

# COMPATIBILITY STUDIES ON POLYMER/WAX AND POLYMER/RESIN-ASPHALTENE BY VISCOMETRY AND PHOTOMICROGRAPHY\*

QIAN Jinwen (钱锦文) QI Guorong (戚国荣) DING Xinzhe (丁兴者)

and YANG Shiling (杨士林)

(Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027)

## ABSTRACT

The compatibility of mixtures of polymeric pour point depressants, i.e. poly(ethylene-co-vinylacetate) (EVA), poly(EVA-graft-octadecylacrylate) (EVA-g-POA), poly(ethylene-co-octadecylacrylate) (EOA) and poly(ethylene oxide-co-propylene oxide) (EO-co-PO) with wax or resin-asphaltene from crude oil have been studied by means of dilute-solution viscometry. It was found that each mixture pair is incompatible, but the degrees of incompatibility are quite different, which are in good agreement with the results from photomicrography.

## INTRODUCTION

Polymeric pour point depressants (PPPDs) are the main additives for viscosity reduction and pour point depression of crude oil<sup>[1]</sup>, both high viscosity and high pour point are caused by the presence of paraffin wax(W) and resin-asphaltene(RA) in crude oil<sup>[2,3]</sup>. Therefore, studying the interaction of PPPD/W and PPPD/RA are very important to understand the role of PPPD. Viscometry, being simple, requiring no expensive equipment, is an attractive method for studying the compatibility of polymer blends<sup>[4]</sup> such as homopolymer/homopolymer, homopolymer/copolymer or graft polymer, copolymer/copolymer or graft polymer, polymer/microemulsion mixtures, and some aqueous polymer blends. Several criteria have been used to assess the compatibility and interaction of polymer/polymer mixtures. The present paper attempts to using an U-interaction parameter proposed by Chee<sup>[5]</sup> to examine compatibility of PPPD with wax( $U_w$ ) or with RA ( $U_{RA}$ ).

\* This work was supported by the National Natural Science Foundation of China.

Received September 18, 1995

## EXPERIMENTAL

The wax with melt point of 49.4°C and RA with  $\overline{M}_n$  of 1160 were obtained from Daqing crude oil, which were measured by Perkin Elmer DSC-7 and Knauer membrane osmometer, respectively. Four kinds of PPPDs were synthesized in our laboratory. And their SEC data were obtained on a Waters model 150C instrument and the compositions were determined by the Carlo Erba 1106 element analyzer. All characterization data are listed in Table 1.

The viscosity measurement was conducted using an Ubbelohde dilution viscometer in xylene at 25±0.02°C.

The mixtures of PPPD/W and PPPD/RA with the weight ratio of ca. 20/80 was dissolved in toluene with the concentration of 0.5 g/dl. Then, a droplet of the solution was spread on a glass slide to form a thin layer, dried at room temperature for more than one week. The photomicrographs for mixtures of PPPD/W and PPPD/RA were taken by using Nikon Phase Contrast Achromat 0.90.

## RESULTS AND DISCUSSION

The relationship between dilute solution viscosity and polymer concentration can usually be expressed by Huggins equation,

$$\eta_{sp}/c = [\eta] + b \cdot c \quad (1)$$

where  $[\eta]$  is intrinsic viscosity, which measures the effective hydrodynamic specific volume of an isolated polymer molecule and reflects the interaction between polymer segment and solvent at infinite dilute solution, whereas the quantity  $b$  represents the interaction between two polymer segments in solution. Similarly, for mixture of two polymers (polymer 1 + polymer 2) in solution, Eq(1) becomes

$$\eta_{spm}/(c_1 + c_2) = [\eta]_m + b_m(c_1 + c_2) \quad (2)$$

Chee<sup>[5]</sup> produced an interaction parameter  $U$ , to determine polymer 1/polymer 2 compatibility

$$U = \frac{b_m - b}{2X_1X_2([\eta]_1 + [\eta]_2)} \quad (3)$$

where  $b = b_1X_1 + b_2X_2$ ,  $X_1$  and  $X_2$  are the weight fraction of polymer 1 and polymer 2.  $U > 0$  signifies compatibility of two polymers whereas  $U < 0$  indicates phase separation.

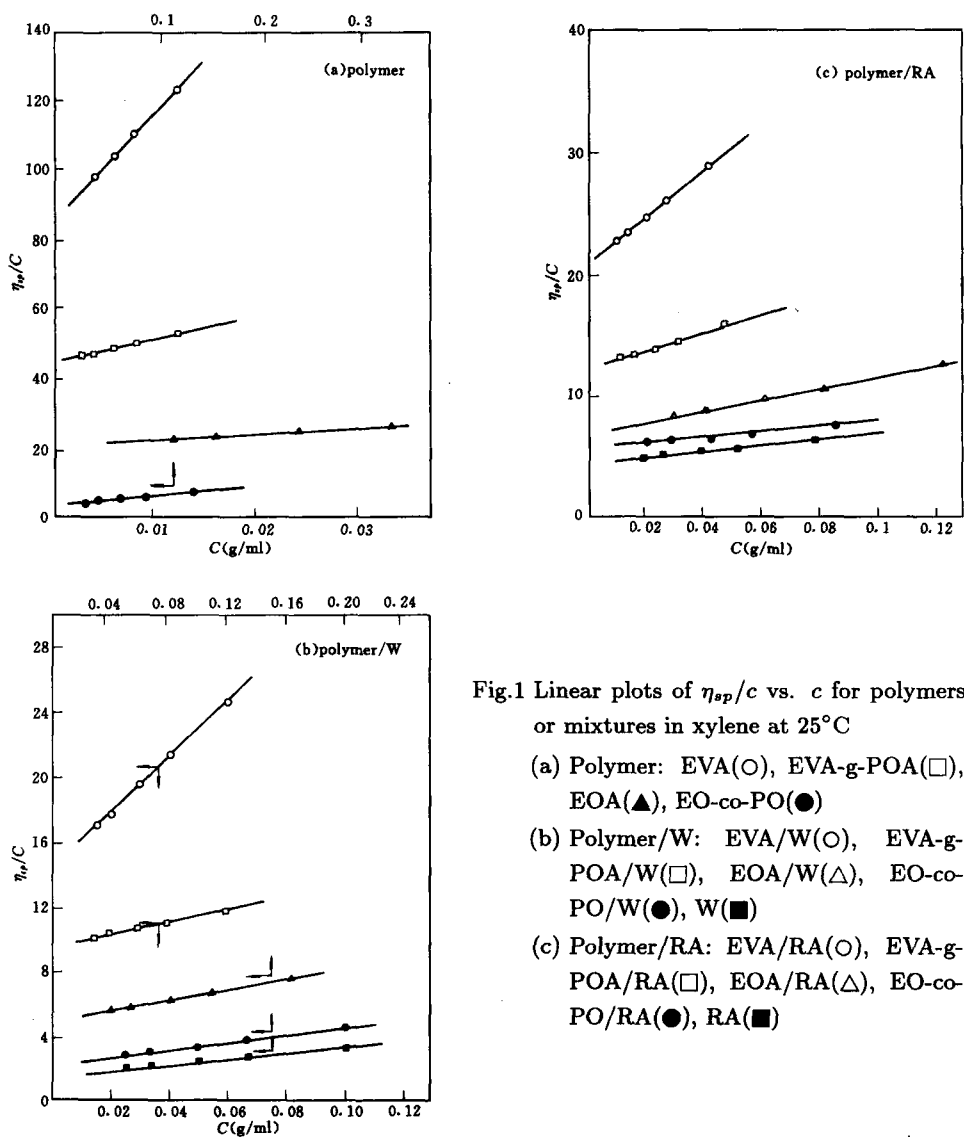


Fig.1 Linear plots of  $\eta_{sp}/c$  vs.  $c$  for polymers or mixtures in xylene at 25°C

(a) Polymer: EVA(○), EVA-g-POA(□), EOA(△), EO-co-PO(●)

(b) Polymer/W: EVA/W(○), EVA-g-POA/W(□), EOA/W(△), EO-co-PO/W(●), W(■)

(c) Polymer/RA: EVA/RA(○), EVA-g-POA/RA(□), EOA/RA(△), EO-co-PO/RA(●), RA(■)

Table 1 Data of the PPPDs characterization and U-parameters

| Polymer                         | EVA-g-POA                      | EVA      | EOA     | EO-co-PO |
|---------------------------------|--------------------------------|----------|---------|----------|
| $\overline{M}_n \times 10^{-3}$ | 32.6                           | 16.9     | 32.0    | 3.0      |
| $\overline{M}_w/\overline{M}_n$ | 9.0                            | 3.39     | —       | —        |
| Composition<br>(wt%)            | E: 59.5<br>VA: 33.5<br>OA: 7.0 | VA: 32.0 | OA: 7.0 | PO: 15.0 |
| $U_w$ (~ 80 wt% W)              | -0.180                         | -0.217   | -0.284  | -4.132   |
| $U_{RA}$ (~ 80 wt% RA)          | -0.178                         | -0.229   | -0.153  | -16.725  |

The concentration dependence of reduced viscosity,  $\eta_{sp}/c$ , of pure polymer and

wax, RA with and without 20 wt% polymer in xylene are shown in Fig.1(a-c), respectively. The intrinsic viscosity  $[\eta]$ , and slope  $b$ , were evaluated by the linear least squares treatment, then,  $U$ -parameters calculated by using Eq(3) were also given in Table 1.

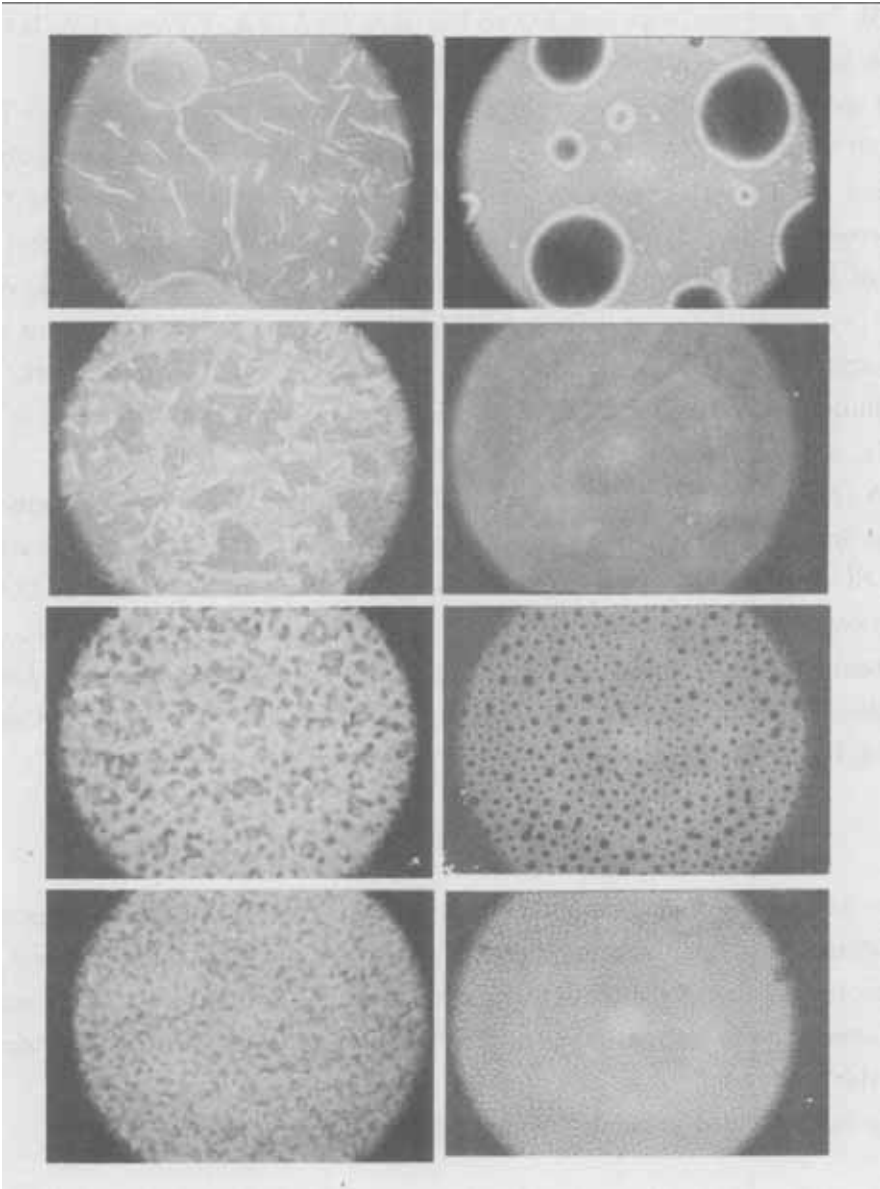


Fig.2 Photomicrographs of PPPD/W (Plate I) and PPPD/RA (Plate II) systems (400x)  
Plate I (a) EO-co-PO/W; (b) EOA/W; (c) EVA/W; (d) EVA-g-POA/W  
Plate II (a) EO-co-PO/RA; (b) EOA/RA; (c) EVA/RA; (d) EVA-g-POA/RA

It can be seen from Table 1, the  $U$  values of the mixtures for polymer/W and polymer/RA are all negative. It means that each pair of polymer/W or polymer/RA is not compatible, namely, the phase separation phenomena are existed to some extent. With increasing of  $U$  values, however, the compatibility of the mixtures becomes better and in the order of EO-co-PO/W, EOA/W, EVA/W, and EVA-g-POA/W for polymer/wax and EO-co-PO/RA, EVA/RA, EVA-g-POA/RA, and EOA/RA for polymer/RA.

Fig.2 shows the photomicrographs for the mixtures of polymer/W (plate I) and polymer/RA (plate II). All these pictures of wax and RA with ca.20 wt% polymers were taken at 25° with a photographic magnification of 400x. According to the photomicrographs of polymer/W mixtures in Fig.2 (plate I), it indicates that compatibility of the PPPD with wax are enhanced in the order of EO-co-PO/W (a), EOA/W (b), EVA/W (c), and EVA-g-POA/W (d), respectively. This result shows that the smaller the  $U$  value obtained from viscometry, and the worse the compatibility. Similarly, the compatibility of polymer/RA mixtures, as illustrated in Fig.2 (plate II), increases with the order of EO-co-PO/RA (a), EVA/RA (c), EVA-g-POA/RA (d) and EOA/RA (b), respectively. This result is also in good agreement with that from the  $U$  values by viscometry. Obviously, the large incompatibility between EO-co-PO and RA or wax is due to some hydrophilicity of EO-co-PO, and the large compatibility between EVA-g-POA and RA or wax may be due to suitable content of polar component of the EVA-g-POA and its wide molecular weight distribution. The compatibility or  $U$ -parameter effect of PPPD/W or RA on the rheological behavior of doped crude oil has been discussed in other paper<sup>[6]</sup>.

## CONCLUSIONS

The mixtures of polymeric pour point depressants with wax or resin-asphaltene are almost incompatible, but the degree of incompatibility are quite different. According to the results of photomicrography, the dilute-solution viscometry may be used for assessing the compatibility of PPPD/wax and PPPD/resin-asphaltene.

### Keywords:

Polymeric pour point depressant; Compatibility; Viscosity; Crude oil

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