

UDC 66.092-977

DOI: 10.15372/CSD2020263

Comparison of Coal Tar Pitch and Petroleum Pitches in the Reactions of Thermal Solvolysis of Thermosetting Polymers

A. S. KABAK^{1,2}, E. I. ANDREIKOV^{1,2}¹*Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russia*

E-mail: kas@ios.uran.ru

²*JSC "VUKhIN", Ekaterinburg, Russia*

Abstract

The thermal solvolysis of epoxy diene resin (ED-20) and glass and carbon fibre reinforced plastics (FRP) in the medium of coal tar pitch and petroleum pitches was studied. The components of liquid-phase decomposition products were identified by gas chromatography-mass spectrometry; solvolysis residues were characterized. The mechanism of thermal solvolysis of epoxy resin in coal tar pitch and in petroleum pitches was proposed. The possibility of carbon and glass fibre recycling as a result of thermal solvolysis of FRP in coal tar pitch and in petroleum pitches was demonstrated. Coal tar pitch and petroleum pitches were compared as solvents for thermal solvolysis.

Keywords: thermal solvolysis, coal tar pitch, petroleum pitch, fiber reinforced plastic, recycling

INTRODUCTION

Thermosetting polymers, in particular those based on epoxy resin, are used in the production of polymer composite materials (PCM). The polymer in PCM is reinforced with glass fibres, carbon, quartz, aramide or other fibres. These materials possess exclusive strength with low density, which provides their wide use in space, aircraft, automobile branches of industry, in construction, in nuclear and alternative power engineering, and in the production of sports equipment [1, 2].

Along with PCM, the production of thermosetting polymers is continuously increasing, which leads to an increase in the amount of wastes. Thermosetting polymers are characterized by a strong cross-linked structure. This brings complications into their processing, unlike for thermoplastic polymers that may be fused and transformed into a new product. Utilization of thermosetting polymers involves chemical and thermal

destruction methods leading to the formation of initial monomers suitable for repeated use. In the case of utilization of PCM based on thermosetting polymers, the problem of extracting reinforcing fibres also arises. Because of this, for the development of an efficient method of PCM utilization, it is necessary not only to destroy the polymer binder obtaining commercial chemical compounds but also to isolate the fibrous filler for secondary use. Chemical methods of PCM utilization including thermal solvolysis are considered to be promising.

Thermal solvolysis involves PCM treatment with chemically active solvents at increased temperatures. This allows complete destruction of the polymer binder and isolation of the filler in the pure form. The solvolysis of PCM in the medium of supercritical liquids is under active investigation [3, 4]. The use of supercritical liquids or gases allows one to achieve high efficiency of destruction of the polymer binder due to an increase in diffusion coefficient, dissolving capacity and mass

exchange rate in comparison with the solvents under normal conditions. The agents of special interest are supercritical water and carbon dioxide which do not have any negative effect on humans and on the environment, and may be recovered.

The active solvents used for solvolysis include also hydroaromatic compounds acting as hydrogen donors. The destruction of PCM based on epoxy resin and reinforced with carbon fibres was studied in tetralin and 9,10-dihydroanthracene [5]. The conversion of epoxy resin at 340 °C was nearly 100 %.

The high cost of the proposed solvents, their toxicity, the necessity to use devices operating at high pressure bring complications into the introduction of thermal solvolysis.

Previously we demonstrated the possibility to use coal tar pitch as an active hydrogen-donor solvent in thermal solvolysis of thermosetting polymers and PCM based on them. Unlike other solvents, coal tar pitch allows carrying out solvolysis at atmospheric pressure and is a cheap large-scale product [6–8]. Its carcinogenic activity due to the presence of carcinogenic polycyclic aromatic hydrocarbons (PAH) and its poor solubility in organic solvents hindering the purification of fibres isolated from PCM may be considered as the disadvantages of its use.

Petroleum pitch may be considered as an alternative agent instead of coal tar pitch because the basis of both kinds is PAH taking an active part in the solvolysis of thermosetting polymers. The content of carcinogenic PAH in petroleum pitch is much lower than in coal tar pitch [9]. At the same time, coal tar pitch and petroleum pitch differ from each other in chemical composition. The fractions of petroleum pitches are characterized by lower aromaticity degree, substantial content of aliphatic substituents in polyaromatic structures, and higher molecular mass. In addition, petroleum pitches contain hydrocarbons with naphthene rings, which are absent from the fractions of coal tar pitch. Some differences in elemental composition are observed; the atomic ratio of C/H for coal tar pitch reaches 1.26–1.52 against 1.14–1.19 for petroleum pitch [10, 11].

So, an experimental test of the possibility to use petroleum pitch as a solvent in the thermal solvolysis of polymers is necessary. The goal of the work was to compare coal tar pitch and petroleum pitch as a hydrogen-donor solvent for thermal solvolysis of epoxy resin and PCM on its basis.

EXPERIMENTAL

Materials

Commercial medium-temperature coal tar pitch was used in the work. Petroleum pitch from heavy gas oil of catalytic cracking (PPG) was obtained by stripping the distillate fractions to the temperature of 430 °C in the tank, with exposure at this temperature for 120 min. Petroleum pitch from the heavy resin of pyrolysis of ethylene production (PPR) was obtained by stripping the distillate fractions to the temperature of 400 °C in the tank without exposure at this temperature. The characteristics of pitches are presented in Table 1.

Epoxy diene resin (ER) of ED-20 grade (with epoxy value 19.2 according to GOST 10587–84) and commercial samples of PCM with 50–60 % content of glass or carbon reinforcing fibres were also used.

Investigation procedure

Thermal solvolysis of epoxy resin in coal tar pitch and petroleum pitches was carried out under isothermal conditions within temperature range 320–380 °C in a metal reactor at atmospheric pressure. The reactor was filled with a mechanical mixture of 45 g coal tar pitch or petroleum pitch and 15 g of epoxy resin; after melting the pitch, mixing with a propeller-type mixer was carried out. The vapours of distillate products that were released during solvolysis were condensed in a glass outlet pipe and collected in the receiving tank. The amount of gas together with possible losses was determined as a difference between the loaded mass and the sum of the masses of distillate products and the residue in the reactor.

TABLE 1

Characteristics of coal tar and petroleum pitches (GOST 10200–2017)

Sample	Characteristics of solvolysis residues			
	T_s , °C	α , %	α_1 , %	V, %
PPG	45	13.2	0.5	71
PPR	81	0.3	0	68
CP	68	27	5	61

Note. Here and in Tables 2–4: 1. CP is coal tar pitch; PPG is petroleum pitch from heavy gasoil from catalytic cracking; PPR is petroleum pitch from heavy resin of pyrolysis from ethylene production. 2. T_p is softening temperature according to the ring and rod procedure; α is the mass fraction of substances insoluble in toluene; α_1 is mass fraction of substances insoluble in quinoline; V is the yield of volatile substances at 850 °C.

During thermal solvolysis of PCM, before being loaded into the reactor, the sample was placed into a metal reticulated cell to fix the fibres released during solvolysis. A PCM sample 1.0–1.5 g in mass was taken for the experiment; the mass of coal tar pitch or petroleum pitches was 60 g. The fibres recovered as a result of solvolysis were washed from the residues of coal tar pitch and petroleum pitches using N-methylpyrrolidone for 120 min under intense mixing, then washed with water, dried to the constant mass at 120 °C, and weighted. The yield of fibres was calculated as a ratio of the mass of isolated fibres to the mass of the initial PCM sample.

Methods of investigation

The composition of distillate products was determined with the help of gas chromatography – mass spectrometry using a Trace GC Ultra DSQ II instrument (Thermo Scientific, USA). Quantitative analysis was using a GC 2010 gas chromatograph (Shimadzu, Japan) with flame ionization detector (GC-FID), quartz capillary column ZB-5 (polydimethylsiloxane, phenyl groups 5 mass %) 30 m long, 0.25 mm in diameter, with film thickness 0.25 µm. Measurement mode: initial column temperature, 40 °C (exposure for 3 min); temperature programming at a rate of 10 °C/min to 280 °C (exposure for 30 min), evaporator temperature: 250 °C, detector temperature: 300 °C. The carrier gas was nitrogen; flow partitioning 1 : 30, the flow rate through the column 1.0 mL/min. Calculations were carried out by means of internal normalization according to the areas of peaks.

The IR spectra of exhaust vapours and gases of epoxy resin and the mixtures of epoxy resin with coal tar pitch, formed during thermogravi-

metric analysis, were recorded with the help of a Nicolet iS10 spectrometer with a TGA/FT-IR attachment (Thermo Scientific, USA).

Initial pitches and the residues from solvolysis were analyzed according to GOST 10200–2017 “Coal tar pitch, electrode grade. Technical conditions”.

RESULTS AND DISCUSSION

The results of the determination of material balance and analysis of distillate products of the pyrolysis of epoxy resin and its thermal solvolysis in coal tar pitch and petroleum pitches are presented in Table 2 and Fig. 1.

The yields of solid residue and distillate products of the pyrolysis of epoxy resin at 380 °C are 49.5 and 43.5 %, respectively. For thermal solvolysis of epoxy resin both in coal tar pitch and in petroleum pitch at this temperature (in comparison with the pyrolysis of the resin alone), the yields of distillate products calculated for resin load increase and exceed 70 %; the total yield of phenol products, phenol and *p*-isopropylphenol also increase, mainly due to the latter compound. Unlike for thermal solvolysis in coal tar pitch, the distillate products of epoxy resin solvolysis in petroleum pitch contain bisphenol A in small amounts, and the fraction of this compound increases substantially with a decrease in process temperature to 360 °C.

Characteristics of the residues of thermal solvolysis of epoxy resin in pitches are shown in Table 3.

Thermal solvolysis of epoxy resin in coal tar pitch leads to a strong change of its characteristics, an increase in softening temperature and the content of substances insoluble in toluene and

TABLE 2

Material balance of pyrolysis and thermal solvolysis of epoxy resin (ER) in coal tar pitch and petroleum pitches

Solvent type	Loaded mass, g		Solvolysis conditions		Amount of products, g		
	Pitch	ER	T, °C	Time, min	Residue in the reactor	Distillate products	Losses and gases
Without solvent	–	40.0	380	60	19.8	17.4	2.6
PPG	44.9	15.0	380	60	47.9	10.8	1.2
PPR	45.2	15.2	380	105	37.8	11.6	11.0
	45.4	14.6	360	105	46.9	8.1	5.1
	45.6	15.6	320	180	50.6	3.5	7.1
CP	45.0	15.0	380	60	47.5	11.4	1.1
	45.0	15.0	320	60	66.2	1.4	1.2

Note. For designations, see Table 1.

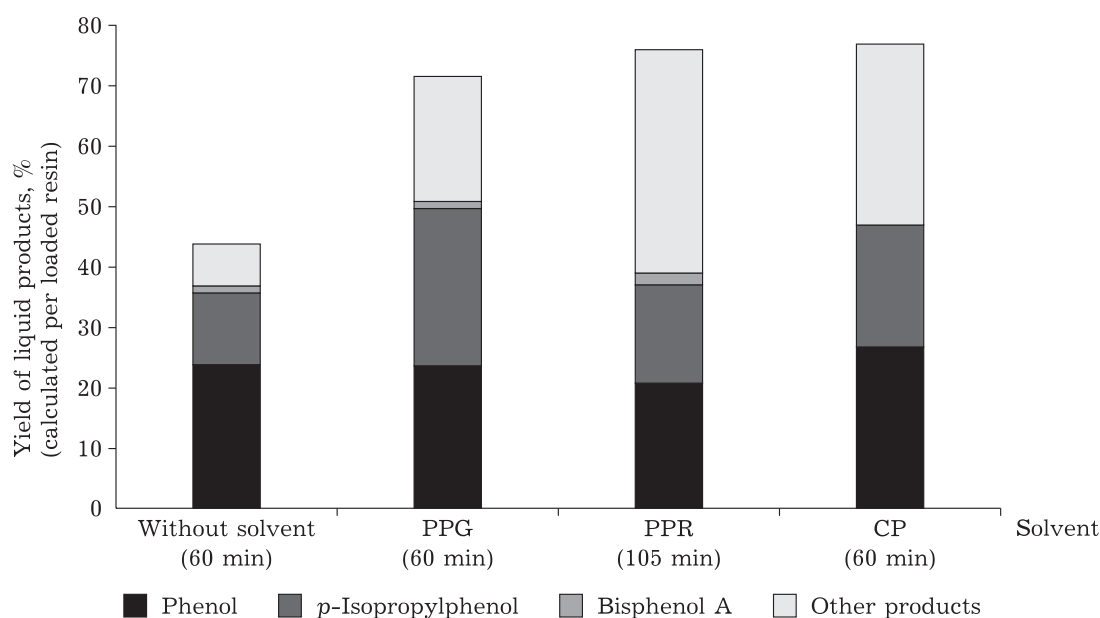


Fig. 1. Yields of distillate products of solvolysis of epoxy resin in coal tar pitch and in petroleum pitches at the process temperature of 380 °C and different process duration. Note. For designations, see Table 1.

quinolone, a decrease in the yield of volatile substances. This occurs as a consequence of dehydrogenation condensation of the compounds in coal tar pitch, initiated by hydrogen transfer from pitch compounds to the products of polymer destruction. The intensity of these reactions is substantially higher than the intensity of thermal reactions in pitches, as one can see in the comparison with the experiments without the addition of epoxy resin, and increases with an increase in the degree of polymer transformation with temperature rise.

Similar changes occur in petroleum pitches during thermal solvolysis of epoxy resin, which allows speaking of dehydrogenation condensation initiated by hydrogen transfer. A similar nature

of the changes in the properties of coal tar pitch and petroleum pitches was previously established for thermal solvolysis of polystyrene in them [12].

So, it was demonstrated that petroleum pitches, similarly to coal tar pitch, form an efficient medium to carry out thermal solvolysis of epoxy resin. The major regularities of the process, namely prevention of the formation of solid residue of epoxy resin pyrolysis, an increase in the yield of phenol products, initiation of solvent condensation reactions, are similar and are determined by hydrogen transfer from polycyclic aromatic compounds of pitches.

To determine the effect of the solvent on the temperature at which the destruction of epoxy resin starts, the vapours of compounds released

TABLE 3

Characteristics of coal tar pitch after pyrolysis and the residues from thermal solvolysis of epoxy resin (ER) in coal tar pitch and in petroleum pitches

Sample	Conditions of thermal treatment		Characteristics of the residue from solvolysis			
	T , °C	Time, min	T_s , °C	α , %	α_1 , %	V , %
CP	400	60	87	36	11	53
PPG + ER	380	60	152	41	6	40
PPR + ER	380	105	>160	44	11	42
	360	105	160	37	5	47
	320	180	133	17	0	60
CP + ER	380	60	154	55	32	44
	320	60	92	38	7	59

Note. For designations, see Table 1.

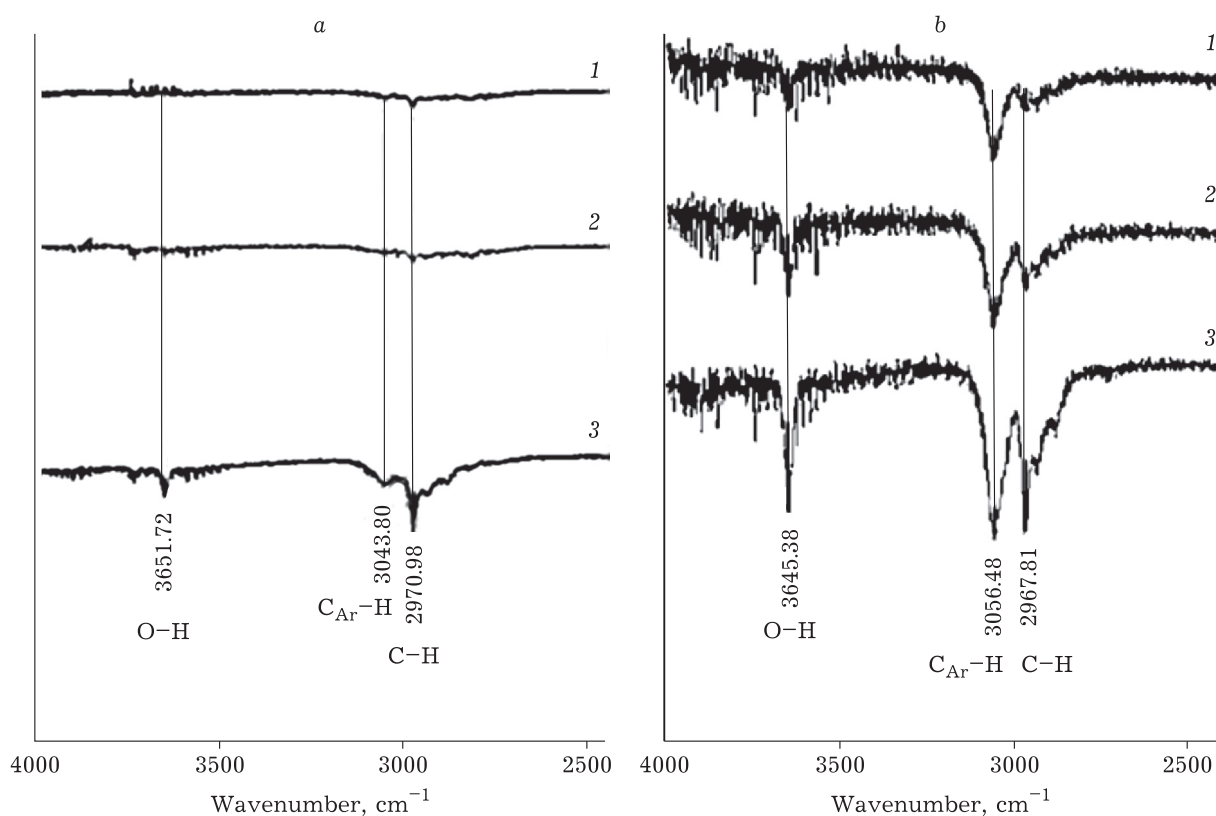


Fig. 2. IR Fourier spectra of gaseous products formed in the thermal treatment of epoxy resin (a) and a mixture of epoxy resin with coal tar pitch (b) at 360 (1), 400 (2) and 440 °C (3).

during the pyrolysis of epoxy resin and its mixtures with coal tar pitch were studied by means of IRT Fourier Transform spectroscopy. The IR Fourier spectra of the compounds evolved into the gas phase during heating the epoxy resin and its mixture with coal tar pitch (mass ratio of epoxy resin to coal tar pitch was 1 : 5) are presented in Fig. 2.

Absorption bands at 2970, 3050 and 3650 cm^{-1} , corresponding to the stretching vibrations of $\text{C}_{\text{al}}-\text{H}$, $\text{C}_{\text{ar}}-\text{H}$ bonds in the aromatic ring and O-H in phenols appear in the gaseous products of the destruction of individual epoxy resin at 440 °C, while in the case of thermodestruction in coal tar pitch they appear at 360 °C. It may be concluded that the use of coal tar pitch as a solvent decreases the temperature of epoxy resin destruction.

The experimental data obtained in the study allow us to propose an integrated mechanism of thermal solvolysis of the bisphenol fragment of epoxy resin in coal tar pitch and petroleum pitches as presented in Fig. 3.

At the first stage, homolytic rupture of the weakest $-\text{C}_{\text{al}}-\text{O}-$ bond in epoxy resin occurs under the action of temperature, resulting in the formation of reactive radicals. As indicated above, the temperature necessary for this process is sub-

stantially lower than the temperature needed for the pyrolysis of epoxy resin without the solvent. The formed phenoxy radical is stabilized due to hydrogen transfer from the compounds present in the pitch. Then two directions of destruction are possible. The first one involves the rupture of the nearest $-\text{C}_{\text{al}}-\text{O}-$ bond, followed by the formation of bisphenol A, which is unstable in coal tar pitch as reported in [13] and reacts with the formation of phenol and *p*-isopropylphenol. The second direction involves splitting of isopropyl group with the formation of phenol and a fragment of polymer chain, so that its further destruction may proceed *via* the formation of intermediate condensed compounds with partial loss of isopropyl group [14]. This explains a decreased mass ratio of *p*-isopropylphenol/phenol in reaction products in comparison with the theoretical value (1.45) for the destruction of bisphenol. At the same time with the formation of phenol products, recombination of Ar. radicals formed from the compounds present in pitches occurs. As a result, intra- and intermolecular dehydrogenation condensation of polycyclic aromatic compounds proceeds in coal tar pitch and petroleum pitch, resulting in an increase in the softening temperature of pitches, in the amount of sub-

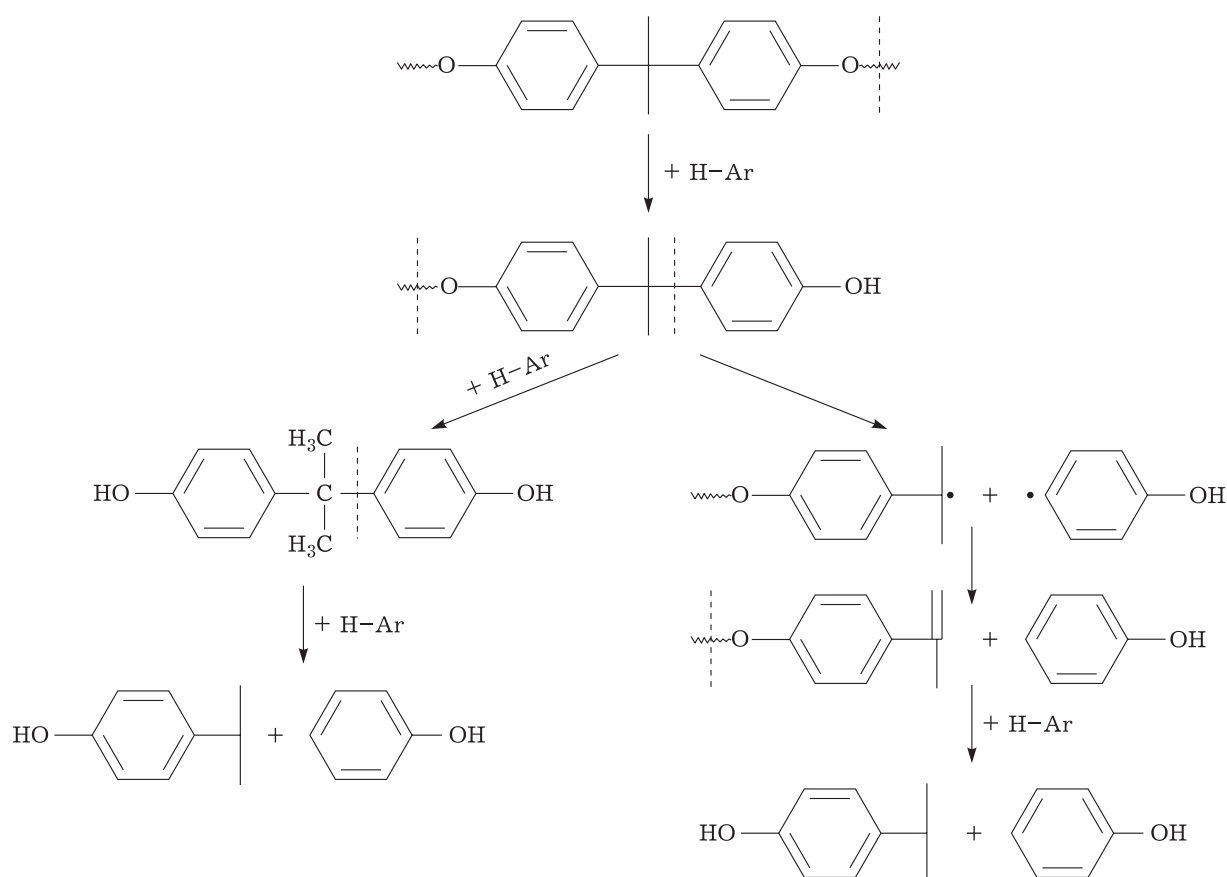


Fig. 3. Reactions proceeding during thermal solvolysis of epoxy resin in coal tar pitch and petroleum pitches. H-Ar are polycyclic aromatic hydrocarbons of coal tar pitch or petroleum pitches.

stances insoluble in toluene and quinolone, and a decrease in the yield of volatile substances.

The obtained experimental data show the activity of petroleum pitches in thermal solvolysis of epoxy resin, which allows us to propose them along with coal tar pitch for the destruction of epoxy matrices in PCM. The reaction proceeds

slower in petroleum pitches, which may be compensated by an increase in solvolysis temperature and/or reaction time.

Comparative results on the yields of the filler isolated from PCM in different pitches are presented in Table 4, and the images of the isolated fibres are shown in Fig. 4. One can see that in

TABLE 4

Results of solvolysis of different polymer composite materials (PCM) in coal tar pitch and in petroleum pitches

Solvent	PCM type	Solvolysis conditions		Yield of isolated filler, %
		T, °C	Time, min	
CP	Carbonplastics	320	60	82
	»	400	60	52
PPG	»	320	60	73
	»	340	60	68
	Glass reinforced plastics	360	90	55
PPR	Carbonplastics	380	90	60
	Glass reinforced plastics	380	90	58

Note. For designations, see Table 1.

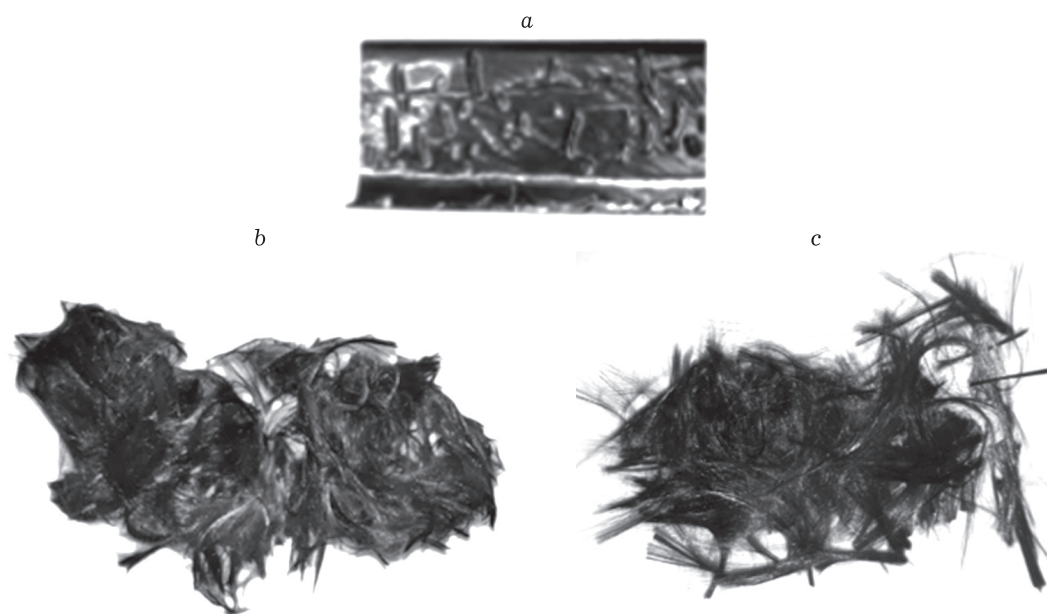


Fig. 4. Initial sample of carbonplastic (a) and carbon fibres isolated from it by means of solvolysis in petroleum pitch (b) and coal tar pitch (c).

both cases the surface of fibres is purified from the polymer binder. The volume of the isolated fibres is much larger than the initial PCM sample, which is due to the removal of the polymer binder holding the fibres in a tight harness, after solvolysis in coal tar pitch and petroleum pitch. The length of the isolated fibres is determined by the size of the composite sample taken for thermal solvolysis. Fibre diameter determined after solvolysis in coal tar pitch with the help of electron microscopy is the same and equals 6–7 μm [7], which corresponds to the diameter of initial carbon fibre.

CONCLUSION

Thus, thermal solvolysis of epoxy resin in coal tar pitch and in petroleum pitch follows the same regularities and may be used for utilization of thermosetting polymers and PCM based on them for the purpose of isolating the filler from PCM wastes. The use of petroleum pitches as the solvents for thermal solvolysis in carbon fibre recycling from PCM wastes is preferable over coal tar pitch because the former are characterized by lower carcinogenic activity and better solubility in organic solvents.

REFERENCES

- Oliveux G., Dandy L., Leeke G., Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties, *Progress in Materials Science*, 2015, Vol. 72, P. 61–99.
- Kumar S., Krishnan S., Recycling of carbon fiber with epoxy composites by chemical recycling for future perspective: A review, *Chemical Papers*, 2020, Vol. 74, P. 3785–3807.
- Kim Young Nam, Kim Young-O., Kim Seong Yun, Park Min, Yang Beomjoo, Kim Jaewoo, Jung Yong Chae., Application of supercritical water for green recycling of epoxy-based carbon fiber reinforced plastic, *Composites Science and Technology*, 2019, Vol. 173, P. 66–72.
- Hyde J., Lester E., Kingman S., Pickering S., Wong K., Supercritical propanol, a possible route to composite carbon fibre recovery: A viability study, *Compos. Part A. Appl. Sci. Manuf.*, 2006, Vol. 37, No. 11, P. 2171–2175.
- Braun D., von Gentzkow W., Rudolf A. P., Hydrogenolytic degradation of thermosets, *Polym. Degrad. Stab.*, 2001, Vol. 74, P. 25–32.
- Kabak A. S., Andreykov E. I., Pervova M. G., Koitov S. A., Seleznev A. M., Disposal of thermoreactive epoxy resin-based polymers by thermal solvolysis in coal tar medium accompanied by chemical raw material receipt [in Russian], *Chemistry for Sustainable Development*, 2018, Vol. 26, No. 2, P. 135–140.
- Andreykov E. I., Kabak A. S., Beilina N. Yu., Mishkin S. I., Research of recycling carbon fibres by thermal solvolysis of polymer composites using coal tar pitch, *Chemistry for Sustainable Development*, 2018, Vol. 26, No. 6, P. 571–575.
- Pat. RU 2600637, 2016.
- Russo C., Cijolo A., Stanzione F., Tregrossi A., Oliano M., Carpentieri A., Apicella B., Investigation on chemical and structural properties of coal- and petroleum-derived pitches and implications on physico-chemical properties (solubility, softening and coking), *Fuel*, 2019, Vol. 245, P. 478–487.
- Babenko E. M., Ilyina M. N., Plevin G. V., Investigation of pyrolysis pitch as binding and impregnating material for the production of graphitized electrodes [in Russian], *Khimiya Tverdogo Topliva*, 1981, No. 4, P. 117–122.
- Kershaw J. R., Black K. J. T., Structural characterization of coal-tar and petroleum pitches, *Energy & Fuels*, 1993, No. 7, P. 420–425.

- 12 Andreykov E. I., Amosova I. S., Dikovinkina Yu. A., Krasnikova O. V., Pervova M. G., Pyrolysis of polystyrene in coal tar pitch and pyrolytic pitch [in Russian], *Zhurn. Priklad. Khimii*, 2012, Vol. 85, No. 1, P. 93–102.
- 13 Safarov L. F., Thermal solvolysis of polycarbonate in coal tar pitch (Thesis Cand Sci. in Technology), Ekaterinburg, 2017. 122 p. (in Russ.).
- 14 Kumagai S., Ono S., Yokoyama S., Kameda T., Yoshioka T., Fate of bisphenol A pyrolysates at low pyrolytic temperatures, *Journal of Analytical and Applied Pyrolysis*, 2017, Vol. 125, P. 193–200.