RANKING ASPHALT BINDERS BY ACTIVATION ENERGY FOR FLOW

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ABSTRACT

The viscosity of neat and modified asphalt binders were measured at temperatures between 110°C and 160°C by rotational viscometry. The Arrhenius relationship was used to analyze the data and obtain the activation energy for flow of the asphalt binders. Activation energies for flow ranged from 44 kJ/mol to 90 kJ/mol. The effects of film thickness, asphalt type, aging, polymer content, and polymer type on the activation energy for flow were studied. A preliminary analysis was conducted to explain these effects. The results indicate that the activation energy for flow can be used to differentiate asphalt binders and rank their temperature susceptibility in a quantitative manner. It is suggested that this asphalt binder ranking can be used to predict the relative compaction effort for these binders in mixes.

INTRODUCTION

Viscous flow in any liquid can be regarded as a thermally activated rate process where molecules must overcome an energy barrier to move to an adjacent vacant site. As temperature increases, the thermal energy of molecules increases and the vacant site or "holes" in the liquid increases. Henry Eyring modeled the concept of an activation energy barrier to flow in 1936 (Eyring, 1936). When a liquid flows, layers of liquid molecules slide over each other and intermolecular forces cause resistance to flow. The viscosity and temperature relationship can then be modeled using an Arrhenius equation (Ward and Hadley, 1993; Painter and Coleman, 1997):

$$\eta = Ae^{\frac{E_f}{RT}} \qquad (1)$$

where η is the viscosity of the asphalt binder, T is temperature in degrees K, A is a constant, E_f is the activation energy for flow, and R is the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$). It is more useful to rewrite equation (1) as

$$\ln\eta = E_f / RT + \ln A \qquad (2)$$

A plot of $\ln\eta$versus (1/T) gives a straight line with a slope of E_f/R.

Recently, the concept of an activation energy was applied to study the properties of asphalt binders and asphalt mixes (Maze, 1996; Partl and Francken, 1998; Pellinen, Witczak and Bonaquist, 2002). Maze measured the activation energy for unmodified and EVA modified binders using rotational viscometry. The typical activation energy determined for an EVA modified bitumen was around 67 kJ/mol (Maze 1996). Pellinen et al. measured an average activation energy for unmodified mixtures to be 205 kJ/mol versus 202 kJ/mol for modified mixtures (Pellinen, Witczak and Bonaquist, 2002).

In this work, asphalt binders from different crude sources and different grades were tested using rotational viscometry to determine their activation energy for flow. A base asphalt binder was modified using different polymers and varying polymer content. The temperature dependence of the viscosity was used to obtain the activation energy for flow from the Arrhenius relationship. The activation energy for the binders was used to rank their temperature susceptibility. This quantitative ranking for the binders can be used to rank the relative compaction effort for a given mix design.

EXPERIMENTAL DESIGN

Materials

Both neat and modified asphalt binders were tested in this study. Three different pen grades (0-pen, 85-100 and 300-400) and six different PG grades (PG52-40, PG58-28, PG64-28, PG70-28, PG76-28) of asphalt binders were selected. Five different SBS polymers (SBS Radial, SBS Linear, SBS Diblock, SBS-1 (20% Styrene), SBS-2 (30% Styrene), 1 to 5) and one EMA polymer were included in this study. Two air blown asphalt binders (PG70-28 AB and PG58-28 AB) were also studied.

Rheology measurement

The rotational viscosity of the selected asphalt binders was measured using a Brookfield DV-III+ programmable viscometer. Three different spindles were used: SC4-18, SC4-21 and SC4-27. The measurements were made at 110°C, 135°C and 160°C for all materials except for the 0-pen and high polymer content (>6%) binders where measurements were done at 135°C, 160°C and 185°C. The shear rate susceptibility of the binders was measured at shear rates of 0.5, 1, 2, 5, 10, 20 and 50 RMP. At each shear rate, ten readings were generated at 1-minute interval. Readings from the last three minutes were averaged and used in the analysis.

RESULTS AND DISCUSSION

Experimental results

Shear rate dependency

Figure 1 shows a plot of the viscosity versus shear rate for the modified asphalt PG58-34. It indicates that at the temperature range studied, modified asphalt binders show non-Newtonian behavior. This shear dependence was typical for all modified binders studied. At the high shear rates, the viscosity reach a plateau. To minimize the effect of shear rate, at each temperature, the viscosity at the plateau measured at the highest shear rate was used for data analysis.

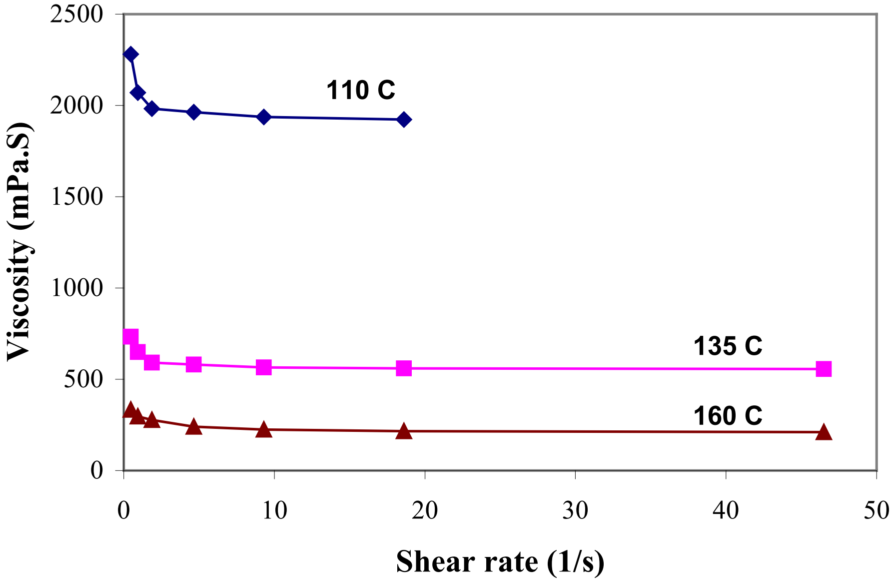

Figure 1. Viscosity versus shear rate for PG58-34

Activation energy of flow

Figure 2 shows an example of a typical Arrhenius plot obtained for the asphalt binders studied.

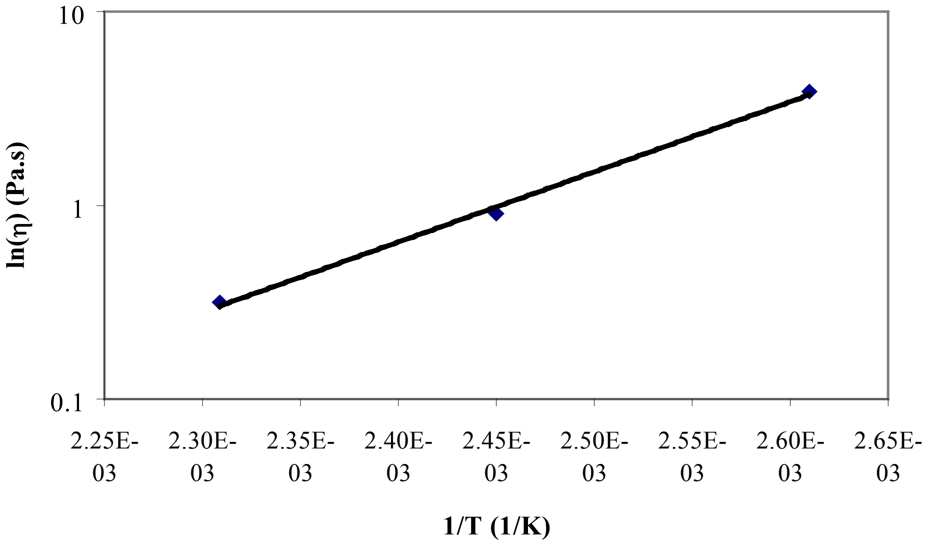

Figure 2: Arrhenius plot for asphalt binder

The activation energy for flow, E_f , was obtained by multiplying the slope of the line by the universal gas constant, R, as discussed above for equation (2).

Effect of film thickness (gap size)

Three different spindles were used to study the effect of sample thickness on the viscosity and the flow activation energy for the asphalt binders. Table 1 shows the corresponding film thickness (gap) for different spindles. As indicated in Figure 3, the effect of gap size is minimal. To normalize the data, the results for the flow activation energy were determined from averaging the results obtained using the three spindles.

Table 1: Different gap sizes created by the spindle used

Spindle	Diameter (mm)	Chamber Diameter (mm)	Gap (mm)
R18	17.48	19.05	0.785
R21	16.79	19.05	1.13
R27	11.76	19.05	3.645

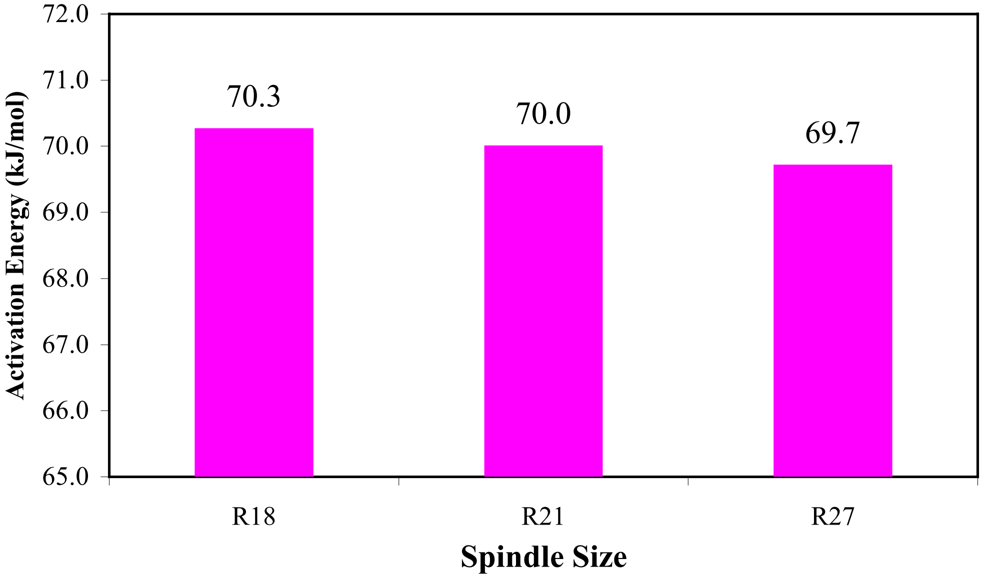

Figure 3: Effect of gap size on the activation energy for flow

Factors that affect the activation energy for flow

Asphalt type

Figure 4 shows the effect of different asphalt crude sources on the activation energy for flow. Although the three asphalt binders have the same PG grade, their activation energies for flow show significant differences. The air blown asphalt has the highest activation energy. This indicates that the chemical composition of the asphalt binders, such as the asphaltene content may have some influence on the activation energy. The viscosity results for these asphalt binders at 135°C and 20 RPM are shown in Figure 4. It appears that the viscosity changes are small compared to their respective activation energies.

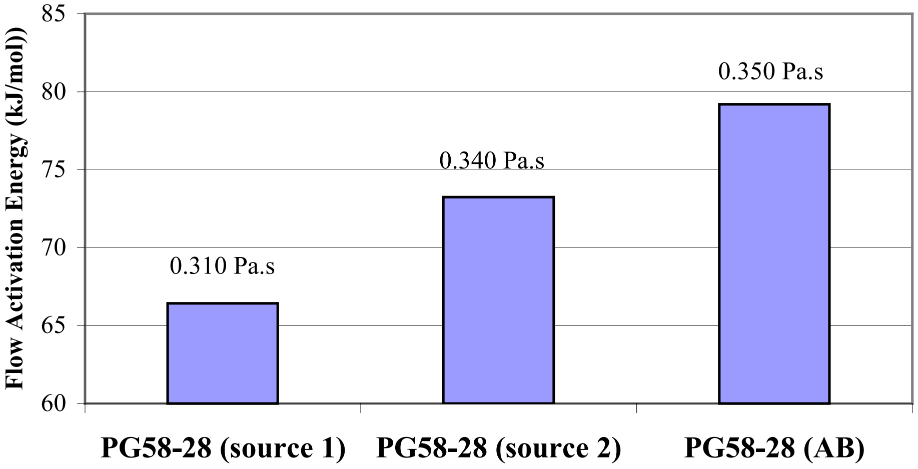

Figure 4: Effect of asphalt type on the activation energy for flow

Aging

Figure 5 shows the effect of aging on the activation energy for flow.

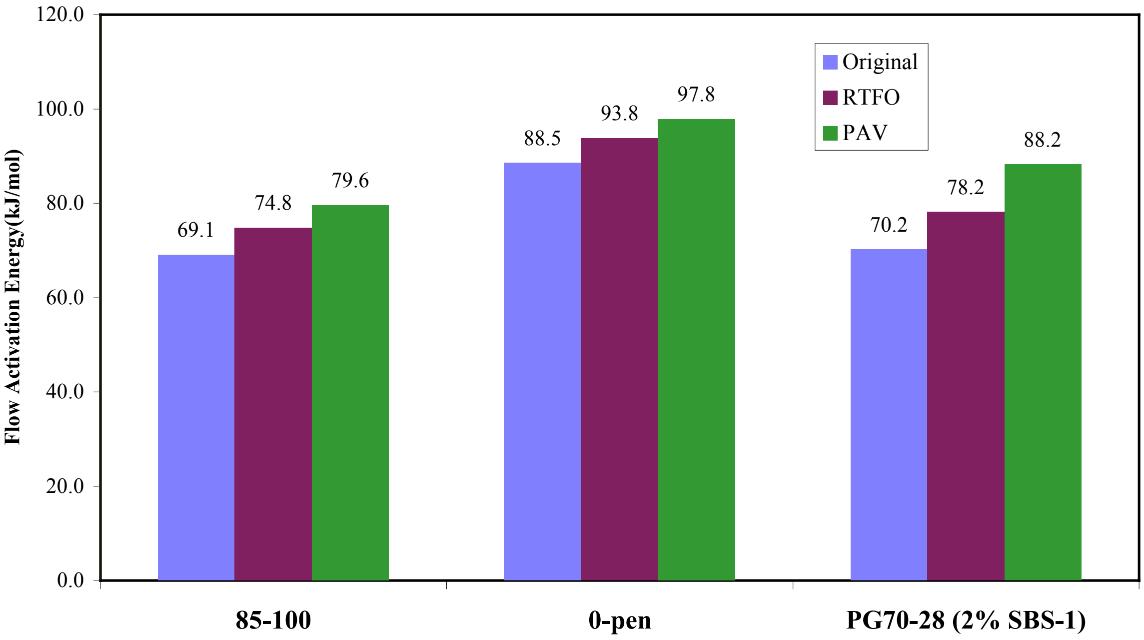

Figure 5: Effect of aging on the activation energy for flow

After aging, asphalt binders show higher activation energy. After PAV aging, the activation energy is at least 10 kJ/mol higher than that of the original binder. Oxidation increases the number of polar molecules in the asphalt binders. The higher concentration of polar molecules increases the intermolecular forces leading to stronger interactions. These stronger interactions within the asphalt binder result in a higher resistance to flow consequently a higher activation energy for flow. The 0-pen material, with an asphaltene content of 25%, shows the highest activation energy for flow. This higher activation energy for flow in this binder can be attributed directly to the higher concentration of the polar asphaltene fraction.

Polymer type

Figure 6 shows the effect of different polymers on the activation energy for flow. All modifications were conducted at the same polymer content and using same base asphalt. All modified asphalt binders were the same PG grade: PG70-28. An air-blown asphalt of the same PG grade was included to compare the effect of different modification. As discussed above the higher activation energy in the air-blown asphalt is a result of the stronger intermolecular interaction between polar molecules.

As shown in Figure 6, different polymer modifiers have different activation energies for flow. This indicates that polymer type influences the activation energy for flow. The air-blown asphalt had the highest activation energy for flow. This is interpreted to mean that different modification of the base asphalt results in a different activation energy for flow.

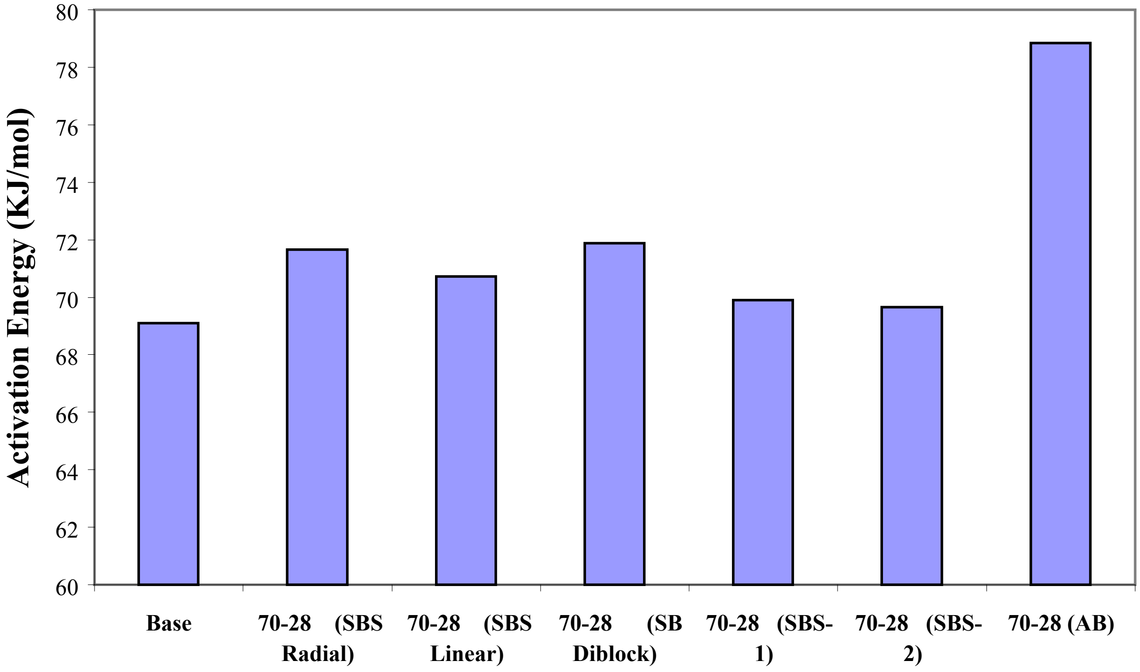

Figure 6: Effects of polymer types on the activation energy for flow

Polymer content

Figure 7 shows the effect of polymer content on the activation energy for flow. When the polymer content is below 4%, the activation energy for flow is within 10 kJ/mol of each other. When the polymer content is larger than 4%, the activation energy for flow decreases significantly. From 4% to 14%, the activation energy changes from 68 kJ/mol to only 44 kJ/mol. It appears that when the polymer content is above a critical value, the activation energy for flow of the asphalt becomes more polymer content dependent. There may be a critical polymer concentration that changes the nature of the interaction between asphalt components and polymer. Compared to the EVA polymer, the SBS polymer shows a much larger drop in the activation energy than that reported previously (Maze 1996). This indicates that polymer content and type influence the interaction between asphalt binder and polymer additives. Further study is needed to understand the impact of polymer content on the activation energy for flow.

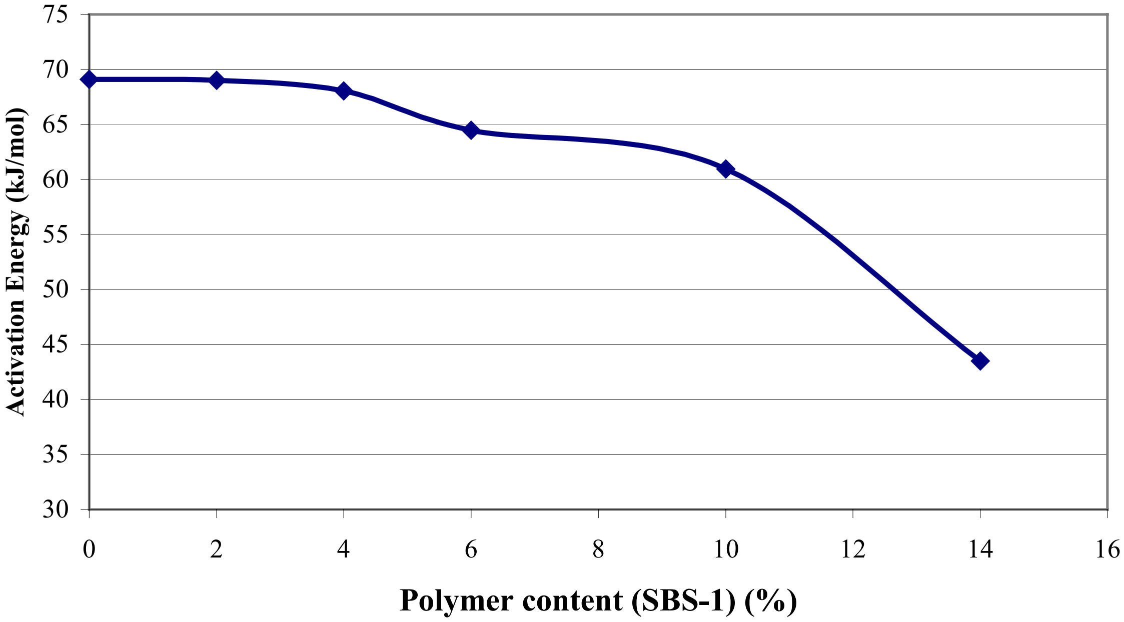

Figure 7: Effect of Polymer content on the activation energy for flow

Flow activation energy ranking

Figure 8 is a summary of the activation energy for flow for the different grades of asphalt binders..

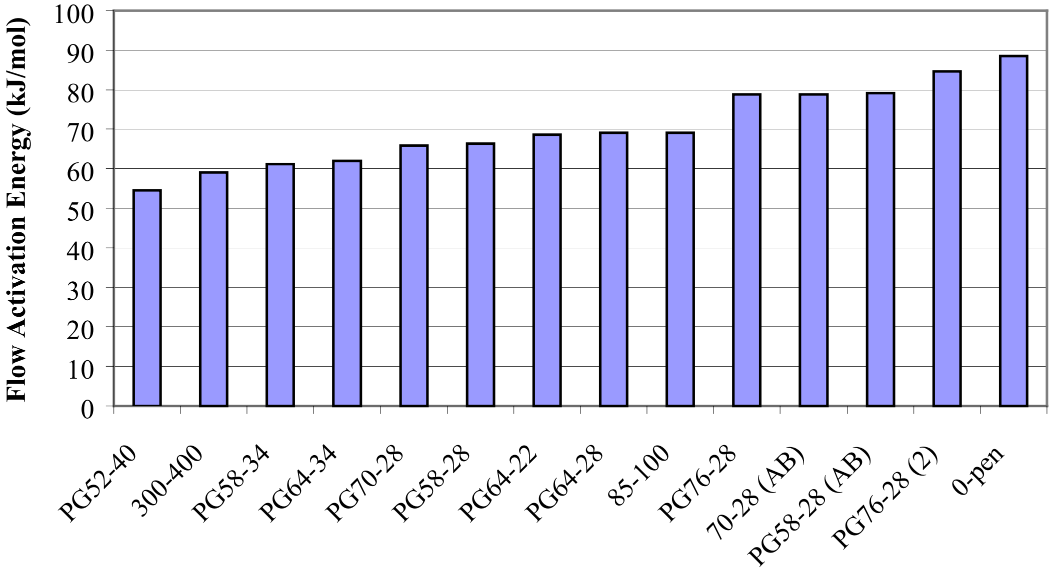

Figure 8: Activation energy for flow of different asphalt binders

Different activation energies for flow are obtained for different asphalt binders. The values range from 55 kJ/mol to close to 90 kJ/mol. For the same PG grade, the activation energies for flow of different asphalt binders can be significantly different. The air-blown asphalt binders have much higher activation energies than asphalt binders of the same PG grade. The activation energy for flow for the air blown binders PG58-28 and PG 70-28 are similar. This is attributed to the fact that the original asphalt binders were from different crude sources and had different susceptibility to air oxidation.

The ranking of the activation energy for flow indicates the relative temperature susceptibility of the different binders. Lower activation energy indicates that the asphalt binder is less sensitive to temperature changes, while higher activation energy shows a higher sensitivity to temperature changes. Different compactive efforts, such as compaction temperature range, compactive pressure (shear force) and rolling patterns may be needed to achieve optimum performance and required density of the mix. Mixture tests using a gyratory compactor are needed to further evaluate the influences of activation energy for flow on the compaction efforts of the mixtures.

CONCLUSIONS

1. Different asphalt sources and polymer types will result in different activation energy for flow. This may be related to the different chemical composition of asphalt binders and the different interaction between polymer and asphalt components.

2. Aging will increase the activation energy for flow. Oxidation increases the number of polar molecules in the asphalt binders resulting in an increase in the intermolecular forces. This may also explain the higher flow activation energies for the air-blown asphalt binders studied.

3. When the polymer content is above a critical polymer concentration, the activation energy for flow decreases. This critical polymer concentration is different for different types of modifiers. This may be caused by the different interactions between polymer molecules and asphalt components.

4. The activation energy for flow for asphalt binders can be used to rank and differentiate asphalt binders. This ranking of asphalt binders may be used to rank the relative compaction effort of asphalt binder mixtures in the field.

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