JANUSZ ZIELIŃSKI[1)], JERZY POLACZEK[2)], DOROTA DOBRZYŃSKA[2)], TOMASZ ZIELIŃSKI[2)],
STANISŁAW DUBRAWSKI[3)], ZOFIA MACHOWSKA[2)]

Hydrocarbon resin/polymer blends as precursors of lustrous carbon

RAPID COMMUNICATION

Summary — Ternary hydrocarbon resin/expanded polystyrene/poly(vinyl chloride) (HR/EPS/PVC) blends and hydrocarbon resin/expanded polystyrene/polycyclic aromatic hydrocarbons (HR/EPS/PAH) were prepared. Softening point and lustrous carbon yield of the blends were studied to evaluate their applicability as lustrous precursors for molding sands manufacturing. The softening points of the blends increased while the lustrous carbon yield showed a flat maximum with increasing of poly(vinyl chloride) content. Both softening point and lustrous carbon yield decreased with increasing temperature of the blending.

Key words: hydrocarbon resin, expanded polystyrene, poly(vinyl chloride), polycyclic aromatic hydrocarbons, blends, lustrous carbon, softening point.

The hydrocarbon resins (HRs) are the oldest and cheapest commercially produced polymers [1]. In the past, coal-derived raw materials were used for HRs manufacturing. Today, petroleum-derived feedstocks play a crucial role in the production of HRs.

The petroleum-derived aromatic HRs are complex low molecular weight copolymers of styrene, α-methylstyrene, vinyl toluenes, indene and methylindenes. They are produced and separated from the liquid residues of thermal or catalytic cracking of straight-run gasoline or aromatic extracts of lubricating oils.

Among many other uses, HRs are added to molding sands as precursors of lustrous carbon (LC), improving the smoothness of the mold and cast surfaces. Their applicability in this area is, however, strongly limited because of the relatively low softening temperatures. After the resin-containing sand mold has been contacted with a hot liquid metal, the resin is destructed to volatile species decomposing then to elementary carbon, hydrogen and low molecular weight hydrocarbons. The carbon is deposited on the sand wall of the mold as LC, the other volatiles leave *via* ventilation systems. The higher is the yield of the elementary carbon, the more efficient is the resin applied for. The chemistry of LC formation has never been studied in detail.

The purpose of this study is to define the influence of other polymers, as example poly(vinyl chloride) or polystyrene, in blends with HRs on softening point and LC yield during the blends pyrolysis. Softenig point of HRs/polymer blend is an important feature because when it is too low (<100 °C) the disturbances in a mill work during molding sand homogenization occur. A method of the blends preparation has been developed [2—4]. Some polycyclic aromatic hydrocarbons (PAHs) were used as model substances.

EXPERIMENTAL

Materials

Hydrocarbon resins were made by *in-situ* thermal polymerization of unsaturated compounds contained in a heavy ("clarified") oil from catalytic cracking residues (OR) and in a furfural extract (FE) of middle petroleum distillates, both supplied by the Polish Petroleum Concern Orlen SA, Płock (Poland). Expanded polystyrene (EPS) waste and suspension S-67 poly(vinyl chloride) (PVC) product of Polish Chemical Work Anwil SA, Włocławek (Poland) were used as high-polymeric components of the blend. Acenaphthene (AC) and fluoranthene (FL), both Fluka's pure reagents, and anthracene (AN) 95 % of purity, POCh, Gliwice (Poland) reagent, were used as PAHs in the study.

[1)] Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry, Institute of Chemistry, ul. Łukasiewicza 17, 09-400 Płock, Poland.
[2)] Industrial Chemistry Research Institute, ul. Rydygiera 8, 01-793 Warszawa, Poland.
[3)] Industrial Institute of Electronics, ul. Długa 44/50, 00-241 Warszawa, Poland.

Preparation of the blends

The components were blended in a stirred 750 mL glass reactor at weight ratio of HR:EPS:PAH = 50:50:10, at 150 °C for 1—3 h or at weight ratio of HR:EPS:PVC = 50:50:0-to-20 at 150—250 °C until complete homogenization of the mixture took place. Small amounts of organic volatiles (styrene monomer) and/or some remarkable amounts of hydrogen chloride were detected in the outlet gas.

Methods

The blends were tested for softening point (Mettler) and for LC precursors (LC yield) determination. The yield of lustrous carbon was determined according to a German standard [5] by using a newly constructed original automatic AWB-500/1000 device [6—8].

LC formation capacities of individual blend components are shown in Table 1.

Table 1. Properties of individual components of the blends

Component		Softening/ melting point, °C	LC yield, %
HR	OR	viscous liquid	below 50
	FE	viscous liquid	below 50
Polymer	EPS	149$^{*)}$	65.0
	PVC	n.d.	n.d.
PAH	AC	95$^{**)}$	71.6
	AN	218$^{**)}$	65.9
	FL	111$^{**)}$	68.3

$^{*)}$ Ring&Ball method. $^{**)}$ Melting point (literature data [9]).
n.d. — not determined.

RESULTS

HR/EPS blends showed higher softening points and LC yields than the pure HRs but lower than the pure EPS. The additivity rule could be applied to estimate the blend properties. The softening points of the blends increased but LC yields decreased as the time of the blending was prolonged (Table 2). This phenomenon can be explained by chemical changes (polycondensation) occurring during the blending at elevated temperatures.

Table 2. Properties of HR/EPS blends (50/50) prepared at 150 °C

Kind of HR	Blending time, h	Blend yield, %	Softening point, °C	LC yield %
OR	1	95.0	102.7	58.8
	2	95.0	116.1	56.6
	3	91.0	120.3	55.9
FF	1	99.1	88.2	53.4
	2	99.0	91.3	52.3
	3	98.7	101.1	50.6

Table 3. Properties of HR/EPS/PAH (50/50/10) blends

PAH	HR	Softening point, °C	LC yield, %
No	OR	116.1	56.6
	FE	91.5	52.3
AC	OR	128.3	70.5
	FE	127.4	60.5
AN	OR	135.6	63.3
	FE	139.6	59.5
FL	OR	192.7	58.8
	FE	194.8	57.4

A relatively small addition of PAHs to HR/EPS blends resulted in a substantial increase in both softening point and LC yield (Table 3). The increase was much higher than expected on the additivity basis.

The ternary HP/EPS/PVC blends showed increasing softening points and LC yields when compared with PVC-free ones. The softening point increased as PVC content in the blend was raised and the time of blending protracted (Figs. 1 and 2). LC yield decreased as the time of blending was prolonged and showed a flat maximum at 2—3 phr of PVC/(HR+EPS) (Figs. 3 and 4).

An increase in the blending temperature was disadvantageous both for the softening points and LC yields

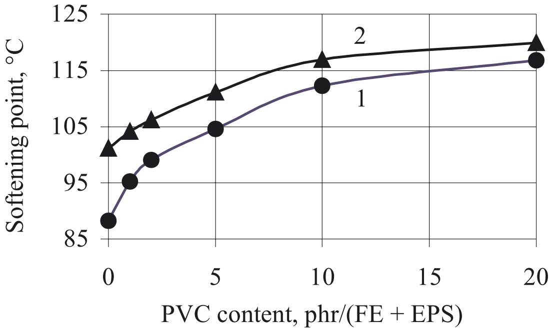

Fig. 1. Effect of PVC content on softening point of FE/EPS/PVC mixtures blended at 150 °C; blending time: 1 — 1 h, 2 — 3 h

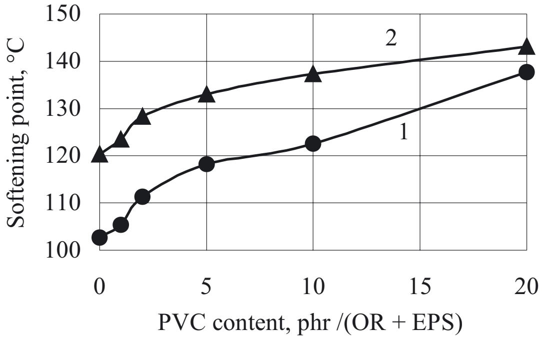

Fig. 2. Effect of PVC content on softening point of OR/EPS/PVC mixtures blended at 150 °C; symbols of curves as in Fig. 1

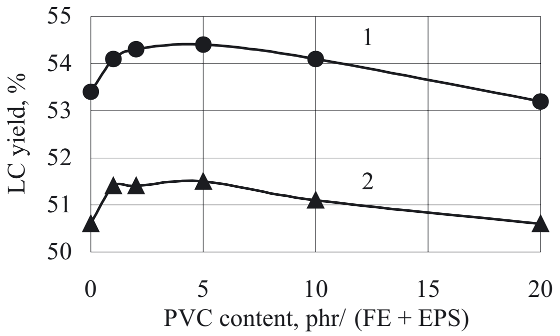

Fig. 3. Effect of PVC content on LC yield of FE/EPS/PVC mixtures blended at 150 °C; symbols of curves as in Fig. 1

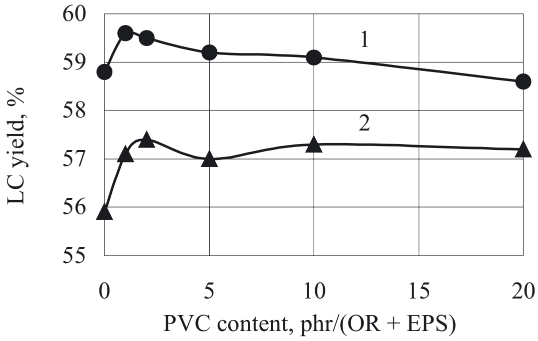

Fig. 4. Effect of PVC content on LC yield of OR/EPS/PVC mixtures blended at 150 °C; symbols of curves as in Fig. 1

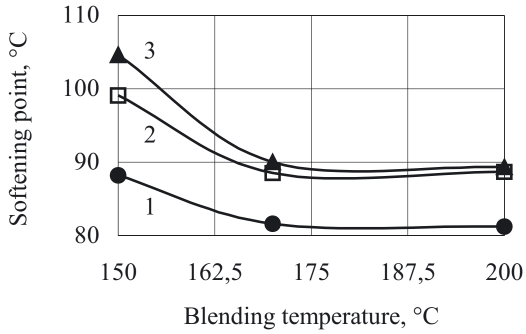

Fig. 5. Softening point of FE/EPS/PVC mixtures in relation to blending temperature. Blending time 1 h, PVC content: 1 — none, 2 — 2 wt. %, 3 — 5 wt. %

of the blends (decreased). This relationship was observed both for the PVC-free and for PVC-containing blends (Figs. 5 and 6).

CONCLUSIONS

The hydrocarbon resin/polymer blends constitute a new class of lustrous carbon-forming materials of practical importance. During the blending, chemical transformations take place. They result in changing of softening points and lustrous carbon yields of the blends. They have to be prepared at temperature below 150 °C and short blending time (below 1 h) to maximize the yield of lustrous carbon.

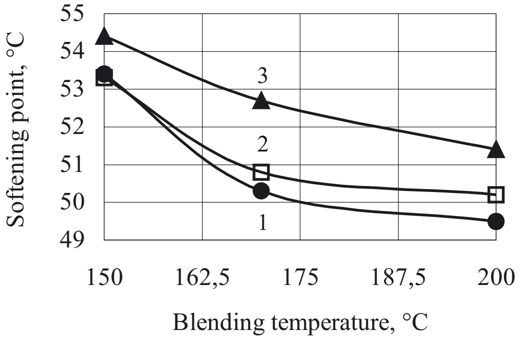

Fig. 6. LC yield of FE/EPS/PVC mixtures in relation to blending temperature. Blending time 1 h, symbols of curves as in Fig. 5

The study was performed as a part of the Polish State Committee for Scientific Research (KBN) Project No 4 T08E 050 22. The rheological properties of the blends, their environmental issues and applicability in sand molds manufacturing will be reported elsewhere.

REFERENCES

1. Mildenberg R., Zander M., Collin G.: "*Hydrocarbon resins*", International Resins Club, Frankfurt/Main 2002.
2. Polaczek J., Machowska Z., Zieliński J., Dobrzyńska D.: International Conference of New Carbon Materials, Ustroń—Jaszowiec, January 1999, proceedings, Paper 13.
3. Zieliński J., Polaczek J., Osowiecka B., Machowska Z.: 38th Macromolecular IUPAC Symp., Warsaw 9—14 July 2000, Vol. III, p. 1387.
4. Zieliński T., Zieliński J., Dobrzyńska D., Polaczek J.: Tworzywa Sztuczne i Chemia 2004, No 1, 8.
5. Verein Deutscher Giessereifachleute: VDG-Markblatt "*Bestimmung von Glanzkohlenstoff*" P 85, Duesseldorf 1980.
6. Industrial Inst. of Electronics, Warsaw, PL, Automatic AWB-50/1000 Analyzer, a leaflet.
7. Dubrawski S., Sawicki J., Nowicki G., Polaczek J., Dobrzyńska D., Witowski A.: *Inż. Mat.* 2003, 10, 287.
8. Zieliński T., Zieliński J., Dobrzyńska D., Polaczek J., Dubrawski S.: *Tworzywa Sztuczne i Chemia* 2003, No 4, 22.
9. Franck H.-G., Stadelhofer J. W.: "*Industrial aromatic chemistry*", Springer, Berlin 1988.

Received 20 X 2004.