The rheological properties of coal bitumens modified by polyesters *(Rapid Communication)*

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Abstract: The purpose of testing was to find changes of rheological properties of coal-tar pitch (CTP) due to modification with chosen polyesters. Poly(ethylene terephthalate) (PET), unsaturated polyester resin (UP) and polycarbonate (PC) were selected for testing. Polymers, in the amounts of 10 and 25 wt %, were mixed with CTP under conditions considered optimal for each modifier type. Properties of CTP-polymer compositions were assessed based on their softening point, content of components insoluble in toluene and quinoline and on rheological properties. Distinct changes of rheological properties, especially changes in viscosity versus shear rate and temperature, as well as viscoelastic properties were observed as results of modifications with all used polyesters. The modification effects became more intensive with increasing amount of the modifier added to CTP.

Keywords: coal-tar pitch, polyesters, modification, rheological properties.

Właściwości reologiczne bitumów węglowych modyfikowanych poliestrami

Streszczenie: Celem badań było określenie zmian właściwości reologicznych paku węglowego (CTP) na skutek modyfikacji poliestrami: poli(tereftalanem etylenu) (PET), nienasyconą żywicą poliestrową (UP) oraz poliwęglanem (PC). Polimery te, w ilości 10 i 25 % mas. mieszano z pakiem w warunkach uznanych za optymalne dla każdego rodzaju modyfikatora. Właściwości kompozycji CTP-polimer oceniono na podstawie ich temperatury mięknienia, zawartości składników nierozpuszczalnych w toluenie i chinolinie oraz właściwości reologicznych. W przypadku każdego poliestru modyfikacja powodowała wyraźne zmiany właściwości reologicznych, w tym zmiany lepkości ze wzrostem szybkości ścinania i temperatury oraz właściwości lepkosprężystych. Efekty modyfikacji nasilały się ze zwiększeniem ilości modyfikatora dodawanego do CTP.

Słowa kluczowe: pak węglowy, poliestry, modyfikacja, właściwości reologiczne.

Particularly important features, especially from the point of view of possible applications of bituminous substances are rheological properties [1]. They allow assessing the performance and suitability of the material for the specific application.

On the other hand, they may indicate changes in materials due to various physical and chemical factors [2, 3]. Modification of bitumen petroleum and coal is now widely used to improve their properties, leading to the preparation of materials that meet the increasingly high quality requirements. In the case of bitumen of coal origin, *i.e.* coal-tar pitch, modification is carried out usually in order to increase its heat resistance, to obtain a suitable viscosity under high-temperature preparation of carbon materials [1].

One way of modification of the coal-tar pitches is mixing them with various macromolecular compounds, and polymer waste. Depending on the physical and chemical modifiers, they can cause various changes in the colloidal structure of the bitumen and thus affect its rheological properties [4, 5].

The aim of this work was to determine the effect of modification of coal-tar pitch with the poly(ethylene terephthalate), unsaturated polyester resin or polycarbonate on selected rheological and physico-chemical properties of the materials obtained.

EXPERIMENAL PART

Materials

The coal-tar pitch (CTP) in granular form supplied by Institute for Chemical Processing of Coal (Zabrze, Poland) was used in this study. As modifiers, the following polymers were selected:

— poly(ethylene terephthalate) (PET), produced by Indorama Polymers Poland Sp. z o.o.,

— unsaturated polyester resin „Estromal 103E" (UP) produced by Zakłady Tworzyw Sztucznych ERG S.A. in Pustków (Poland),

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T a b l e 1. The conditions of preparation, physicochemical and selected rheological properties of CTP/polyester compositions

Composition	Conditions of preparation		Physicochemical properties				Rheological properties		
	temp., °C	time, min	*ST*, °C	*TI*, wt %	*QI*, wt %	*CV*, wt %	η^*_{min}, Pa · s	$T\eta^*_{min}$, °C	$T_{G'=G''}$, °C
CTP	—	—	107.0	34.21	7.14	53.0	3.01	192.6	264.0
CTP+10 wt % PET	260	30	128.0	55.18	13.31	53.62	75.80	217.2	130.0
CTP+25 wt % PET	260	30	141.0	63.04	29.43	50.10	125.30	253.0	194.0
CTP+10 wt % UP	100—105	30	88.0	51.13	5.43	49.60	1.35	182.9	260.0
CTP+25 wt % UP	100—105	30	86.0	66.35	4.34	49.35	8.05	209.2	206.0
CTP+10 wt % PC	220	60	117.5	43.00	6.03	46.70	1.24	206.7	278.0
CTP+25 wt % PC	255	60	120.0	34.20	7.14	40.70	0.47	270.4	270.0

— waste polycarbonate (PC) originating from automotive industry, granulated by Drewnex Recycling Plastics Company (Poland).

Pitch-polymer compositions containing 10 or 25 wt % of polymer were prepared in the conditions allowing obtaining homogeneous and stable mixtures. Depending on the polymer applied, the components were homogenized in the temperatures ranging between 105 and 260 °C, for 30 to 60 min. The preparation conditions of all compositions are listed in Table 1.

Analytical methods

For CTP and CTP-polymer compositions the following physicochemical properties were determined:

— softening temperature (*ST*) with „ring and ball" method according to the PN-EN 1427:2001 standard;

— coking value (*CV*) according to the PN-C-97093:1993 standard;

— content of components insoluble in toluene (*TI*) according to the method elaborated in the Institute of Chemistry, Warsaw University of Technology in Plock;

— content of components insoluble in quinoline (*QI*) according to the PN-C-97058:1999 standard.

The rheological properties were examined using AR 2000 rheometer (TA Instruments Inc.) equipped with parallel plates fixture (plate radius: 2.5 cm). Measurements were carried out in the steady state mode and oscillation mode. Measurements in the steady shear mode were carried out at the temperature of 130 °C, at a controlled shear rate in the range between $1.25 \cdot 10^{-3}$ and 125 s^{-1}. Oscillation mode measurements were carried out at the temperature of 130 °C in the frequency range between 0.01 and 100 Hz. The top plate oscillated with strain amplitude of 0.25 %. Measurements in a function of temperature were carried out in the range between 80 and 300 °C, at strain amplitude of 0.5 % and frequency of 1 Hz.

RESULTS AND DISCUSION

Selected relations of the rheological properties determined for CTP-polymer compositions are presented in Figs. 1 and 2. The set physicochemical properties and selected rheological properties, *i.e.* the minimum viscosity (η^*_{min}), achieving the minimum viscosity temperature ($T\eta^*_{min}$), the temperature equalization characteristics viscous and elastic ($T_{G'=G''}$), are summarized in Table 1.

Tested unmodified CTP and CTP-polymer compositions at the temperature of 130 °C showed a non-Newtonian fluid properties and shear thinning (Fig. 1). The observed dependencies of complex viscosity, storage (*G′*)

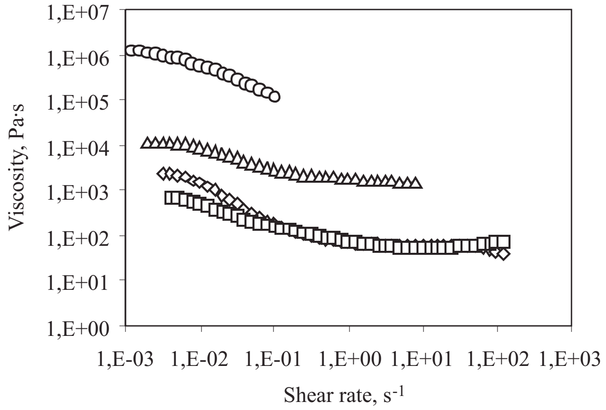

Fig. 1. Viscosity curves determined at 130 °C for CTP-polymer compositions: ◇ — CTP, □ — CTP+25 wt % PET, ○ — CTP+25 wt % UP, △ — CTP+25 wt % PC

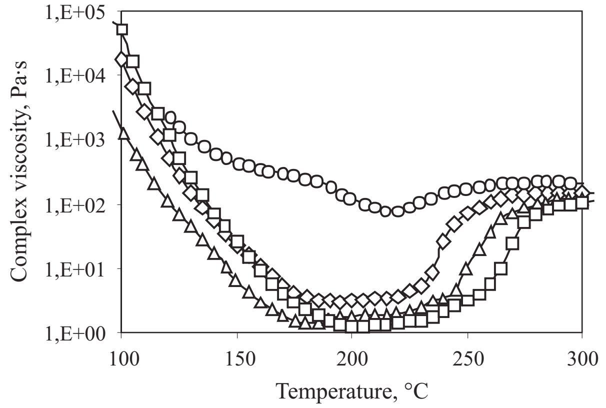

Fig. 2. The plots of complex viscosity versus temperature determined for CTP-polymer compositions: ◇ — CTP, □ — CTP+10 wt % PET, ○ — CTP+10 wt % UP, △ — CTP+10 wt % PC

and loss moduli (G'') of CTP on temperature in the range between 100 and 300 °C showed the similarity to the corresponding dependencies for thermosets. As the temperature increases the viscosity of the first decreased to the minimum value, then increased to achieve a virtually constant value. At the same time the G'' value at lower temperatures exceeded the G' value, which indicated prevailing viscous characteristics. As the temperature increases occurred equalization modules and then G' received higher values than G''. Initially, therefore there was liquefaction of CTP, and then after reaching the minimum viscosity (η^*_{min}), probably there was started the process of resolidification as a result of chemical reactions, such as polymerization or polycondensation, and evaporation of the lighter components. This led likely to increase in the average molecular weight of bitumen.

Addition of PET to CTP caused increase in *ST*, and changes in the group composition of bitumen resulted in increased quantity of components insoluble in toluene and quinoline. These changes were accompanied by significant changes in the rheological properties, escalating with increasing amount of polymer in the composition. There was a clear increase in viscosity. Compositions containing PET had a prevalence of the elastic properties in a wide temperature range. For compositions containing 10 wt % of PET this range has included temperature above 134 °C. The viscosity of CTP initially decreased with increasing temperature reaching the minimum value. Both values η^*_{min} and $T\eta^*_{min}$ were higher in the case of CTP-PET compositions compared to the unmodified CTP.

The UP resin, which is a solution of UP in styrene, added to CTP resulted in a decrease of *ST* by approximately 30 °C. The composition is prepared at the temperature of 105 °C, which prevented the crosslinking reaction of UP at the stage of preparation. The reduction of *ST* was probably due to dissolution of CTP components in styrene. Dissolution of some components in styrene may also be the cause of a decrease in the content of quinoline insoluble components (*QI*). The viscosity of the CTP-UP composition at 130 °C increased in comparison to the value determined for CTP.

Probably UP resin mixed with CTP at 130 °C has been partially crosslinked, which increased the viscosity of the composition. As in the case of CTP the viscosity of the composition first decreased with increasing temperature to a minimum value and then increased. At temperatures up to 260 °C (CTP+10 wt % UP) and 206 °C (CTP+25 wt % UP) compositions showed the advantageous characteristics of viscous ($G'' > G'$). Above these temperatures elastic properties predominated.

Addition of PC to CTP caused an increase in the *ST*. In the case of PC used as the modifier, the addition of 10 wt % of PC had a little effect on rheological properties of the composition, but slightly larger changes were observed for composition with 25 wt % of PC. The viscosities of the CTP-PC compositions were lower than the viscosity of unmodified CTP which indicated that PC caused plasticization of CTP. Similarly to the viscosity of CTP, viscosity of CTP-PC compositions decreased with increasing temperature.

CONCLUSIONS

The direction of changes in the properties of CTP after addition of different polymers from the group of polyesters depends on chemical and physical properties of the polymer applied. For all compositions with polyesters there were observed distinct changes in rheological properties, especially the viscosity changes as a function of the shear rate and temperature, as well as viscoelastic properties. For all polymers, the modification effects intensify with increasing amount of the modifier added to CTP. Among the used polymers only PC had the plasticizing effect on CTP. For other compositions an increase in viscosity was observed. The largest increase in viscosity occurred under the influence of PET, which caused an increase in the minimum value of complex viscosity attained during the heating of the bitumen and simultaneously decrease in the temperature of equalization of viscous and elastic characteristics. CTP-PET compositions in a wide temperature range have a prevalence of the elastic characteristics. Modification of CTP with polyesters changes the group composition of CTP and its thermorheological properties. Research efforts suggest that CTP-polymer compositions can be used to obtain for example carbonaceous adsorbents [6—8] or an insulating and sealing material [9]. Modification of CTP with polymers allows utilization of waste plastics and low-quality CTP.

REFERENCES

[1] Ciesińska W.: *Przem. Chem.* **2012**, *91*, 2164.

[2] Daguerre E., Nauguier F., Py X.: *Carbon* **1999**, *37*, 1189. http://dx.doi.org/10.1016/S0008-6223(98)00311-X

[3] Diaz M.C., Edecki L., Steel K.M., Patrick J.W., *et al.*: *Energy Fuels* **2008**, *22*, 471. http://dx.doi.org/10.1021/ef7004628

[4] Ciesińska W., Zieliński J., Brzozowska T.: *J. Therm. Anal. Calorim.* **2009**, *95*, 193. http://dx.doi.org/10.1007/s10973-008-9090-3

[5] Ciesińska W.: *J. Therm. Anal. Calorim.* **2008**, *93*, 747. http://dx.doi.org/10.1007/s10973-008-9193-3

[6] Ciesińska W., Makomaski G., Zieliński J., Brzozowska T., *et al.*: *Pol. J. Environ. Stud.* **2009**, *1B*, 27.

[7] Makomaski G., Ciesińska W., Zieliński J.: *Polimery* **2012**, *57*, 635. http://dx.doi.org/10.14314/polimery.2012.635

[8] Makomaski G., Ciesińska W., Zieliński J.: *J. Therm. Anal. Calorim.* **2012**, *109*, 767. http://dx.doi.org/10.1007/s10973-01-2373-8

[9] Brzozowska T., Zieliński J., Ciesińska W.: *Karbo* **2004**, *2*, 80.

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