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Stabilization Mechanisms in Polyolefine-Asphalt Emulsions 1. Temperature Susceptibility of Chlorinated Polyethylene-Modified Asphalts

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폴리올레핀－아스팔트 에멀젼의 안정화 메카니즘 1. Chlorinated Polyethylene으로 개질된 아스팔트의 온도 의존성

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Abstract: The physical characteristics of polymer modified asphalt depend on many parameters, such as, the polymer nature, polymer content and the asphalt properties. The objective of this study is to investigate the temperature susceptibility of polymer modified asphalt. The asphalts employed in this study were two different grades : a soft(200/300) grade and a hard(85/100) grade. And chlorinated polyethylene of two different characteristics were used : plastomer(Tyrin 2552) and elastomer(Tyrin CM0730). Temperature susceptibility of asphalt is a fundamental feature for characterizing asphalt and modified asphalt. It can be quantified by the penetration index(PI) and pen-vis number (PVN). These indices were obtained from the measurements of penetration and viscosity of the asphalt samples. For both of asphalts, the addition of the polymers increases the value of PI and PVN. Plastomer modified asphalt shows higher value of PI and PVN than elastomer modified asphalt. Soft grade shows more temperature susceptibility than hard grade at elevated temperatures.

요 약: 고분자로써 개질을 시킨 아스팔트의 물리적 특성은 여러 가지 매개변수에 의존한다. 예를 들어 고분자의 특성, 고분자의 사용량 및 아스팔트의 물성 등에 의하여 좌우된다. 본 연구의 목적은 고분자로써 개질된 아스팔트의 온도 의존성을 고찰하는데 있다. 아스팔트는 연질의 200/300과 경질의 85/100 2가지 종류를 사용하였으며 개질을 위한 고분자는 염화 폴리에틸렌으로 플라스틱 성질을 갖는 Tyrin 2552와 탄성체 성질을 갖는 Tyrin CM0730 2가지 종류를 사용하였다. 온도에 대한 의존성은 아스팔트나 고분자로 개질된 아스팔트의 특성을 결정하는 기본적인 요인 중 하나이다. 따라서 온도 의존성은 penetration index(PI)와 penetration-점도수(PVN) 등의 지수에 의하여 결정되어지는데 이들 지수들은 개질된 아스팔트의 penetration과 점도를 측정하여 이론식에 대입하여 계산함으로서 얻었다. 2종류의 아스팔트는 개질을 위한 고분자를 첨가하였을 경우 PI와 PVN이 동시에 증가하였다. 그리고 Plastomer로 개질시킨 아스팔트에 비하여 PI및 PVN이 더 큰 값을 나타내었다. 아울러 연질의 아스팔트가 경질의 아스팔트에 비하여 온도 의존성이 더 큰 것으로 나타났다.

1. Introduction

Asphalt is a thermoplastic material : elastic solid at low temperatures, and viscous liquid at high temperatures. This characteristic creates a need to improve the performance of an asphalt to minimize the stress cracking that occurs at low temperatures and the plastic deformation at high temperatures. One of the best way to improve the properties of asphalt is its modification with small amounts of polymers.

The advantages of polymer modification are numerous; most polymer systems provide reduced temperature susceptibility, improved low temperature flexibility, and better tensile properties to the asphalt. Therefore, modified asphalt exhibits varying degrees of reduced rutting, longer fatigue life, increased stripping resistance, higher stiffness at high temperatures, and improved resistance to cracking[1-3].

The idea of using polymers in asphalt to improve its properties has been around for a long time. As reported by Zanzotto et al[4] and Anderson et al [5], the first patent for a polymer modified asphalt was authorized and the first road employing rubber -modified asphalt was constructed in France in 1902. Since then, great efforts have been made in the development of modified asphalt technology and use of modified asphalt, most notably in France and Austria as discussed by Terrel and Walter[6]. Among various types of polymer amenable to asphalt modification, styrene-butadiene-styrene(SBS) copolymer has probably been the most widely used up to now[7]. The major effect of incorporating a SBS copolymer into an asphalt is a significant decrease in the temperature susceptibility. As reported by Leunget et al[8], methods used to define temperature susceptibility over various temperature ranges have been reviewed extensively.

A process of incorporating LDPE into asphalt was pioneered by the Richard Felsinger Corporation in Austria. The process is patented and the product is called Novophalt[9].

Many different types of polymers have been suggested. These polymers can be classified in two main groups, elastomers and plastomers. Elastomers give a more resilient, flexible pavement, while plastomers result in mixture of higher stabilities and stiffness moduli[10].

The physical characteristics of polymer modified asphalt depend on many parameters, as for example, the polymer nature, polymer content, the asphalt properties, and mixing process. Many investigations have been carried out to determine the advantages expected from the modification of asphalt properties by the incorporation of polymer [11].

Therefore, the objective of this study is to investigate the temperature susceptibility of polymer modified asphalt. As discussed before, polymer plays an important role, not only as a filler, but, more importantly, as an agent for enhancing the properties of the asphalt. In this regard, miscibility of the polymer with asphalt can be critical for the final rheological properties of the mixture. Thus, chlorinated polyethylene is used as a modifier in this study. Moreover, there is little data available regarding the characteristics of asphalt which is modified by this type of polymer.

2. Theory

Asphalt is a thermoplastic material. In other words, its consistency changes with temperature. Temperature susceptibility is, more precisely, defined as the rate at which the consistency of an asphalt changes with a change in temperature and is a very important property of asphalt[12].

One measure of the temperature susceptibility of an asphalt can be written quantitatively by a expression that was designated penetration index(PI) by Pfeiffer and Van Doormaal[13]. Penetration, which is a depth of penetration by a needle, can be measured at two temperatures to obtain the index. Logarithm of penetration is plotted against the test temperature. The plot normally gives a straight line. The slope A of this line is calculated as follows :

$A = \log Pen.\ at\ T_1 - \log Pen.\ at\ T_2 / T_1 - T_2$

The following empirical expression is then used to calculate the PI :

$PI = 20 - 500\ A/1 + 50\ A$

The lower the PI value of an asphalt, the higher its temperature susceptibility. Asphalt with a PI below -2 are highly temperature susceptiblity, usually exhibit brittleness at low temperatures, and are very prone to transverse cracking in cold climates.

As an another criterion for expressing the temperature susceptibility of an asphalt, McLeod proposed Pen-Vis Number(PVN)[14]. This number is based on penetration at 25℃ and viscosity in centiskokes at either 135℃ or 60℃. The following formula is used to calculate PVN :

$PVN = ((\log L - \log X)/(\log L - \log M)) * (-1.5)$

where

X = the viscosity in centistockes measured at 135℃.
L = the viscosity at 135℃ for a PVN of 0.0.
M = the viscosity at 135℃ for a PVN of -1.5.

The viscosity values of L and M can be read from the graph obtained by McLeod by plotting penetration at 25℃ against viscosity at 135℃ for typical asphalts. However, the following equations can be used to calculate more accurate values of L and M. The equations for the line representing a PVN of 0.0 and -1.5 respectively are

$L = \log V = 4.25800 - 0.79670 \log Pen.$
$M = \log V = 3.46289 - 0.61094 \log Pen.$

Where V is the viscosity in centistokes at 135℃, Pen. is the penetration at 25℃.

The lower the PVN values of an asphalt, the higher its temperature susceptibility.

3. Experimental

3. 1. Materials

Two different grades of asphalt(85/100, 200/300) were obtained from Esso Petroleum, Canada. They represents a hard and soft grades of asphalt, respectively. $AlCl_3$(Aldrich Chemical Co.) was used as received. Polymers used in this study are Tyrin 2552 and Tyrin CM 0730(Dow Chemical Co.). They are chlorinated polyethylenes. Properties of them are shown in Table 1.

Table 1. Physical Properties of Tyrin 2552 and Tyrin CM0730

	Physical properties	Value
Tyrin 2552	Chlorine conten(%)	25
	Heat of fusion(cal/g)	8
	Specific gravity	1.1
	Melt viscosity(190℃, 144sec^{-1} (poises))	1250
	100% modulus(psi)	500
	Ultimate tensile(psi)	1500
	Ultimate elongation(%)	800
Tyrin CM0730	Chlorine content(%)	30
	Moony viscosity, ML_{1+4}(121℃)	8
	Residual crystallinity(%)	<2
	Specific gravity	1.13
	Tensile strength(psi)	2600
	200% modulus(psi)	1400
	Ultimate elongation(%)	800
	Hardness, shore A	75

3. 2. Preparation of the Polymer Modified Asphalt

Polymer modified asphalt is typically prepared by mixing the polymer with asphalt in 1.5 liter reactor, followed by heating and stirring. The mixer(Polytron Mixer, Brinkman Insruments) is equipped with high shear agitation and a speed of up 4000 rpm. The mixing temperature is 195℃ and the maximum mixing time is 4 hours.

3. 3. Measurement of Penetration and Viscosity

General procedure of penetration measurement (ASTM D5) : sample is placed under a needle of given dimensions. The needle is loaded with a 100g weight and is allowed to penetrate the sample for 5 seconds. The depth of penetration is measured in units of 0.1 mm and is reported as penetration unit.

Viscosity is typically measured as follows : viscosity measurement is obtained using coaxial cylinder geometry(Brookfield Engineering Laboratories, Thermosel system, RVT). Sample is put into sample chamber and the temperature of sample chamber is controlled thermostatically at prescibed temperature.

From these results, the penetration index, and the penetration viscosity number are calculated.

4. Results and Discussion

4. 1. Rheological Properties

The asphalts employed in this study represents two different kind of grades : soft(200/300) and hard(85/100) grades. And the polymers are also of two different characteristics : plastomer(Tyrin 2552) and elastomer(Tyrin CM0730). To modify the temperature susceptibility of the asphalts, the asphalts are blended with the polymers in the presence of $AlCl_3$. When the asphalt is mixed with polymer, not only the individual type of asphalt and polymer, but the miscibility of the two components can affect the characteristic of the mixture. One way of improving miscibility of two components is linking asphalt and polymer chemically. By using $AlCl_3$, it may be expected that $AlCl_3$ catalyze the grafting reaction of polymer to asphalt.

Penetration and viscosity of thus prepared asphalts are investigated and tabulated in Table 2 and 3. To better discern the differences caused by the factors, which are affecting the rheological properties of the blends, the penetration data are plotted

Table 2. Penetration Data for Two Grade Asphalts and Polymer Modified Asphalts

Materials				Log Pentration				
Asphalt	Catalyst	Modifer (Polymer)	Mixing Time(hr)	Temperature(℃) 10	20	25	30	40
85/100 (Hard Type)	–	–	–	1.423	1.703	1.816	2.031	2.390
	$AlCl_3$ (0.5%)	–	2	1.352	1.607	1.771	1.940	2.300
		–	4	1.312	1.580	1.748	1.908	2.279
		Tyrin 2552(5%)	1	1.176	1.423	1.498	1.672	1.937
			2	1.114	1.398	1.477	1.653	1.857
			3	1.114	1.398	1.462	1.562	1.785
			4	1.114	1.312	1.389	1.512	1.677
		Tyrin CM0730(5%)	2	1.161	1.398	1.484	1.574	1.892
			4	1.204	1.332	1.455	1.550	1.771
200/300 (Soft Type)	–	–	–	1.820	2.116	2.276	2.420	–
	$AlCl_3$ (0.5%)	–	2	1.667	1.914	2.059	2.230	–
		–	4	1.562	1.857	2.004	2.170	–
		Tyrin 2552(3%)	2	1.491	1.781	1.878	1.949	2.188
			4	1.447	1.724	1.813	1.898	2.093
		Tyrin 2552(5%)	1	1.389	1.633	1.716	1.789	2.017
			2	1.380	1.667	1.740	1.860	2.135
			3	1.380	1.667	1.736	1.863	2.134
			4	1.371	1.638	1.720	1.799	1.989
		Tyrin CM0730(3%)	2	1.580	1.903	2.029	2.041	2.204
			4	1.505	1.771	1.875	2.041	2.204
		Tyrin CM0730(5%)	2	1.512	1.744	1.848	1.991	2.241
			4	1.470	1.760	1.857	2.011	2.260

Table 3. Viscosity Data for Two Grade Asphalts and Polymer Modified Asphalts

Materials				Log Viscosity			
Asphalt	Catalyst	Modifer (Polymer)	Mixing Time(hr)	Temperature(℃)			
				80	100	120	135
85/100	–	–	–	4.176	3.544	2.903	2.544
	$AlCl_3$ (0.5%)	–	2	4.505	3.708	3.079	2.716
		–	4	4.531	3.740	3.114	2.740
		Tyrin 2552(5%)	1	5.949	5.255	4.041	3.602
			2	6.041	5.204	4.021	3.602
			3	5.973	5.230	4.097	3.663
			4	–	6.041	4.869	4.267
		Tyrin CM0730(5%)	2	5.009	4.176	3.556	3.176
			4	5.158	4.322	3.681	3.279
200/300	–	–	–	3.771	3.097	2.602	1.813
	$AlCl_3$ (0.5%)	–	2	4.051	3.398	2.778	2.477
		–	4	4.161	3.447	2.903	2.544
		Tyrin 2552(3%)	2	4.892	4.097	3.380	3.000
			4	5.505	4.146	3.431	3.041
		Tyrin 2552(5%)	1	6.134	5.398	3.954	3.477
			2	6.008	5.301	3.903	3.447
			3	6.000	5.279	3.978	3.531
			4	5.892	5.190	4.011	3.568
		Tyrin CM0730(3%)	2	4.415	3.633	3.097	2.498
			4	4.820	3.978	3.398	3.041
		Tyrin CM0730(5%)	2	5.000	4.176	3.556	3.176
			4	5.146	4.322	3.681	3.279

from Fig. 1 to Fig. 4 ; the viscosity ones from Fig. 5 to Fig. 8. By adding $AlCl_3$ to asphalt, the resulting penetration values decrease compared to those of asphalts before adding $AlCl_3$ for both of the asphalts as shown in Table 2. But viscosities in Table 3. increase. Therefore, it may be said that $AlCl_3$ causes some reactions among asphalts, leading to the increase of molecular weight. In Fig. 1. 2. 5. and 6 , the effect of mixing time on penetrtion and viscosity is shown. For Tyrin 2552 modified 200/300 asphalt, both penetration and viscosity does not change with increasing mixing time. However, for Tyrin 2552 modified 85/100 asphalt, the slope of penetration line for mixing time shows a decreasing trend as temperature increases, while viscosities seem to be unchanged up to 3hr mixing time. The effect of adding $AlCl_3$ and the polymers to asphalts on penetration and viscosity is illustrated in Fig. 3. 4. 7 and 8. Both of asphalts qualitatively show a decrease in penetration and an increase in viscosity when $AlCl_3$, or $AlCl_3$+Tyrin 2552 or $AlCl_3$+ Tyrin CM0730 is added to the asphalts. Quantitatively, they show a difference: a) for 200/300 asphalt, the slope of penetration line of $AlCl_3$+Tyrin CM0730 is more pronounced than that of $AlCl_3$+ Tyrin 2552, b) for 85/100 asphalt, the slope of penetration line decreases for both of the polymers. The influence of the amount of polymer added on penetration and viscosity for 200/300 asphalt is shown is Fig. 4 and 8. As expected, by increasing the amount of polymer viscosity increases. but for Tyrin 2552, penetration decreases as the polymer content increases. Tyrin 2552 shows more conspicuous effect on viscosity than Tyrin CM0730 does.

The effect of type of asphalt and polymer on penetration and viscosity is seen in Fig. 3 and 7. For Tyrin CM0730, the type of asphalt has no effect on viscosity. Penetration data show following decreasing order, 200/300 asphalt+Tyrin CM0730>200/300 asphalt+Tyrin 2552>85/100+Tyrin CM0730

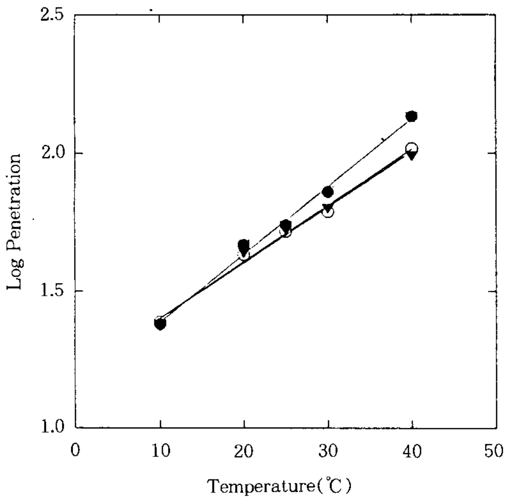

Fig. 1. Log penetration as a function of temperature for Tyrin 2552(5%) modified 200/300 after different mixing time : 1hr (○), 2hr (●), 3hr (▽), 4hr (▼).

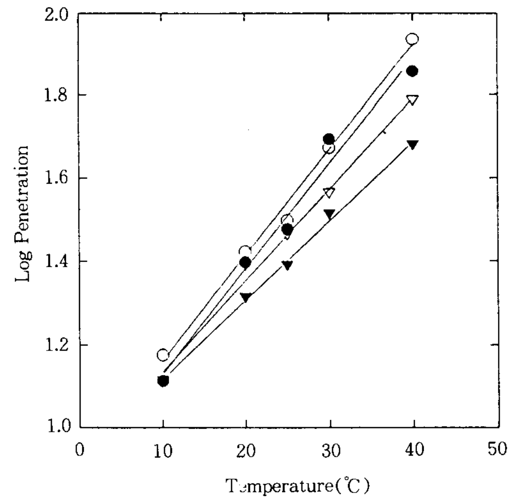

Fig. 2. Log penetration as a function of temperature for Tyrin2552(5%) modified 85/100 after different mixing time : 1hr (○), 2hr (●), 3hr (▽), 4hr (▼).

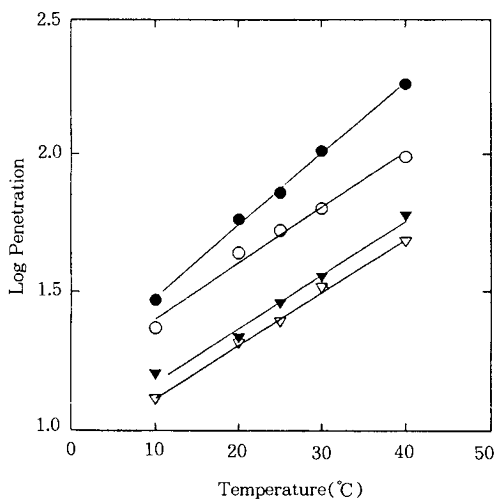

Fig. 3. Log penetration as a function of temperature for various asphalt(4hr mixing) : 200/300+$AlCl_3$+Tyrin 2552(5%) (○), 200/300+$AlCl_3$+Tyrin CM0730(5%) (●), 85/100+$AlCl_3$+Tyrin 2552(5%) (▽), 85/100+$AlCl_3$+Tyrin CM0730(5%) (▼).

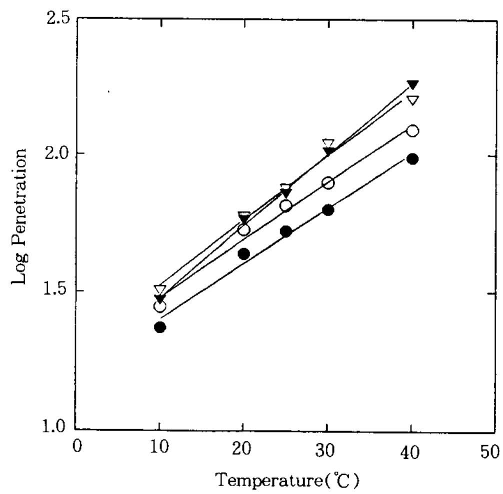

Fig. 4. Log penetration as a function of temperature for 200/300 and $AlCl_3$ with different chlorinated polyethylene(4hr mixing) : Tyrin 2552 (3%) (○), Tyrin 2552(5%) (●), Tyrin CM0730(3%) (▽), Tyrin CM0730(5%) (▼).

>85/100 asphalt+Tyrin 2552. It seems that the type of polymer has a significant effect on the penetration.

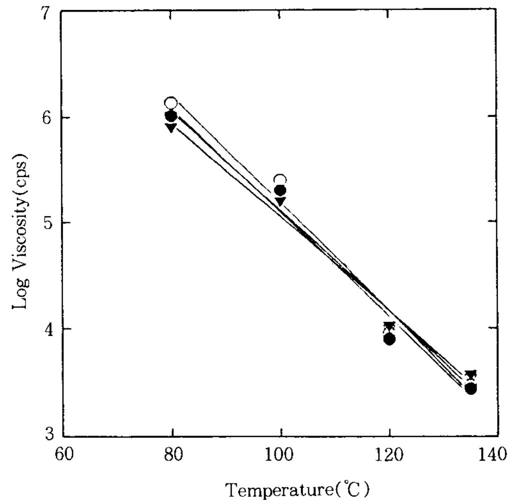

Fig. 5. Log viscosity as a function of temperature for Tyrin 2552(5%) modified 200/300 asphalt (○), 1hr mixing (●), 2hr (▽), 3hr (▼), 4hr.

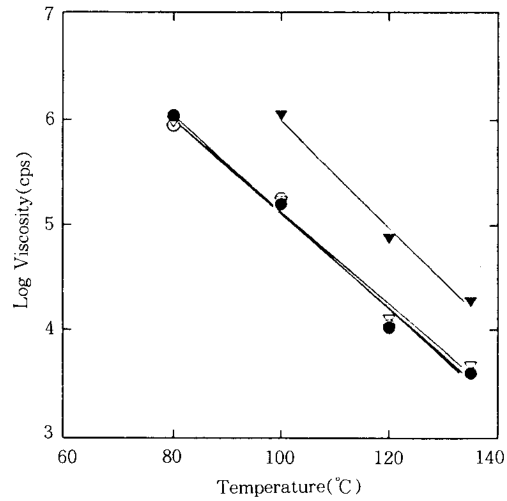

Fig. 6. Log viscosity as a function of temperature for Tyrin 2552(5%) modified 85/100 after different mixing time : 1hr (○), 2hr (●), 3hr (▽), 4hr (▼).

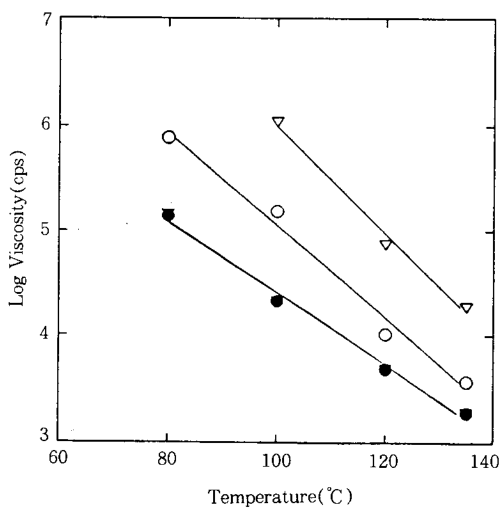

Fig. 7. Log viscosity as a function of temperature for various asphalt(4hr mixing) : 200/300+$AlCl_3$+Tyrin 2552(5%) (○), 200/300+$AlCl_3$+Tyrin CM0730(5%) (●), 85/100+$AlCl_3$+Tyrin 2552(5%) (▽), 85/100+$AlCl_3$+Tyrin CM0730(5%) (▼).

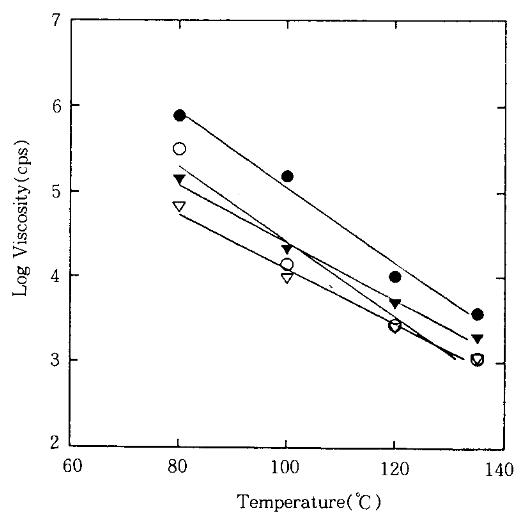

Fig. 8. Log viscosity as a function of temperature for 200/300 and $AlCl_3$ with different chlorinated polyethylene(4hr mixing) : Tyrin 2552 (3%) (○), Tyrin 2552(5%) (●), Tyrin CM0730(3%) (▽), Tyrin CM0730(5%) (▼).

4. 2. Temperature Susceptibility

As discussed before, temperature susceptibility takes on a fundemental meaning for characterizing asphalt and modified asphalt. It can be quantified by the penetration index(PI) and pen-vis number (PVN). These indices are obtained from the measurements of penetration and viscosity of the asphalt samples. From preceding penetraion and viscosity data, PI and PVN of the chlorinated polyethylene modified asphalts are tabulated in Table 4 and shown in Fig. 9 to Fig. 12.

In Fig. 9. the effect of adding $AlCl_3$ to asphalt is shown. PVN values are increased for both of asphalt as $AlCl_3$ is used. But the extent of the increment is bigger for 200/300 asphalt than for 85/100 asphalt. And PI values show no change. The influence of mixing time for Tyrin 2552 modified asphalts is seen in Fig. 10. It seems that the values of PI and PVN are essentially independent of mixing time for modified 200/300 asphalts, whereas both values of PI and PVN increase with mixing time for modified 85/100 asphalts.

When polymeric material is mixed with asphalt, the resulting modified asphalt is naturally expected to show changes in PI and PVN compared to the unmodified asphalt. The quantitative effect of modification by Tyrin 2552 and Tyrin CM0730 for 200/300 and 85/100 asphalt is illustrated in Fig. 11. For both of asphalts, the addition of the polymers sharply increases the values of PI and PVN. A slight difference exerted by the type of polymers is noticed : Tyrin 2552 modified asphalt shows higher

Table 4. PI and PVN Data for Two Grade Asphalts and Polymer Modified Asphalts

Materials				PI[a)]	PVN[b)]
Asphalt	Catalyst	Modifer(Polymer)	Mixing Time(hr)		
85/100	–	–	–	+1.47	−0.87
	$AlCl_3$ (0.5%)	–	2	+1.58	−0.48
		–	4	+1.47	−0.40
		Tyrin 2552(5%)	1	+3.25	+1.56
			2	+3.39	+1.50
			3	+4.32	+1.63
			4	+5.42	+3.12
		Tyrin CM0730(5%)	2	+4.35	+0.29
			4	+5.31	+0.51
200/300	–	–	–	+1.98	−2.45
	$AlCl_3$ (0.5%)	–	2	+2.10	−0.51
		–	4	+1.98	−0.41
		Tyrin 2552(3%)	2	+4.08	+0.80
			4	+4.60	+0.74
		Tyrin 2552(5%)	1	+4.85	+1.85
			2	+3.45	+1.83
			3	+3.45	+2.08
			4	+4.96	+2.94
		Tyrin CM0730(3%)	2	+3.48	+0.51
			4	+3.73	+0.93
		Tyrin CM0730(5%)	2	+3.54	+1.29
			4	+2.99	+1.67

a) PI : Penetration Index
b) PVN : Penetration Viscosity Number

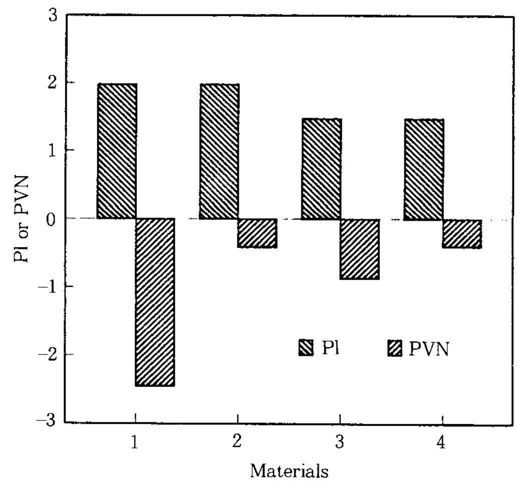

Fig. 9. Bar diagrams of PI and PVN for various asphalt(4hr mixing) : (1) 200/300, (2) 200/300+$AlCl_3$, (3) 85/100, (4) 85/100+$AlCl_3$.

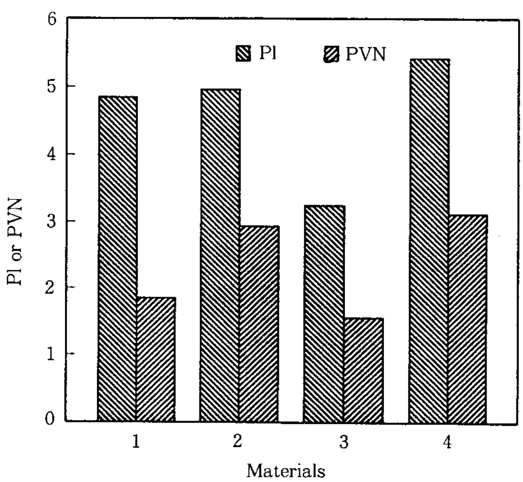

Fig. 10. Bar diagrams of PI and PVN for TYRIN 2552(5%)modified asphalt after different mixing time : (1) 1hr(200/300), (2) 4hr(200/300), (3) 1hr(85/100), (4) 4hr(85/100).

values of PI and PVN than Tyrin CM0730 modified one does for 200/300 asphalt, while the type of polymer does not make differences in PI values but Tyrin 2552 modified asphalt displays higher PVN values than Tyrin CM0730 modified one does for

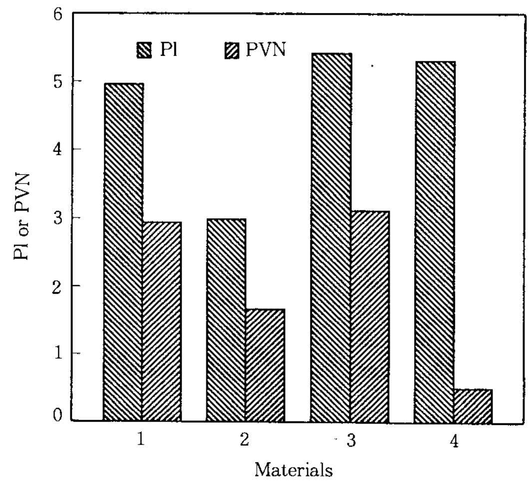

Fig. 11. Bar diagrams of PI and PVN for chlorinated polyethylene modified asphalt(4hr mixing) :(1) 200/300+$AlCl_3$+TYRIN 2552(5%), (2) 200/300+$AlCl_3$+TYRIN CM0730(5%), (3) 85/100+$AlCl_3$+TYRIN 2552(5%), (4) 85/100+$AlCl_3$+TYRIN CM0730(5%).

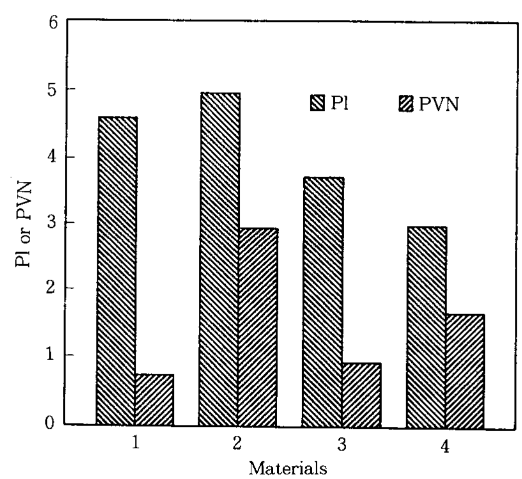

Fig. 12. Bar diagrams of PI and PVN for 200/300+$AlCl_3$ with different chlorinated polyethylene(4hr mixing) : (1) TYRIN 2552(3%), (2) TYRIN 2552(5%), (3) TYRIN CM0730(3%), (4) TYRIN CM0730(5%).

85/100 asphalt. The effect of amount of polymer added for 200/300 asphalt plotted in Fig. 12. It seems that the values of PI essentially do not change with the amount of polymer for both of polymers, whereas the values of PVN increase with the content of polymer.

5. Conclusion

Two grade of asphalts qualitatively show a decrease in penetration and an increase in viscosity when Tyrin 2552 or Tyrin CM0730 is added to the asphalts. Quantitatively, they show a difference : a) for 200/300 asphalt, the slope of penetration line for Tyrin CM0730 modified one is more pronounced than that for Tyrin 2552 modified one, b) for 85/100 asphalt, the slope of penetration line decreases for both of the polymers modified ones.

For two grade of asphalts, the addition of the polymers sharply increases the values of PI and PVN. A slight difference exerted by the type of polymers is noticed: Tyrin 2552 modified asphalt shows higher values of PI and PVN than Tyrin CM0730 modified one does for 200/300 asphalt, while the type of polymer does not make differences in PI values but Tyrin 2552 modified asphalt displays higher PVN values than Tyrin CM0730 modified one does for 85/100 asphalt.

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