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THERMORHEOLOGICAL STUDIES ON POLYMERIC BLENDS

*Wiesława Ciesińska**

Warsaw University of Technology, Institute of Chemistry, Łukasiewicza 17, 09-400 Płock, Poland

Two petroleum-derived aromatic hydrocarbon resins (HRs) were blended (1:1) with expanded polystyrene (EPS) waste and small amounts (up to 10 mass%) of poly(vinyl chloride) (PVC) to increase both the lustrous carbon (LC) yield and softening point of the blends without any deterioration of their rheological characteristics. The blends were prepared and tested for LC content, softening points, shear stress and apparent viscosity to check their applicability as LC precursors under industrial conditions.

The properties of polystyrene compositions with bitumen fractions depend primarily on composition and viscosity of oil fraction. Additional modification by poly(vinyl chloride) improves the blends' properties, like bright coal content, softening point and viscosity, and opens new possibilities of plastics' wastes utilization.

Keywords: *expanded polystyrene, polymeric blends, poly(vinyl chloride), thermorheological properties*

Introduction

Bitumen substances, including heavy oil ends, are valuable raw materials for obtaining materials with wide scope of use in many fields of economy like building industry, highway engineering, motorization. Increasing requirements, connected with quality of these materials, force to do modifications of bitumens properties, give them expected using properties conditioned by requirements and place of use. Especially positive changes of using properties of bitumens can be obtained by their physical modifications by polymer additives [1]. It concerns especially modifications of oil asphalts and coal-tar pitches. The role of trade polymers as bitumens modifiers is more often taken by adequate type plastics wastes.

The tests of use, for example wastes of bitumens from secondary processing of oil, as by-products, like furfural extract or pyrolytic oil, for obtaining using materials were made during last few years. Polymer-bitumen mixtures were considered in aspect of plastics wastes utilization [2–5] and recepis preparation for insulating and flooding sands for building industry and binders for briquetting loose materials for metallurgy and coke engineering. Products like resins characterized by increased bright coal content are made in preliminary mild thermolysis process, what has special meaning in foundry engineering [6–8].

Carriers of bright coal are an important component of modern moulding sand in foundry engineering.

Effectiveness of carriers of bright coal in processes in foundry engineering depends not only on the content of this coal, but also on its thermal and rheological properties.

The aim of the researches was to determine thermal and rheological properties of expended polystyrene or poly(vinyl chloride) compositions and preliminary estimation of these compositions as precursors of bright coal.

Experimental

Materials

Hydrocarbon resins were made by *in-situ* thermal polymerization of unsaturated compounds contained in a heavy (clarified) oil from catalytic cracking residues (OS) and in a furfural extract of middle petroleum distillates (EF), both supplied by the Polish Petroleum Concern ORLEN, Płock. EPS waste and suspension S-67 PVC, product of ANWIL S.A., Włocławek, PL, were used as high-polymeric components of the blends.

Preparation of blends

The components were blended in a stirred 750 mL glass reactor at the mass proportion of HR:EPS:PVC= 50:50:0-to-20 at 150°C for 2 h 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. The blends were primarily tested for softening point (Mettler) and for LC precursors (Table 1).

* w.ciecinska@pw.plock.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 The selected properties of the polymeric blends

Composition/mass%		Thermolysis yield/%	LC yield/%	Softening point/°C			Fraction of structural viscosity in apparent viscosity (110°C)	Flow activation energy (shear rate 1 s^{-1})/kJ mol^{-1}
Blend	PVC			Mettler	Vicat	Ring&Ball		
Blend OS/EPS (1:1)+PVC								
100	0	95.0	56.6	116.1	30.4	87.0	50.6	81.92
99	1	92.3	57.7	118.9	29.3	87.0	70.2	57.17
95	5	91.4	58.2	131.7	35.0	103.0	54.6	137.93
90	10	83.2	58.4	134.4	53.6	111.5	97.8	80.22
Blend EF/EPS (1:1)+PVC								
100	0	99.0	52.3	91.5	52.4	103.5	50.4	–
90	10	92.0	53.2	116.4	42.7	90.0	98.7	–

Analytical procedures

Softening points of the blends were determined according to:

- Ring-and-Ball (R&B) method (PN-EN 1427, 2001), an automated RK 2 device with electromagnetic release of the ball (prod. Petrotest Instruments GmbH and CoKG) was used.
- Vicat method (PN-93/C-89024, method A), Vicat device type FWV 633.10 with 1 mm^2 needle (German product) was used. Rectangular samples of the blends (10×15×4 mm) were prepared by pressing at 140°C (EF/EPS), 85°C (EF/EPS/ 10%PVC, OS/EPS and OS/EPS/1%PVC) or 100°C (OS/EPS/5%PVC) under 15 to 100 kg cm^{-2} for 15 s to 3 min. For determination of Vicat softening points, the load of 10 N and heating rate 50°C h^{-1} were used.
- Mettler method (ASTM D3104) an FP900 system (product of Mettler Toledo) was used.

The yield of lustrous carbon was determined according to German Standard by using a newly constructed automatic AWB-500/1000 device [9, 10].

The rheological properties of the blends were determined on the rheoviscometer Rheotest RN 3.1 (product of Haake Meidingen Germany). Measurements were carried out under controlled shear rate at changing temperatures (90–150°C). The shear rate was changed up to 1000 s^{-1}. Flow curves, temperature and shear rate relationships of dynamic viscosity, and thixotropic properties were determined for each blend. The temperature relationship of viscosity was determined at shear rate 1 s^{-1} at 90–150°C and described by the Arrhenius equation: $\eta=Ae^{E/RT}$, where E denotes the efficient activation energy of viscosity, J mol^{-1}; R is gas constant; and A is a constant depending on the medium studied. From the $\ln\eta=(1/T)$ curve, the activation energy of flow was calculated after linearization: $\ln\eta=\ln A+E/RT$. Thixotropic properties were evaluated by applying hysteresis loop test.

Results and discussion

Results of the studies of blends are collected in Table 1.

In OS/EPS/PVS blends, PVC added had a substantial effect on the softening points T_V, $T_{R\&B}$ and T_M, as compared with PVC-free OS/EPS blend. Mettler softening point increased from 116.1°C for OS/EPS to 134.4°C in the blend containing 10 mass% of PVC. Simple relationships between the particular softening points $T_M=T_{R\&B}+28.15$ and $T_{R\&B}=T_V+45.9$ were established to hold over the whole range of PVC contents. The strength of the blends increased in parallel with increasing PVC content. This can be explained by an inhomogeneity of the system containing PVC.

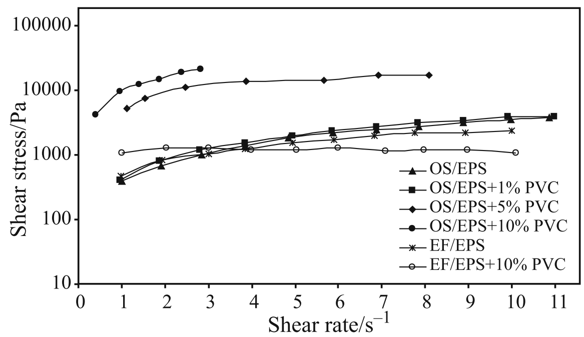


Fig. 1 Flow curves of the OS/EPS and OS/EPS/PVC blends at 110°C

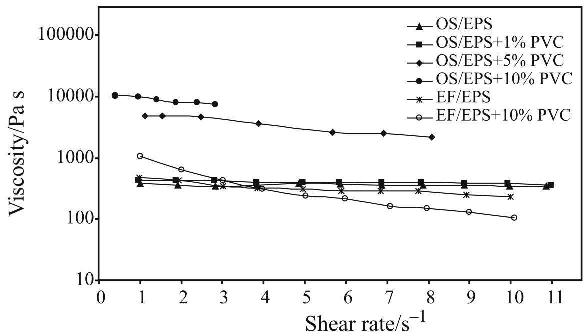


Fig. 2 The effect of shear rate on the viscosity of polymeric blends at 110°C

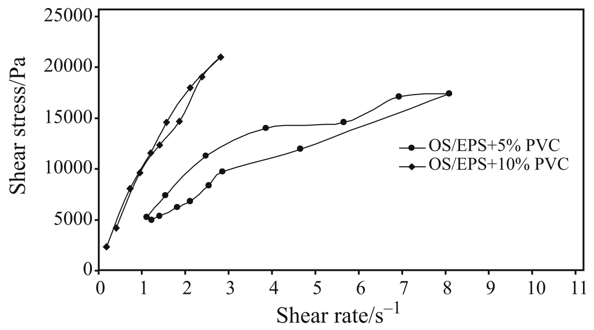
As expected, EF/EPS/PVC blends were found to be less convenient for their use as LC precursors in foundry engineering. PVC addition indeed resulted in the increase in Mettler softening point (from 91.5 to 116.4°C), but the R&B and Vicat softening points decreased from 103.5 to 90°C and from 52.4 to 42.7°C, respectively. The system was inhomogeneous.

The selected results of viscosity studies of OS/EPS/PVC and EF/EPS/PVC blends are presented in Figs 1 and 2.

For the OS/EPS/PVC blends, the measurements at 90°C were possible only for the PVC-free blends and blends containing 1 mass% of PVC. The other blends were studied at higher temperatures (up to 150°C). The OS/EPS/PVC blends were typical shear-thinned non-Newtonian liquids. Their shear range became broader as the temperature of measurement was raised. The rheological behavior of the blends was described by the Bingham and Ostwald de Waele models.

Temperature relationships of apparent viscosity were determined for each blend studied. The linearized relationship $\ln\eta=f(1/T)$ was used for determining the flow activation energy in the OS/EPS blends and EF/EPS blends (Table 1). No correlation was established between the PVC content and the flow activation energy.

The course of hysteresis loops (determined at 110°C) pointed to the thixotropic properties of the OS/EPS blends and EF/EPS blends (Fig. 3). Similar



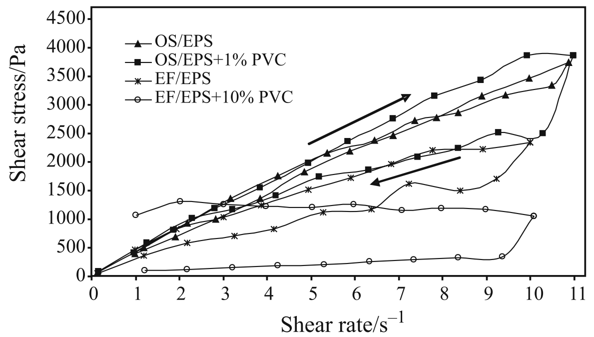


Fig. 3 Hysteresis loops determined for the polymeric blends at 110°C

courses of the hysteresis loops were also observed at higher temperatures.

Addition of PVC to the OS/EPS blends resulted in a substantial change of their rheological properties. The range of shear rates where measurements were possible narrowed, the resistance of the blends against shearing decreased with increasing temperature. The blends showed properties of shear-thinned non-Newtonian fluids with a flow limit. The addition of PVC resulted also in an increase in the blend viscosity.

Addition of PVC to the EF/EPS blends gave similar effects. The PVC-containing blends showed also properties of a shear-thinned non-Newtonian fluid.

The fraction of structural viscosity in the apparent viscosity (as calculated from the formula: $\%\eta_{str}=100(\eta_{max}-\eta_{min})/\eta_{max}$, where η_{str} is the structural viscosity, Pa s, η_{max} maximum apparent viscosity, Pa s; and η_{min} minimum apparent viscosity, Pa s) are given in Table 1. The internal structure of the blends and the interaction between their components were destroyed under action of the shearing stress-inducing forces. The lowest fraction of the structural viscosity in the apparent viscosity was found at 110°C in the PVC-free blend (about 50%). The shear rate velocity relationships of the apparent viscosity of the EF/EPS blends showed a course similar to the formerly presented relationships of the OS/EPS blends. The function $\ln\eta(1/T)$ for the PVC-free EF/EPS blend had a linear course. The flow activation energy was determined and values are given in Table 1. Rheological parameters of the blends are available elsewhere.

Addition of PVC (10 mass%) to the EF/EPS blend resulted in a dramatic change of its rheological properties. The PVC-containing blend behaves as a typical rheologically unstable, shear-thinnable non-Newtonian fluid. The EF/EPS/PVC blend showed structural viscosity η_{str} higher than 98% over the whole range of measurement temperatures. The $\ln\eta$ $(1/T)$ relationship was non linear and, therefore, the flow activation energies could not be determined.

Conclusions

The blends of petroleum-derived HRs with EPS, especially those improved by addition of PVC, showed not only an increased yield of lustrous carbon and preferable softening points but also an advantageous rheological characteristics.

The type of bitumen fraction influence the properties of bitumen-polymer compositions, particularly flowability depended on the temperature and elements of operative shearing forces and high temperature load resistance.

Composition containing expended polystyrene and cleared oil is characterized by higher bright coal content and softening point, compared to furfural extract-expanded polystyrene compositions. Simultaneously compositions containing cleared oil undergoes a deformation easier in all temperatures of measurement under the influence of shearing forces and is characterized by lower viscosity.

Modification by poly(vinyl chloride) of furfural extract-expanded polystyrene composition causes the increase of Mettler softening point and bright coal content. Simultaneously the homogeneity of mixture deteriorates with PVC addition. Composition containing furfural extract, expended polystyrene and poly(vinyl chloride) is a heterogeneous mixture.

Poly(vinyl chloride), added to cleared oil-expanded polystyrene composition, influence the increase of softening point and bright coal content. Besides, the addition of poly(vinyl chloride) increases the shear stress resistance, viscosity and improves thixotropic properties of composition. Thermal-rheological properties of cleared oil-expanded polystyrene composition change regularly with the increase of modifier quantity.

Cleared oil-expanded polystyrene-poly(vinyl chloride) compositions are macroscopic homogeneous mixtures, which viscosity decreases with the increase of the temperature.

It can be assumed that differences of polystyrene with bitumen fractions compositions properties comes from different oil fraction content and their viscosity.

The OS-derived HRs were found much more convenient for the manufacturing lustrous carbon carriers than the EP-derived ones. Therefore, the OS/EPS/PVC blends can be recommended as useful raw materials for making high-quality molding sands for use in foundry engineering.

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