ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 9, pp. 1624–1629. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.I. Andreikov, A.A. Lyapkin, I.S. Amosova, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 9, pp. 1523–1528.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Modification of Coal Tar Pitch by High-Temperature Treatment with Polyvinyl Chloride

E. I. Andreikov, A. A. Lyapkin, and I. S. Amosova

Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia

Received February 16, 2009

Abstract—Properties of residues from joint pyrolysis of poly(vinyl chloride) and coal tar pitch at 300 and 400°C were studied.

DOI: 10.1134/S1070427209090213

Utilization of steadily growing amounts of polymeric wastes, of which polyvinyl chloride (PVC) makes a considerable fraction, is a topical problem [1, 2]. Such widely used utilization procedure like incineration [3] is unsuitable for PVC-containing wastes because of possible emission of highly toxic dioxins [4].

Preliminary pyrolysis of PVC allows removal of the major fraction of chlorine via thermal dehydrochlorination [5]. The resulting pyrolysis product can be incinerated safely [6]. Heating of PVC to 420°C leads to the formation of so-called polyvinyl chloride pitch (PVC pitch) [7] which is suggested for use for preparing carbon fibers. Use of heat-treated PVC for this purpose was also suggested in [8–10]. Mochida et al. [11] used PVC pitch prepared by PVC pyrolysis at 360–450°C for modification of mesophase coal tar and petroleum pitches.

Published data on pyrolysis of PVC in high-boiling solvents are lacking, except a paper by Ali and Siddigni [12] who showed that, after thermal dehydrochlorination of PVC in petroleum pitch, the product can be subjected to thermal or catalytic cracking.

In this study we examined thermal degradation of PVC in the medium of coal tar pitch and the properties of the resulting modified pitches. This process is also of interest as an approach to utilization of spent PVC. The advantages of heat treatment of PVC in coal-tar pitch are high boiling onset temperature of this pitch (>380°C), allowing the process to be performed at atmospheric pressure, and prospects for using modified pitch similarly to coal tar pitch proper, namely, as a raw material for production of graphitic carbon items and carbon-containing composites [13, 14].

EXPERIMENTAL

We used a commercial sample of PVC, S-70 grade, with a particle size smaller than 0.5 mm, prepared by radical suspension polymerization of the monomer, and a commercial sample of high-temperature coal tar pitch (HTP) of grade V [GOST (State Standard) 10200–83].

A glass reactor was charged with PVC, HTP, or HTP + PVC mixture (1 : 1 or 4 : 1) in an amount of up to 10 g. A water-cooled distillate condenser was connected to the reactor through a side neck, and a test tube for distillate collection was connected to the condenser. Nitrogen was fed to the reactor at a rate of 20 ml min^{-1}. The gas leaving the condenser was passed through a bottle filled with an aqueous alkali solution, to trap the released hydrogen chloride. The reactor was placed in an electrically heated furnace. The reactor temperature was controlled with a temperature-control device and a thermocouple.

The amount of the released hydrogen chloride was determined by the absorption with an alkali solution (0.1 N NaOH), followed by back-titration with an acid. The characteristics of the starting substances (PVC, HTP) and products obtained (modified pitches) were determined by elemental analysis, IR Fourier spectroscopy, and in accordance with GOST 10200–83. The IR spectra were taken from solid samples in

the diffuse reflection mode with a Perkin–Elmer Spectrum BX-II Fourier transform spectrometer. The spectra were interpreted using the known band assignments for organic compounds [15].

Figure 1 shows the curve of hydrogen chloride release in the course of PVC pyrolysis and thermal degradation of PVC in the medium of coal tar pitch at 215°C. In PVC pyrolysis, the amount of the HCl released in 120 min was 7.2% of its theoretical content in PVC (56.8%). In joint heat treatment of PVC in coal tar pitch under the same conditions, 84.7% of HCl was released. Heat treatment of PVC in coal tar pitch at 300°C for 120 min results in the release of more than 99% of HCl, compared to 89.6% without pitch. The data on thermal degradation of PVC taken separately are consistent with the data of [16]. Pyrolysis of PVC in coal tar pitch allows the PVC dehydrochlorination rate to be increased and its temperature to be decreased.

Data on the elemental composition of the initial substances (HTP and PVC), and also the yields and characteristics of PVC pitches obtained at 300 and 400°C and of coal tar pitch heat-treated at 400°C are given in Table 1. Heat treatment at 300°C does not affect the properties of coal tar pitch. The chlorine content of PVC pitch samples obtained by heat treatment at 300 and 400°C for 120 min is 1 and 0.3%, respectively. The H/C ratio in the PVC pitch sample obtained by heat treatment at 300°C is 0.97, which is close to the theoretical value equal to unity for completely dehydrochlorinated PVC. At 400°C, the H/C ratio in PVC pitch decreases to 0.89, which is considerably higher than for coal tar pitch (0.60).

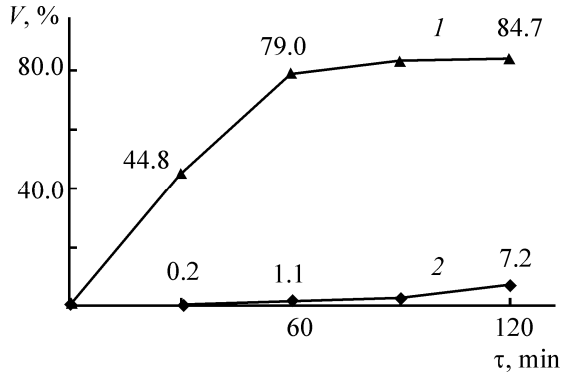

Fig. 1. Percentage of the HCl released from PVC at 215°C as a function of time τ. Pyrolysis of (*1*) PVC : pitch = 1 : 1 mixture and (*2*) individual PVC.

The yield of PVC pitch prepared at 300°C is 38% at a theoretical HCl content in the starting polymer of 56.8%. It is known that PVC pyrolysis at temperatures of up to 300°C is accompanied by the release, along with HCl, of benzene and other aromatic compounds [5, 17]. The PVC pitch obtained at 300°C is virtually fully insoluble in toluene but partially soluble in quinoline. It does not melt up to 300°C. The infusibility and insolubility of the pitch obtained at 300°C suggest its three-dimensional structure formed by cross-linking of polymer chains [5] in the course of thermal dehydrochlorination with the formation of conjugated double bonds [18–20].

The yield of PVC pitch at 400°C is 25%. This pitch has a softening point of 186°C and low, compared to coal tar pitch, content of substances insoluble in toluene and quinoline, in agreement with the data from [8, 9]. This fact indicates that an increase in the heat treatment temperature to 400°C leads to degradation of three-dimensional structures formed at lower tem-

Table 1. Characteristics of high-temperature coal tar pitch, polyvinyl chloride, and pitches obtained by their heat treatment

Pitch preparation conditions	Pitch yield, %	Content, wt %			H/C	Parameters according to GOST 10200–83[a]			
		C	H	Cl		α-fraction, wt %	α_1-fraction, wt %	V^g, wt %	T_s, °C
Initial HTP	–	90.1	4.6	–	0.61	32.3	4.5	53.4	90
HTP, 400°C, 120 min	71	–	–	–	–	58.1	27.3	33.2	190
Initial PVC	–	38.1	4.8	56.8	1.51	–	–	–	–
PVC, 300°C, 120 min	38	89.5	7.3	1.0	0.97	98.3	64.8	73.1	>300
PVC, 400°C, 120 min	25	92.7	6.9	0.3	0.89	5.4	2.6	62.0	186

[a] α-Fraction: substances insoluble in toluene; α_1-fraction, substances insoluble in quinoline; V^g, yield of volatiles at 850°C; T_s, ring-and-rod softening point.

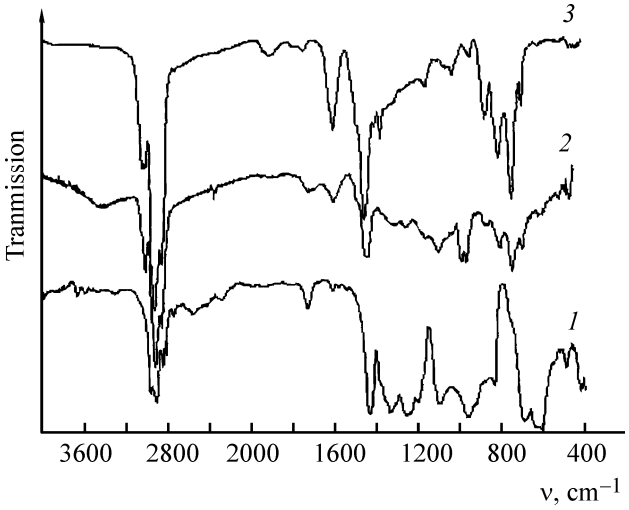

Fig. 2. IR spectra of (*1*) PVC and of PVC pitches obtained by heat treatment of PVC at (*2*) 300 and (*3*) 400°C for 120 min. (T) Transmission and (ν) wavenumber; the same for Fig. 3.

peratures, with an increase in the solubility of PVC pitch in toluene and quinoline.

The IR spectra of the initial PVC and of PVC pitch are shown in Fig. 2. The IR spectrum of the PVC pitch obtained at 300°C differs significantly from that of the initial PVC. The differences are due to elimination of the major amount of chlorine. The absorption of the C–Cl bond at 616–692 cm^{-1} and the bands at 2970 and 2912 cm^{-1}, corresponding to the C–H bonds in the –CHCl– group and in the adjacent $–CH_2–$ group, disappeared. The bands at 2923 and 2856 cm^{-1} belong to the methylene group, as also does the band at 1447 cm^{-1}. A series of new absorption bands (3016, 911, 965 cm^{-1}) are indicative of the formation of double bounds: that in terminal vinyl group (991 cm^{-1}) and trans-vinylene bond. The bands at 748, 810, and 880 cm^{-1} apparently belong to substituted vinylidene groups [21]. The new absorption band at 1599 cm^{-1} is usually attributed to formation of conjugated double bonds in the course of PVC dehydrochlorination [22]. It can also belong to aromatic structures. Weak absorption (shoulder) at 3048 cm^{-1} most probably belongs to an aromatic C–H bond, as this band becomes stronger in PVC pitch obtained at 400°C and is characteristic of coal tar pitch.

In the IR spectrum of a sample of PVC pitch obtained at 400°C, the prevalent bands in the range of absorption of aliphatic C–H bonds are those of $–CH_2–$ groups (2926, 2838, 1452 cm^{-1}). Bands of aromatic C=C bonds appear at 1600 cm^{-1}, and vibrations of aromatic C–H bonds are observed at 3049, 3020, and 700–900 cm^{-1}. In contrast to the IR spectrum of the PVC pitch obtained at 300°C, the absorption bands of double bonds at 991 and 965 cm^{-1} are absent.

The preparation conditions, yields, and properties of coal tar pitches modified by heat treatment with the initial PVC or with PVC pitches are given in Table 2. Two series of experiments, at 300 and 400°C, were done. In the modified pitches (HTP : PVC ratio 1 : 1) obtained at 300 and 400°C, the residual Cl content is 0.6 and 0.2%, respectively. As the properties of the initial coal tar pitch noticeably change upon heat treatment at 400°C, data for the coal tar pitch heat-treated at 400°C for 120 min are also given in Table 2.

The softening points of the modified pitches are in the range 190–200°C, except for the pitch obtained at 300°C and HTP : PVC ratio of 1 : 1, which does not undergo softening up to 300°C.

For the yields of the modified pitches and their characteristics in accordance with GOST 10200–83, along with the experimental results we present the corresponding additive values calculated from data in Table 1.

Table 2 shows that, when thermal degradation of PVC is performed in the medium of coal tar pitch, the yields and properties of the modified pitches obtained are essentially nonadditive. The processes are characterized by the formation at 300°C of insoluble three-dimensional cross-linked structures in the amount exceeding the sum of insoluble compounds in the separately heat-treated PVC and coal tar pitch. Hence, these structures are formed, at least partially, by reactions between the compounds formed by thermal degradation of PVC and components of coal tar pitch. With an increase in the temperature to 400°C, three-dimensional structures decompose with the formation of higher-molecular-weight compounds that are less soluble in toluene (the content of the α-fraction increases nonadditively), compared to the initial coal tar pitch.

The IR spectra of the modified pitches obtained at 300 and 400°C are shown in Fig. 3. The IR spectra of the modified pitches differ from that of the initial coal tar pitch in stronger absorption at 2924 and 2857 cm^{-1} (stretching vibrations of C–H bonds in methylene groups). The intensity ratio of the absorption bands of aliphatic C–H bonds at 2850–2925 cm^{-1} and of

Table 2. Characteristics of modified pitches

Conditions of pitch preparation	Yield of modified pitch, %	H/C	Cl, %	α-Fraction, wt %	α_1-Fraction, wt %	V^g, %	T_s, °C	Pitch yield,[a] %
HTP:PVC = 1:1, 400°C, 120 min	53	0.48	0.2	51.0/44.0[b]	5.5	41.0/40.6	205	48
HTP:PVC = 4:1, 400°C, 120 min	68	–	–	52.0/49.0	15.4	38.0/35.0	188	62
HTP:PVC = 1:1, 400°C, 60 min	56	–	–	56.6/44.0	5.6	46.0/40.6	211	–
HTP:PVC = 4:1, 300°C, 120 min	82	–	–	57.0/38.0	19.4/13.0	48.0/55.0	189	88
HTP:PVC = 1:1, 300°C, 120 min	63	0.47	0.6	74.0/51.0	19.1/19.0	49.0/59.0	>300	69
HTP:PVC = 1:1, 300°C, 60 min	65	–	–	73.8/51.0	19.5/19.0	51.0/59.0	223	–
HTP:PVC_{300}[c] = 1:2, 400°C, 60 min	80	0.47	–	38.1	8.0	48.8	174	–
HTP:PVC_{300}[c] = 1:2, 300°C, 60 min	95	0.52	–	63.0/57.0	14.7	58.5/60.0	151	–
HTP:PVC_{400}[c] = 1:2, 400°C, 60 min	84	–	–	31.8	4.3	51.6	165	–
HTP:PVC_{400}[c] = 1:2, 300°C, 60 min	96	–	–	22.6/23.0	7.5	55.9/56.0	154	–
HTP, 400°C, 120 min	71	–	–	58.1	27.3	33.2	190	–
Initial HTP	–	–	–	32.3	4.5	53.4	90	–

[a] Calculated additive values. [b] In the denominator are the calculated additive values. [c] PVC_{300} and PVC_{400} are PVC pitches obtained by heat treatment of PVC at 300 and 400°C, respectively.

aromatic C–H bonds at 3000–3100 cm^{-1} for the modified pitch obtained at 300°C is lower than for the pitch obtained at 400°C.

The possible cause of higher intensity of aromatic C–H vibration bands at 3000–3100 cm^{-1} relative to the intensity of aliphatic C–H vibration bands at 2850–2925 cm^{-1} for the modified pitches obtained at 300°C may be weaker IR absorption of $–CH_2–$ groups incorporated in three-dimensional cross-linked structures of the PVC pitch obtained at 300°C. This assumption was confirmed by recording the IR spectra of model mechanical mixtures of HTP and PVC pitches obtained at 300 and 400°C.

Comparison of the properties of the modified pitches obtained by heat treatment for 60 and 120 min (Table 2) shows that, at 300°C, an increase in the heat treatment time to 120 min strongly increases the

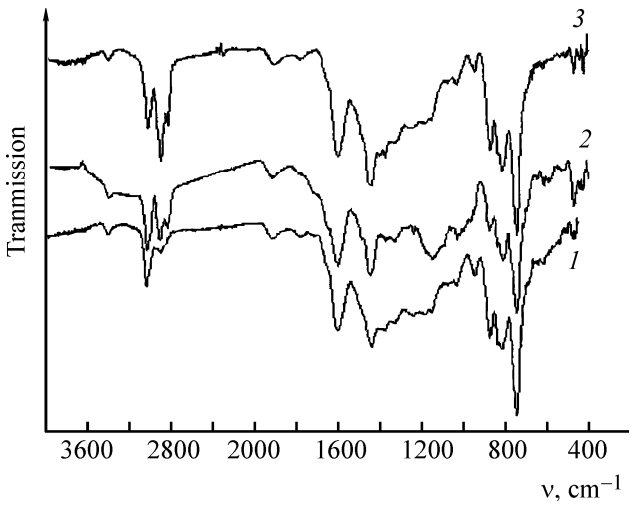

Fig. 3. IR spectra of (*1*) HTP and of modified pitches obtained by pyrolysis of 1 : 1 mixture of HTP and PVC at (*2*) 300 and (*3*) 400°C for 120 min.

softening point of the modified pitch. This may be due to an increase in the extent of cross-linking of the oligomeric molecules. The other properties change insignificantly.

An increase in the time of heat treatment of a PVC–coal tar pitch mixture at 400°C somewhat decreases the softening point, α-fraction content, and yield of volatiles. These changes may be associated both with chemical changes in the structures obtained by the reaction of thermal degradation products of PVC and pitch and with more efficient removal of low-boiling compounds from the reactor.

To determine whether nonadditive changes in the properties of the modified pitches are due to reaction of primary products of PVC thermal degradation with components of coal tar pitch or to reaction of PVC pitches with coal tar pitch, we performed experiments on heat treatment of mixtures of PVC pitches and coal tar pitch. The characteristics of the products we obtained are given in Table 2.

The α-fraction content and yield of volatiles for the modified pitch obtained at 300°C at a PVC pitch (obtained at 300°C) to HTP ratio of 1 : 2 differs from the calculated additive values insignificantly: 63 against 37% and 58.5 against 60%, respectively, and with the PVC pitch obtained at 400°C, at the same ratio of PVC pitch to HTP, these characteristics coincide with the calculated additive values (23 and 56%).

The pitches prepared at 400°C by heat treatment of mixtures of preliminarily prepared PVC pitches with HTP have a considerably lower α-fraction content and higher yield of volatiles, compared to the pitches prepared by the heat treatment of HTP with straight PVC at 400°C. For the modified pitch prepared by heat treatment of HTP with PVC pitch obtained at 300°C, these parameters are somewhat higher, as for the pitch prepared by the heat treatment of HTP with PVC at 300°C.

CONCLUSIONS

(1) Pyrolysis of polyvinyl chloride in the medium of coal tar pitch occurs at a higher rate, and the temperature of thermal dehydrochlorination is lower, as compared to the pyrolysis of polyvinyl chloride taken separately.

(2) Primary products of thermal degradation of polyvinyl chloride actively react with components of coal tar pitch. The content of high-molecular-weight α-fraction in the modified pitches increases, and the physical and coking characteristics of the pitch change.

(3) Preparation of pitches with a high α-fraction content and a low content of compounds insoluble in quinoline seems promising for the use in production of graphitic articles and carbon composites.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 08-08-00260-a).

REFERENCES

1. *Marketingovoe issledovanie rynka polimernykh otkhodov: Obzor Departamenta marketingovykh issledovanii RESEARCH* (Marketing Study of Polymer Waste Market: Review of the RESEARCH Department of Marketing Studies), TECHART, 2007.
2. Shah, N. and Huffman, G.P., *Energy Fuels*, 2005, vol. 19, pp. 1580–1586.
3. Bernardiner, M.N. and Sapfirov, E.S., *Khim. Prom–st*., 1996, vol. 73, no. 6, pp. 60–67.
4. Vehlow, J., Bergfeldt, B., and Hunsinger, H., *Waste Manag. Res*., 2006, vol. 24, pp. 404–420.
5. Minsker, K.S. and Fedoseeva, G.T., *Destruktsiya i stabilizatsiya polivinilkhlorida* (Degradation and Stabilization of Polyvinyl Chloride), Moscow: Khimiya, 1972.
6. Zevenhoven, R., Axelen, E.P., and Hupa, M., *Fuel*, 2002, vol. 81, no. 4, pp. 507–510.
7. Otani, S., *Carbon*, 1965, vol. 3, pp. 31–34.
8. Qiao, W.M., Song, Y., Yoon, S.H., et al., *Carbon*, 2005, vol. 43, pp. 2022–2025.
9. Qiao, W.M., Yoon, S.H., Korai, V., et al., *Carbon*, 2004, vol. 42, pp. 1327–1331.
10. Qiao, W.M., Yoon, S.H., Mochida, I., and Yang, J.H., *Waste Manag. Res*., 2007, vol. 27, no. 12, pp. 1884–1890.
11. Mochida, I., Toshima, H., Korai, V., and Matsumoto, T., *J. Mater. Sci.,* 1988, vol. 23, pp. 670–677.
12. Ali, M.F. and Siddigni, M.N., *J. Anal. Appl. Pyrol*., 2005, vol. 74, pp. 282–289.
13. Privalov, V.E. and Stepanenko, M.A., *Kamennougol'nyi pek* (Coal Tar Pitch), Moscow: Metallurgiya, 1981.

14. Fialkov, A.S., *Uglerod, mezhsloevye soedineniya i kompozity na ego osnove* (Carbon and Intercalation Compounds and Composites Based on It), Moscow: Aspekt, 1997.
15. Nakanishi, K., *Infrared Absorption Spectroscopy, Practical,* San Francisco: Holden-Day, 1962.
16. Ma, S., Lu, J., and Gao, J., *Energy Fuels*, 2004, vol. 16, pp. 338–342.
17. Matushek, G., Milanov, N., and Kettrup, A., *Thermochim. Acta*, 2000, vol. 361, pp. 77–84.
18. Troitskii, B.B. and Troitskaya, L.S., *Usp. Khim*., 1985, vol. 54, no. 8, pp. 1287–1311.
19. Marongiu, A., Faravelli, T., Bossana, G., et al., *J. Anal. Appl. Pyrol*., 2003, vol. 70, pp. 519–553.
20. Bacalogiu, R. and Fisch, M., *Polym. Degrad. Stab*., 1995, vol. 47, no. 1, pp. 33–57.
21. Beltran, M. and Marcilla, A., *Eur. Polym. J.,* 1997, vol. 33, no. 7, pp. 1135–1142.
22. Chirinos-Padron, J.A. and Von Schoettler, G.A., *Polym. Degrad. Stab*., 1991, vol. 33, pp. 213–227.