

ASPHALT BINDER FLOW ACTIVATION ENERGY AND ITS SIGNIFICANCE FOR COMPACTION EFFORT

DELMAR SALOMON, HUACHUN ZHAI

Idaho Asphalt Supply, Inc.

2627 Brandt Ave., Nampa, ID 83687, USA

TEL 208-442-7742, FAX 208-463-0679, e-mail:dsalomon@idahoasphalt.com

ABSTRACT

The temperature dependence of viscosity of neat and modified asphalt binders were evaluated between 80°C and 200°C using rotational viscometry. The activation energy for flow was determined for these asphalt binders using the Arrhenius equation. Different types of polymer and polymer contents were selected to study the effects of polymer type and concentration on the activation energy for flow. Attempts were made to use a global model to evaluate the relationship between polymer content and viscosity. The effect of aging was also discussed. The results indicate that the flow activation energy can be used to rank the temperature susceptibility of different asphalt binders. It is suggested that this ranking may be used to predict the relative compaction effort for the different asphalt binders studied. Densification curves for different asphalt binders at a compaction temperature of 138 °C are discussed in relation to their activation energy for flow.

Keywords: flow activation energy, asphalt binder, Arrhenius equation, polymer, compaction effort

1. INTRODUCTION

The determination of mixing and compaction temperatures of asphalt mixes, especially for polymer modified asphalt binders have generated great interests in recent years [1-4]. Much of the interest has been focused on the temperature and shear rate dependence of the viscosity of asphalt binders. However, most researches have been directed to empirical fitting of the experimental data. It is important to find a method that not only can relate the experimental factors, but also can explain the nature of the rheological behaviors that relate to the quantity and structure of the modifiers used in asphalt.

In 1936, Henry Eyring [5] modeled the concept of an activation energy barrier for viscous flow of liquids. Viscous flow in any liquid can be regarded as a thermally activated rate process where atoms, molecules or groups of molecules (flow units) must overcome an energy barrier to move to an adjacent vacant site or “hole”. When a liquid flows, layers of liquid molecules slide over each other, where intermolecular forces oppose the motion and cause resistance to flow. This results in an activation energy barrier for viscous flow that must be overcome. As temperature increases, the fraction of molecules with the necessary activation energy increases, which makes the energy barrier becomes easier to overcome. Alternatively, the increase in temperature increases the number of vacant sites or “holes” in the liquid thus expands the volume of the holes. As a result, the resistance to flow or the viscosity decreases. The viscosity and temperature relationship can then be modeled using an Arrhenius equation [6, 7]:

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

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

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

A plot of $\ln\eta$ versus (1/T) would be linear with a slope of E_f/R . This equation assumes that the shear stress (load) is not an important factor in the viscous flow of the binder.

The concept of activation energy for flow has been applied to study the properties of asphalt binders and asphalt mixes [8-11]. Herrin and Jones [8] used the absolute rate theory based on Eyring's concept to measure the size of the flow unit in unmodified asphalt binders. They indicated that at normal and higher temperature regions, the relationship of between temperature and viscosity could be predicted using the absolute rate theory, while at lower temperature range (below 12°C), significant deviations were observed. Maze measured the activation energy for flow for unmodified and EVA modified binders using rotational viscometry. The typical activation energy determined for an EVA modified bitumen was around 67 kJ/mol [9]. Pellinen et al. measured average activation energy for unmodified asphalt mixtures to be 205 kJ/mol versus 202 kJ/mol for modified mixtures [10].

In this work, asphalt binders from different crude sources and different grades were tested using rotational viscometry to determine their activation energy for flow. The temperature dependence of the viscosity was used to obtain the activation energy for flow from the Arrhenius relationship. A base asphalt binder was modified using different polymers and at varying polymer contents. The relationship between activation energy for flow and the polymer content was investigated. The activation energy for flow for the binders was used to rank their temperature susceptibility. Several different asphalt binders were selected for mix design based on their different activation energy for flow. This quantitative ranking for the binders based on the activation energy for flow is used to correlate their relative compaction effort for the mix design with these binders.

2. EXPERIMENTAL DESIGN

2.1 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. Six different SBS polymers, SBS Radial 1 to 4 (SBS-1 (20% Styrene), and SBS-2 (30% Styrene)), SBS Linear, SBS diblock, and one EMA polymer were included in this study. Four air blown asphalt binders (PG70-28 AB, PG70-22 AB, PG64-22 AB and PG58-28 AB) and two acid modified asphalt binders (PG70-28 acid 1 and acid 2) were also studied. A sulfur based cross link agent was used to study the effect of crosslinking on the activation energy for flow.

2.2 Rheology measurement

The rotational viscosity of selected asphalt binders was measured using a Brookfield DV-III+ programmable viscometer. Three different spindles were used: SC4-18, SC4-21 and SC4-27. Measurements were made at 80°C, 95°C, 110°C, 125°C, 140°C, 155°C, and 170°C for all materials except for the 0-pen and high polymer content (>6%) binders where measurements were started at 110°C and ended at 200°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 one-minute interval. Readings from the last three minutes were averaged and used in the analysis.

2.3 Mix design

Single stockpile of Idaho Class III aggregate was selected for the mix design. Asphalt content was 5.9%. The mixes were prepared at 163 °C (325 °F) and compacted at 138 °C (280 °F). Each mix was compacted using a Superpave Gyratory compactor for 200 gyrations.

3. RESULTS AND DISCUSSION

3.1 Experimental results

3.1.1 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 rate dependence was typical for all modified binders studied. At higher shear rates, the viscosity reaches 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.

3.1.2 Geometry dependency

Three different spindles were used to study the effect of film thickness on the viscosity and the flow activation energy for the asphalt binders. The gap sizes for the three spindles are: 0.785 mm (Spindle R18), 1.13 mm (Spindle R21) and 3.645 mm (Spindle R27). As indicated in Figure 2, 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.

3.2 Factors affecting the activation energy for flow

3.2.1 Aging

Figure 3 shows the effect of aging on the activation energy for flow for asphalt binders. 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 and consequently a higher activation energy for flow. The acid modified material shows the highest activation energy for flow compared to the original binder. After RTFO and PAV aging, the acid modified asphalt show much more significant increase (> 20 kJ/mol) in the activation energy for flow. This higher activation energy for flow in this binder may be attributed directly to the higher concentration of the polar fraction in the asphalt. The presence of acid may accelerate the formation of the polar fraction during aging.

3.2.2 Polymer type

Figure 4 shows the effect of different polymers on the activation energy for flow for a PG 70-28 binder. All modifications were conducted at the same polymer content (2%) and using the same base asphalt. All modified asphalt binders were the same PG grade: PG70-28. No crosslinking agent was used. An air-blown asphalt and two acid modified asphalt binders of the same PG grade were included to compare the effect of different modifications. The air-blown and acid modified asphalts show the highest activation energy for flow. As discussed above the higher activation energy values for these asphalts are the result of the stronger intermolecular interaction between polar molecules.

As shown in Figure 4, different polymer modifiers have different activation energy for flow. This indicates that polymer type influences the activation energy for flow. This is interpreted to mean that different polymers may have different interactions with asphalt molecules, which result in different flow unit structures in the system. These differences in flow unit structures may cause the differences in the activation energy for flow.

3.2.3 Polymer content

Figure 5 shows the effect of polymer content on the flow activation energy (same base asphalt). When the polymer content is below 4%, the flow activation energy is within 2 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 69 kJ/mol to 44 kJ/mol for SBS-1 and from 69kJ/mol to 58kJ/mol for SBS-2. It appears that there is a critical polymer concentration (styrene butadiene copolymer) (close to 4% for SBS-1 and 4 to 6% for SBS-2). The existence of a critical polymer concentration has been found in other researches [13-17]. In a recent study on the steady state viscosity of asphalt binders, Rasmussen et al. found that the steady-state viscosity increases up to 5 % SBS modification of binders, but above 5 % no increase was found [13]. By using transmission electron microscopy to study SBS modification of asphalt, Chen et al. reported that at 5 % of modification that a critical network is formed contributing to a large increase in the complex modulus of the modified binder [14]. Rowe's work on the steady state viscosity of modified binders indicated that at 5 % SBS modified binder that the steady-state viscosity increases up to 5%. This was thought to be due to the formation of a critical network polymer formation at 5% [15]. G. Kraus and his colleagues reported that a critical network polymer concentration is formed at 6-8 % in asphalt when using SBS as a modifier [16, 17].

Above this critical polymer content, the nature of the interaction between asphalt components and polymer changes and the activation energy for flow of the asphalt becomes strongly polymer content dependent. Compared to the EVA polymer, the SBS polymer shows a much larger drop in the activation energy than that reported previously [9]. Figure 5 also shows that SBS-1 and SBS-2 have different effect on the activation energy for flow. This indicates that polymer content and type influence the interaction between asphalt binder and polymer additives.

Modified Arrhenius equations have been used to describe the effects of different factors (pressure, polymer concentration) on the activation energy for flow [9, 12]. To correlate polymer content, a modified Arrhenius equation was proposed:

$$\eta = A' e^{\frac{E_f + E_p \phi}{RT}} \quad (3)$$

where A' is a constant, ϕ is the polymer content (%), which is larger than or equal to a critical polymer concentration (for this study, 4% was selected), and E_p is the activation energy for flow related to polymer and asphalt interaction. E_f is the activation energy for flow of neat asphalt that is 69.1 kJ/mol. By plotting $(\ln \eta - E_p / (RT))$ versus ϕ/T at a fixed temperature and varying polymer content, the slope determines E_p/R and the intercept determines $\ln A'$.

The regression parameter determined using equation (3) for SBS-1 modified asphalt binder at different temperatures are listed in Table 1. From the data, both A' and E_p are temperature related. Since the difference between A' factors is fairly small, the A' factor is considered a constant. The E_p factor, on the other hand, shows temperature dependence. The effect of temperature on E_p is shown in Figure 6.

Based on the relationship shown in Figure 6, equation (3) can be modified as follows:

$$\eta = A' e^{\frac{E_f + (AT+B)\phi}{RT}} \quad (4)$$

where A and B are constants related to polymer.

It is not unreasonable to consider the temperature dependence of E_p to be related to the temperature dependence of the interaction between polymer and asphalt. Polymer forms separated phase or domains in asphalt. As temperature increases, the formation of the domains of the polymer phase changes. As a result, the interaction between asphalt and polymer will be different, which causes the E_p to change accordingly.

3.2.4 Crosslink agent

Table 2 indicates the effect of crosslink agent on the activation energy for flow of polymer-modified asphalt. As the amount of agent increases, the value of the activation energy increases. The crosslink agent couples the polymer and the asphalt through chemical bonds and creates a chemical network through the asphalt [18]. The formation of the network restricts the relative motion between the flow units, which increases the energy barrier and results in higher activation energy for flow.

3.3 Activation energy for flow ranking and compaction effort

Figure 7 shows a summary of flow activation energy for different grades of asphalt binders tested. Different flow activation energies are obtained for the different asphalt binders. The values range from 55 kJ/mol to 90 kJ/mol. Based on Figure 6 and 7, acid modified asphalt binders have the highest activation energy for flow.

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 compaction profile, such as compaction temperature range, compaction pressure (shear force) and rolling patterns may be needed to achieve optimum performance and a similar required density of the mix. To correlate the activation energy ranking to the relative compaction effect, four different asphalt binders were selected based on their activation energy for flow values (PG52-40, PG 76-28 SBS, PG70-28AB and PG70-28 Acid 1). Figure 8 shows the densification curves for these four asphalts. From the curves, the ranking for compaction effort is defined as the number of gyration needed to achieve 6% air voids. Higher gyration number means the mix is more difficult to compact. Table 3 shows the relationship between the activation energy values to the ranking of compaction effort. From the data, higher activation energy demands a higher compaction effort, or alternatively, the higher the activation energy, the more difficult the compaction becomes. When the activation energy increases from 70 to 80 kJ/mol, the compaction effort increases exponentially (from less than 30 to more than 100 gyrations). These preliminary findings indicate that the activation energy for flow can be used as a guideline to evaluate the compaction effort for asphalt mixes.

4. CONCLUSIONS

1. 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 and acid modified asphalt binders studied.
2. Different 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.
3. When the polymer content is above a critical 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 addition of crosslink agent will increase the activation energy for flow. The increase is caused by the formation of a network between polymer and asphalt molecules.
5. The activation energy for flow for asphalt binders can be used to rank and differentiate asphalt binders. This ranking of asphalt binders could be used to rank the relative compaction effort of asphalt binder mixtures in the field.

6. ACKNOWLEDGEMENTS

The authors would like to thank Mr. Jack Youtcheff of the FHWA for providing asphalt samples and Mr. Lars Colberg from Strata for supplying aggregate. The help of Mr. Frank Castellanos in obtaining the rotational viscometry measurements is appreciated.

REFERENCES

- [1] D. Sybilski, *Transportation Research Record*, 1535, 15-21, 1996
- [2] Y. Yildirim, M. Solaimanian and T.W. Kennedy, *Journal of the Association of Asphalt Paving Technologists*, 69, 34-71, 2000.
- [3] A. Khatri, H.U. Bahia, and D.I. Hanson, *Journal of the Association of Asphalt Paving Technologists*, 70, 368-403, 2001.
- [4] A. Shenoy, *International Journal of Pavement Engineering*, 2(1), 33-47, 2001
- [5] H.Eyring, *Journal of Chemical Physics*, 4, 283-291, 1936.
- [6] I.M. Ward, and D.W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley, New York, 1993.
- [7] P.C. Painter, and M.M. Coleman, *Fundamentals of Polymer Science – An Introductory Text*, Technomic Publishing Co. Inc., Lancaster, PA, 1997.
- [8] M. Herrin and G. Jones, *Journal of the Association of Asphalt Paving Technologists*, 32, 82-105, 1963.
- [9] M. Maze, *No. 5170, Section 5, Euraspahlt & Eurobitume Congress*, 1996.
- [10] T.K. Pellinen, M.W. Witzak, and R.F. Bonaquist, *15th ASCE Engineering Mechanics Conferences*, Columbia University, New York, NY, June 2-5, 2002.
- [11] M.N. Partl, and L. Francken, L., *Introduction, RILEM Report 17, Bituminous Binders and Mixes*, pp 2-10, London, 1998
- [12] G. Zhou, J.L. Willett and C.J. Carriere, *Rheol Acta*, 39, 601-606, 2000
- [13] R.O. Rasmussen, R.L. Lytton, G.K. Chang, *Journal of Materials in Civil Engineering*, May/June 2002, pp 246-252.
- [14] J.S. Chen, M.C. Liao, M.S. Shiah, *Journal of Materials in Civil Engineering*, May/June 2002, pp 224-229.
- [15] G. Rowe, *40th Petersen Asphalt Research Conference*, Laramie, Wyoming, July 14-16, 2003.
- [16] G. Kraus, D.S. Hall, *Symposium on Block Polymers: Science and Technology*, Michigan Molecular Institute, August, 1979.
- [17] G. Kraus, K. W. Rollman, *International Rubber Conference*, Nurnberg, Germany, September, 1980.
- [18] Y. Becker, M.P. Mendez, and Y. Rodriguez, *Vision Tecnologica*, 9(1), 39-50, 2001

Temperature (C)	110	125	140	155	170	185
Ep (kJ/mol)	15.36	20.30	25.69	31.49	37.65	44.14
A' (Pa.s)	1.16E-09	1.03E-09	9.29E-10	8.41E-10	7.66E-10	7.01E-10

Table 1. Regression parameters in polymer content modified Arrhenius equation (SBS-1)

	2.1% SBS-4	2.1% SBS-4 + 0.1% Agent	2.1% SBS-4 + 0.5% Agent
E _f (kJ/mol)	67.83	74.80	81.23

Table 2. Effect of crosslink agent on activation energy for flow (SBS-4)

Asphalt	PG 52-40	PG 76-28 SBS	PG 70-28 AB	PG 70-28 acid
E _f (kJ/mol)	54.6	76.8	78.8	83.5
No. of Gyration to 6% air voids	20	23	29	105

Table 3. Relation between activation energy for flow ranking and compaction effort

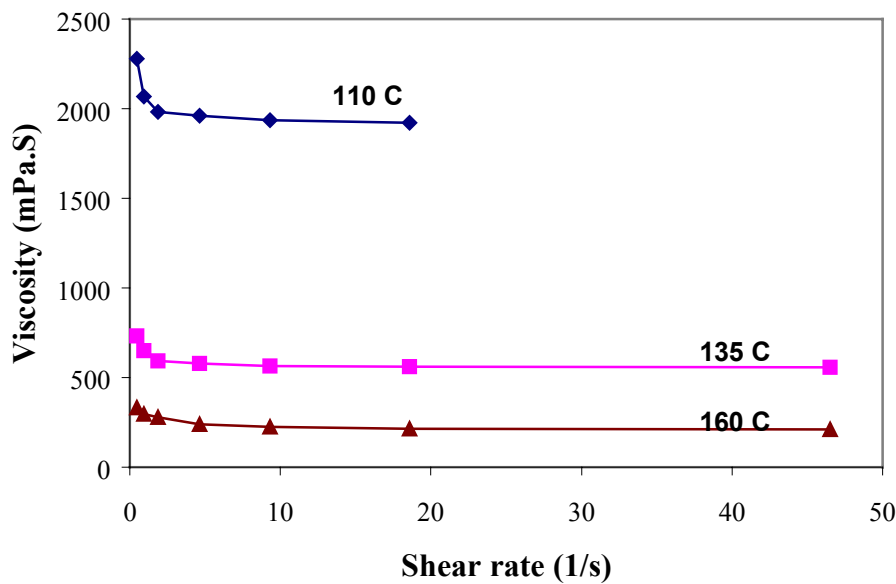


Figure 1. Viscosity dependence on shear rate for PG58-34

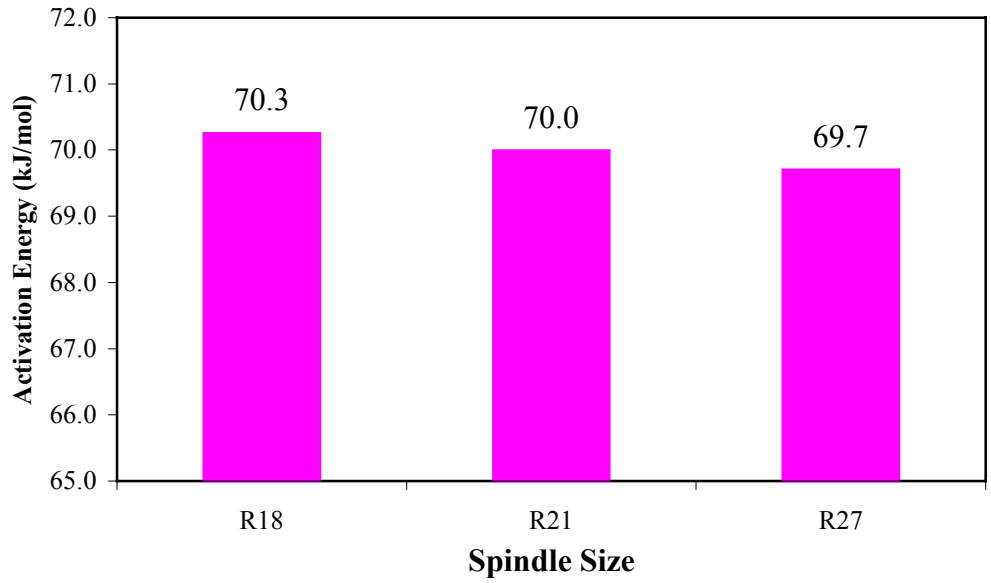


Figure 2: Effect of gap size on the activation energy for flow

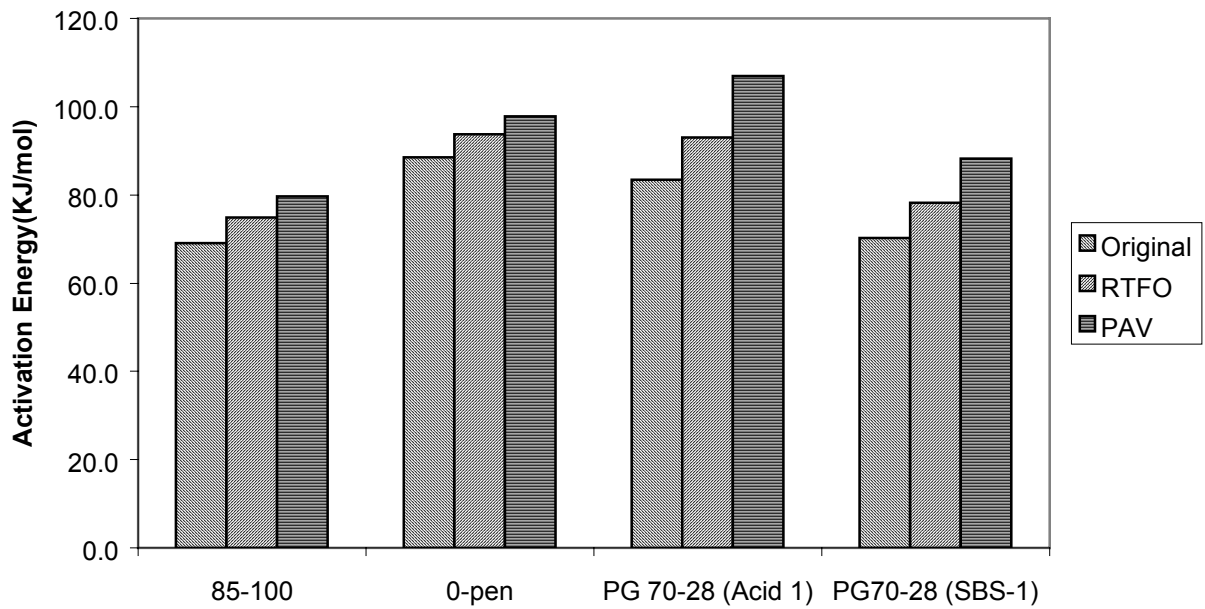


Figure 3: Effect of aging on the activation energy for flow

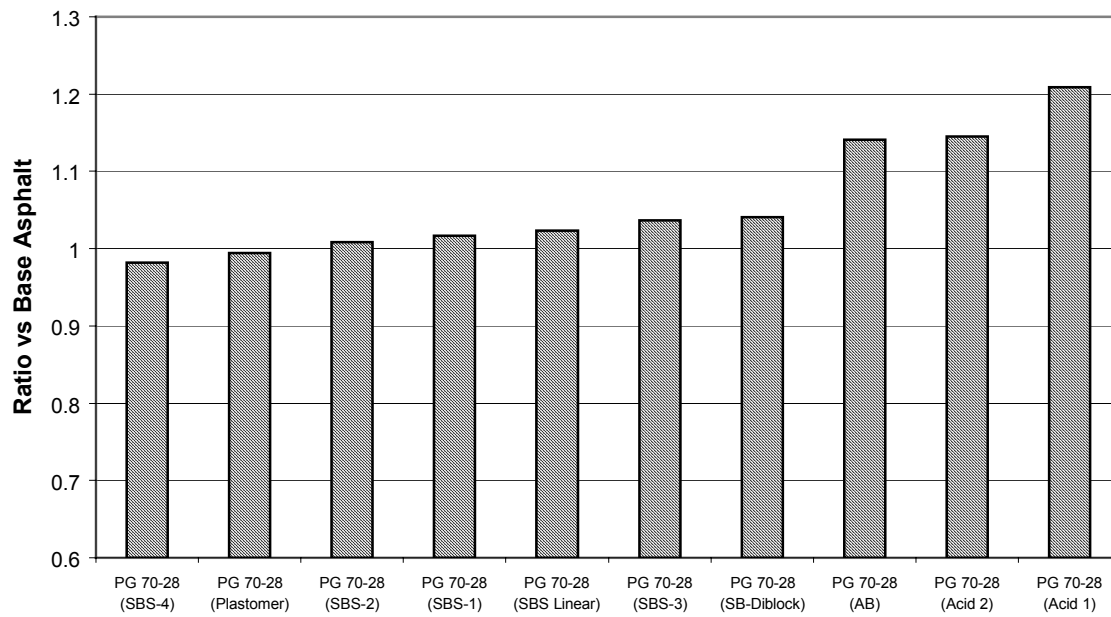


Figure 4: Effects of polymer types on the activation energy for flow for PG 70-28

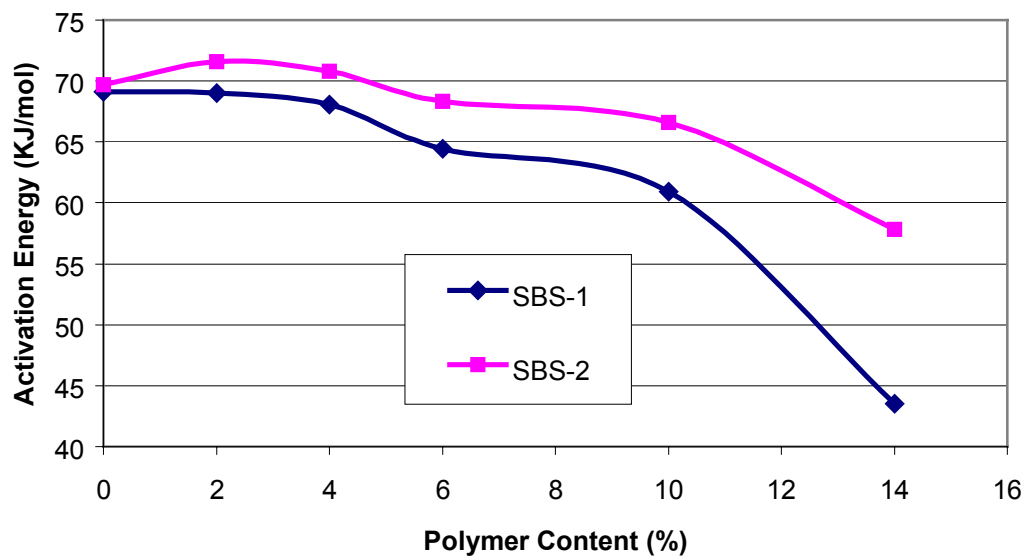


Figure 5: Effect of polymer content on the activation energy for flow

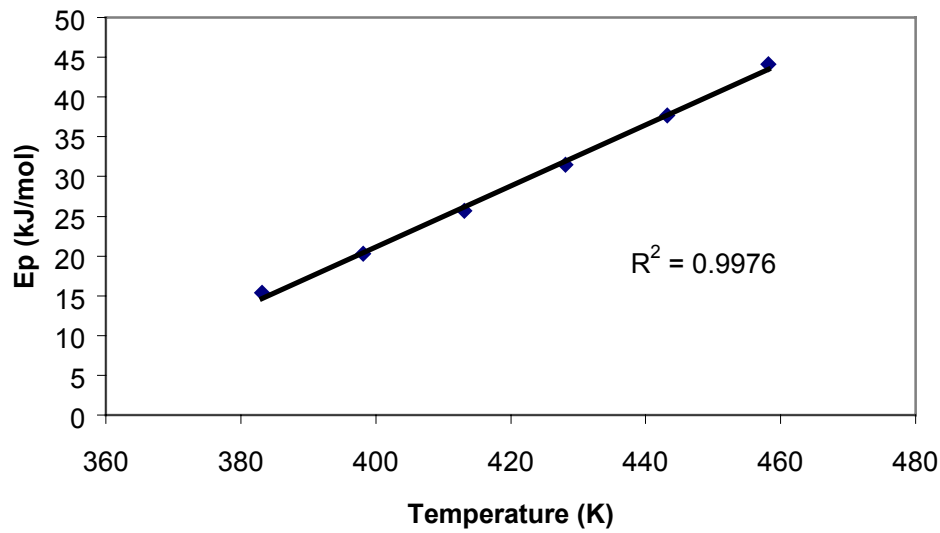


Figure 6: Effect of temperature on polymer/asphalt interaction flow energy, E_p

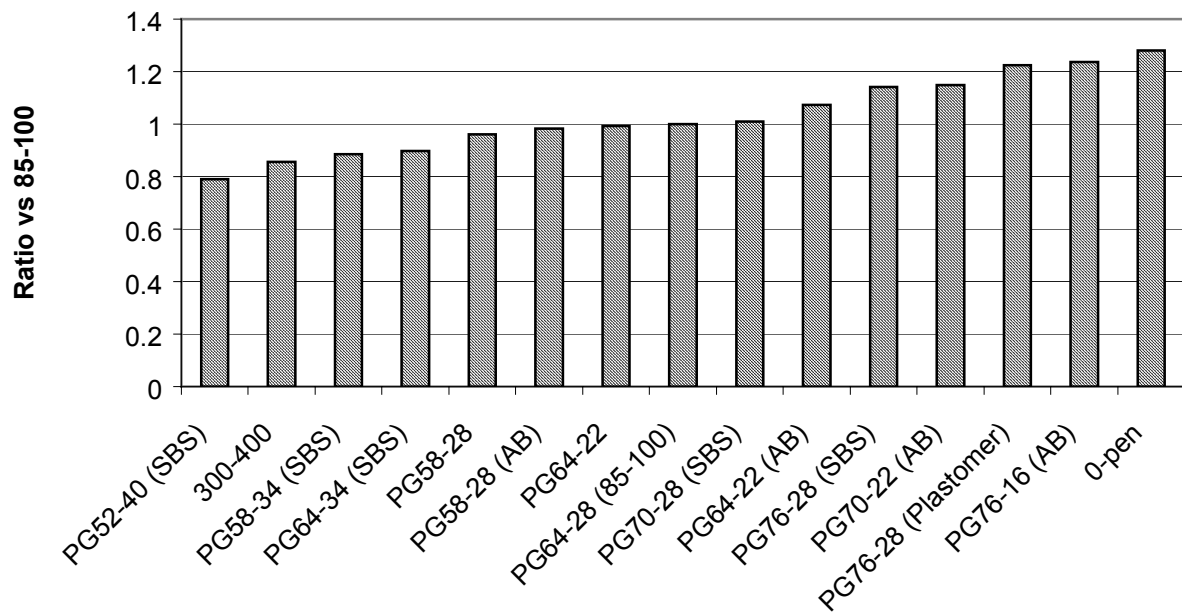


Figure 7: The activation energy for flow for different asphalt binders

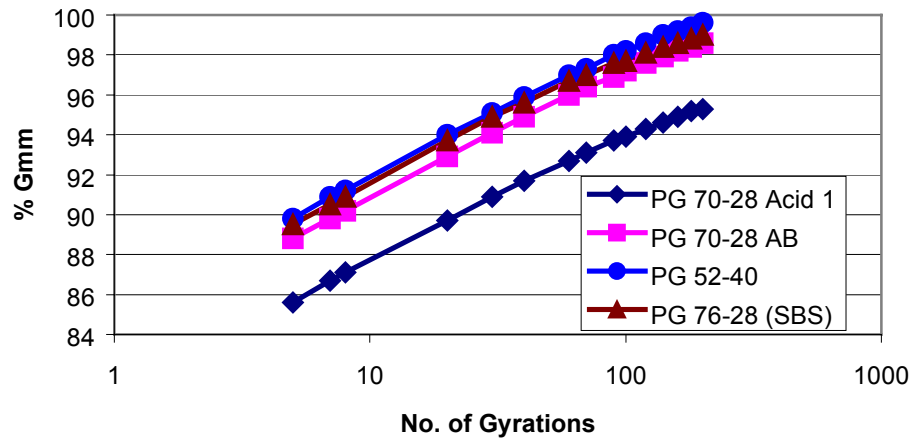


Figure 8: Densification curves for different asphalt binders at a compaction temperature of 138 °C