

# Solvent Effect on the Action of Ethylene–Vinyl Acetate Copolymer Pour Point Depressant in Waxy Solutions

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## SYNOPSIS

The flowability and thermal behavior of waxy solutions with and without an ethylene–vinyl acetate copolymer (EVA) have been studied. The drastic changings of pour point depression ( $\Delta T_{pp}$ ) and the crystallization in four waxy solutions were observed. These changes were linear with the U-interaction parameters between EVA and wax in different solvents, suggesting that the efficiency of EVA pour point depressant depends on its compatibility with wax, which is affected by solvent. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymers such as ethylene–vinyl acetate copolymer (EVA) are the main pour point depressant for crude oil.<sup>1</sup> However, it should be noted that not all polymers have necessary or equal effectiveness to oil.<sup>2–5</sup> The mechanism of pour point depression of crude oil with EVA is not exactly clear up to now. Usually, a polymer is considered to be an inhibitor of wax crystallization.<sup>6–9</sup> We have observed the structure effect of EVA on the flowability of oil,<sup>10,11</sup> but there are few studies dealing with the solvent effect. Recently, Srivastara et al.,<sup>12</sup> using photomicrography, reported that the nature of the solvent has a great effect on the crystallization characteristics of wax. Here, one EVA sample was chosen to examine the solvent effect of EVA on the pour point depression and the crystallization of the waxy solutions.

## EXPERIMENTAL

The EVA sample, purchased from Shanghei Chemical company, had a molecular weight of 16,900, a molecular weight distribution of 3.29, and a vinyl

acetate (VA) content of 32 (wt) % measured by Knauer VPO, Waters model 150 C SEC instrument and Carlo Erba 1106 element analyzer, respectively. The wax was supplied by the institute of the refined oil company in Hangzhou and purified by petroleum ether, which was normal paraffin with a melting temperature of 49.4°C according to its differential scanning calorimetric (DSC) curve. All solvents used for investigation were of reagent grade.

A Ubbelohde dilution viscometer was used for measuring the viscosity of the polymer, wax, and polymer–wax (1/1) solutions in four types of solvents at 25°C. The kinetic energy correction was considered.

The DSC measurements were performed in a Perkin Elmer DSC-7, and the scanning rate was 5 K/min.

The pour points (PP) were detected by a Bly Thermoelectric Cooling Freezing Pour Point Tester. The temperature at which the sample solutions entered the tester was ca. 30°C.

## RESULTS AND DISCUSSION

### Rheological Study

The values of PP and  $\Delta T_{pp}$  of different waxy solutions (10 wt % wax) with or without EVA of 300 PPM were summarized in Table I. From Table I, a drastic solvent dependence of the action of EVA was clearly observed. We supposed that the difference

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of  $\Delta T_{pp}$  must be caused by the changing interaction between EVA and wax. It is the same as in miscibility of a polymer-polymer blend<sup>13</sup> or the phase separation between two polymers,<sup>14</sup> in which the solvent plays a determining role. Therefore, it was believed that any difference of the interaction between EVA and wax in various solvents could be caused by the solvent.

Usually, by the aid of viscosity measurements for the polymer-polymer-solvent ternary system, some parameters<sup>15-19</sup> and treatments<sup>20-23</sup> were obtained and proposed to judge the interaction or compatibility between two polymers. In this article, Chee's  $U$ -parameter<sup>18</sup> was used to assess the interaction between EVA and wax in various solvents.

It is well known that for binary systems, the relationship between dilute solution viscosity and polymer concentration is usually expressed by Huggins equation:

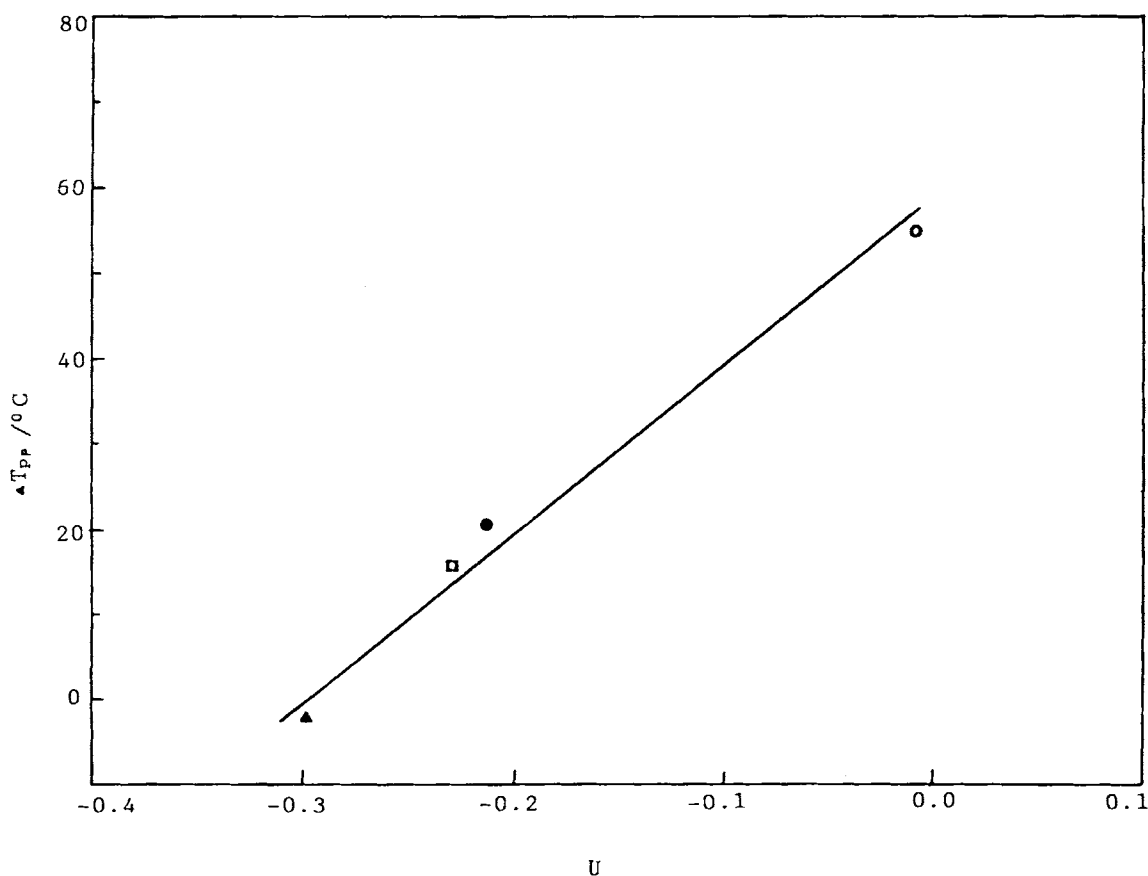
$$\eta_{sp}/c = [\eta] + b \cdot c \quad (1)$$

**Table I** Pour Points of 10 wt % Waxy Solutions With or Without EVA

Solvent	PP (°C), EVA Added		$\Delta T_{pp}$ (°C)
	Nil	300 PPM	
1,2-Dichloroethane	25.0	-30.0	55.0
Toluene	10.0	-11.0	21.0
Xylene	9.0	-7.0	16.0
Chloroform	10.0	12.0	-2.0

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 the mixture of two polymers (polymer 1 + polymer 2) in solution, eq (1) becomes



**Figure 1**  $U$  parameter dependence of pour point depression of waxy solutions in various solvents: chloroform (▲), xylene (□), toluene (●), and 1,2-dichloroethane (○).

**Table II** Viscometric and Thermodynamic Data for Binary or Ternary Systems

Solvent	$X_2$	$[\eta]_1$ (mL/g)	$[\eta]_2$ (mL/g)	$b_1$	$b_2$ (mL/g) <sup>2</sup>	$b_m$	$U$
1,2-Dichloroethane	0.510	2.23	63.01	8.65	860.6	428.3	-0.008
Toluene	0.496	2.17	81.44	4.01	2811.4	730.3	-0.212
Xylene	0.488	1.80	84.84	7.40	3230.3	790.0	-0.229
Chloroform	0.499	3.02	89.11	6.10	3983.7	886.0	-0.298

1, wax; 2, EVA.

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

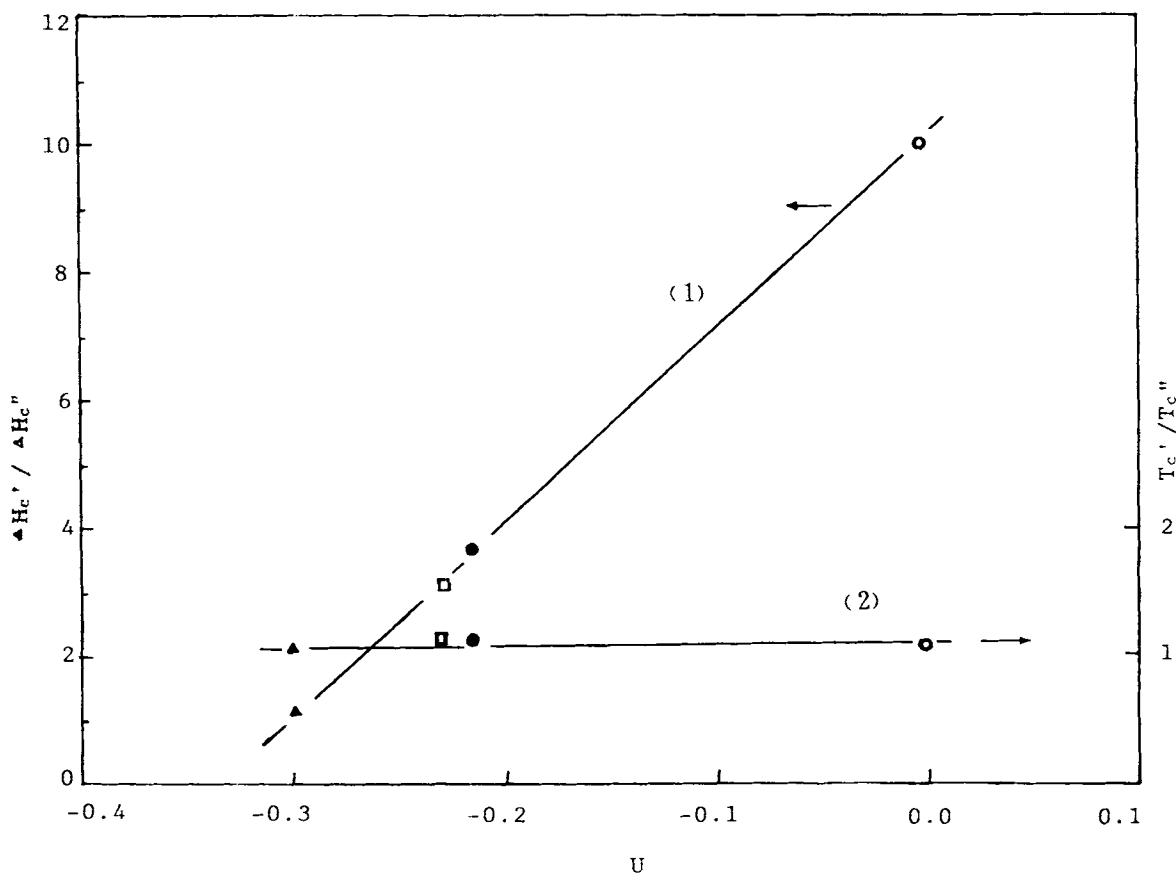
Chee<sup>18</sup> produced an interaction parameter,  $U$ , to determine polymer 1-polymer 2 compatibility

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

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.

The intrinsic viscosity,  $[\eta]$  or  $[\eta]_m$ , and slope,  $b$  or  $b_m$ , were evaluated by the linear least-squares treatment according to eqs (1) or (2). The  $U$ -interaction parameters were calculated by using eq (3) for each solvent system and the values are given in Table II.



**Figure 2**  $U$  parameter dependence of the ratio of the changing of enthalpies (curve 1) or of the peak temperatures (curve 2) in wax crystallization with or without EVA in various solvents: chloroform (▲), xylene (□), toluene (●), and 1,2-dichloroethane (○).

The approach led to negative but different values of  $U$ , which might be due to a certain degree of incompatibility between EVA and wax in different solvents; in other words, the solvents would increase the degree of compatibility between EVA and wax in the order of chloroform, xylene, toluene, and 1,2-dichloroethane, viz., the  $U$  parameter from more negative toward less negative. Figure 1 shows the relation between  $\Delta T_{pp}$  and  $U$ . Obviously, the different interaction would induce different pour point depression, viz., the system of EVA-wax-solvent with larger  $U$  value would give higher  $\Delta T_{pp}$  value such as 55 and  $-2^\circ\text{C}$  of  $\Delta T_{pp}$  for  $-0.008$  and  $-0.298$  of  $U$  in 1,2-dichloroethane and chloroform, respectively. The reason would probably be due to their poor (1,2-dichloroethane) and good (chloroform) solvation for both of EVA and wax, respectively.

### Thermal Behavior Study

By using DSC, the thermal behavior of waxy solution containing 5 wt % wax with or without 1000 PPM EVA were displayed in Figure 2. The  $\Delta H'_c/\Delta H''_c$  is a ratio of the changing of enthalpy of the system with ( $\Delta H'_c$ ) or without ( $\Delta H''_c$ ) EVA in crystallization. The ratio  $\Delta H'_c/\Delta H''_c$  increased with increasing  $U$ , and this result confirmed that stronger interaction between EVA and wax in 1,2-dichloroethane (lower  $\Delta H''_c$ ) could reduce waxy crystallability much more, compared with chloroform (larger  $\Delta H''_c$ ). Otherwise, the ratio of  $T'_c/T''_c$ , peak temperature of wax crystallization with ( $T'_c$ ) or without ( $T''_c$ ) EVA in solvent was always larger than unity, but it was almost independent on the  $U$  parameter. Pour point depressant mainly alters the morphology of wax crystallites.<sup>5,12</sup>

In addition, due to waxy oil or crude oil being multiple component systems, the relation between the efficiency of EVA pour point depressant for them and the  $U$  interaction parameters are complicated, which are to be discussed in another study.

### Conclusions

The solvent effect on the action of EVA pour point depressant has been observed from both rheological behavior ( $\Delta T_{pp}$ ) and thermal behavior ( $\Delta H'_c/\Delta H''_c$ ) of waxy solutions with different solvents. An induced  $U$  parameter presented the interaction between EVA and wax and, directly affected by solvent property, is linearly linked to  $\Delta T_{pp}$  and  $\Delta H'_c/\Delta H''_c$  of waxy solutions at low temperature, viz., EVA/wax/solvent system with larger  $U$  value would give higher values of  $\Delta T_{pp}$  and  $\Delta H'_c/\Delta H''_c$ .

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