treatment of polymers with coal tar are mainly presented by compounds of the initial coal tar that are undergone chemical transformations. As be seen from the data of Table 2, solvolysis residues of P-S-17-420-60 and P-S-17-380-60 samples are comparable with high-temperature coal tar (TU 1104-345352-164–98) according to standard indicators.

Varying the mass resin/coal tar ratio and thermal solvolysis temperature, one can produce modified coal tars with specified characteristics and high softening point for their further use as industrial raw materials [22].

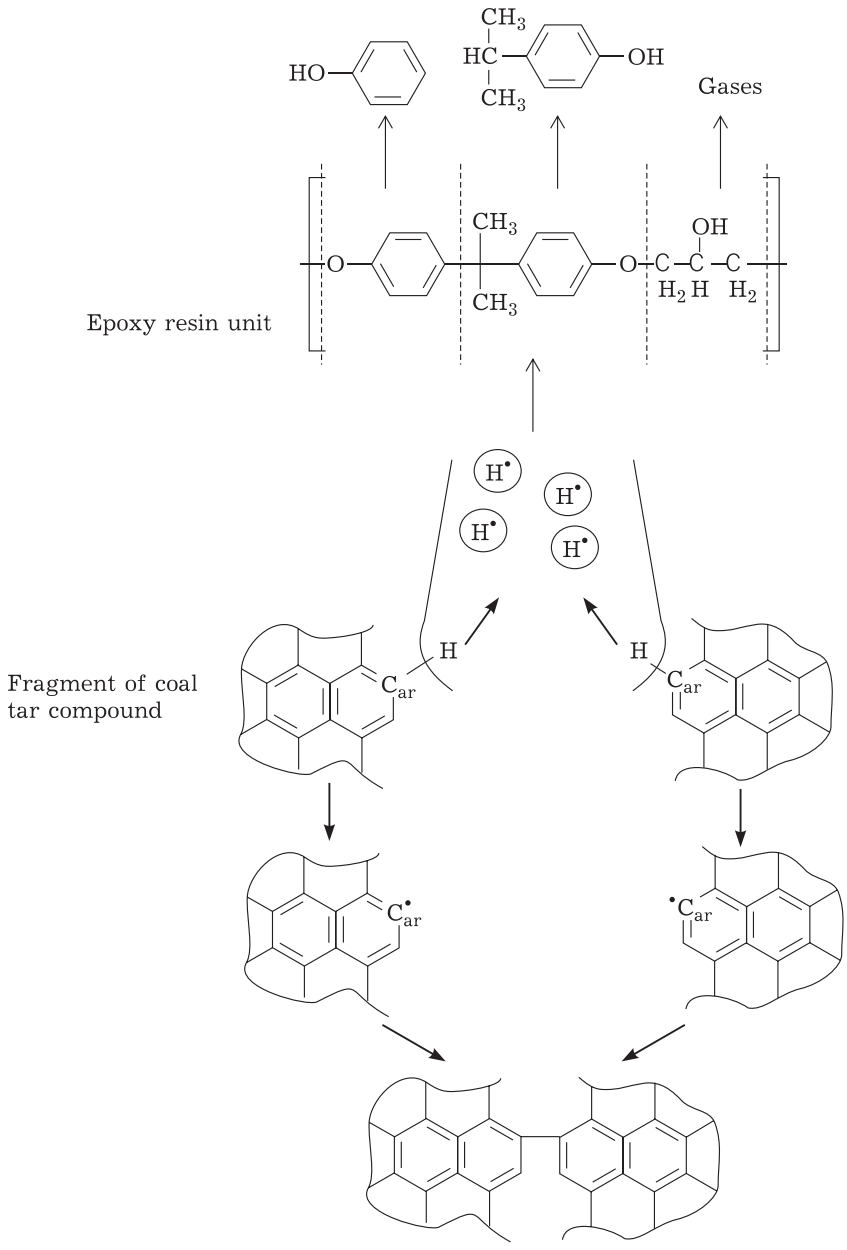

Fig. 2. Schematic diagram of reactions that proceed during thermal solvolysis of epoxy resin in coal tar.

CONCLUSION

Compared to pyrolysis without a solvent, thermal solvolysis of thermoreactive polymers based on epoxy resins in coal tar medium increases the selectivity for products of decomposition of the bisphenolic fragment of the polymer, phenol, and *n*-isopropylphenol. Radical species generated during thermal decomposition of polymers are stabilised owing to hydrogen transfer from polycyclic aromatic compounds of coal tar and form phenolic products. The isolated compounds can serve as chemical raw materials for the production of phenolic resins.

Due to a high degree of decomposition of polymers under study during thermal solvolysis, coal tar may be used as a solvent to dispose of polymer materials based on epoxy resins including polymeric composites.

Residues in the reactor generated after carrying out thermal solvolysis are high-temperature coal tars.

TABLE 2

Characteristics of heat-treated coal tar and residues produced during thermal solvolysis of polymers in coal tar medium

Sample	T_p, °C	α, %	α_1, %	V^r, mass %
P-400	87	36	11	53
P-S-17-380-60	139	54	17	45
P-S-17-420-60	141	52	32	44
P-SP-17-380-60	114	42	12	49
P-SV-12-380-60	110	42	13	50
P-SV-12-400-60	115	52	19	47
P-SV-25-360-120	150	53	36	40
HTCT*	135–145	46–54	20–30	40–46

*High-temperature coal tar (TU 1104-345352-164–98).

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