Evaluation of Aging Characteristics of Selected PMA using HP-GPC

HP-GPC를 이용한 폴리머개질 아스팔트의 노화특성 분석

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요 지

산화는 아스팔트에서 대형분자(LMS : Large Molecular Size) 양의 증가를 야기하고 바인더의 경화에 주요 원인이 되므로 바인더 산화를 저감시키면 도로 및 공항 포장의 공용수명 연장을 기대할 수 있다. 바인더 산화는 혼합물을 도로에 깔기 전에 가열된 골재와 혼합하는 동안과 아스팔트 포장이 시공된 후 공용기간 동안에 일어난다. 본 연구에서는 바인더를 단기 및 장기노화 처리 후 LMS의 양적 증가를 HP-GPC (High-Pressure Gel-Permeation Chromatography)의 자료에 근거하여 해석하였다. 개질 아스팔트는 LMS의 증가율이 아스팔트의 종류에 따라 다를지라도 단기노화 후 LMS의 20-30% 증가, 장기노화 후 2배 이상의 증가를 나타냈다. 본 연구에서 개질 아스팔트의 노화특성을 관찰하기 위하여 사용된 개질제는 선행 연구에서 큰 역학적 특성 향상을 보인 LDPE(Low-Density Polyethylene)와 SBS(Styrene-Butadiene-Styrene block copolymers) 를 사용하였다. LDPE로 개질한 바인더는 단 장기노화 후 LMS의 증가 비율이 상당히 낮았다. 이와 같이 낮은 LMS의 증가는 LDPE 개질 아스팔트가 노화 처리되는 동안에 일반 아스팔트보다 덜 노화가 진행된다는 것을 의미한다. 이는 아스팔트 시멘트 내에 분산된 LDPE 입자가 산화 노화작용을 방해하기 때문인 것으로 보인다.

핵심용어 : 아스팔트, 폴리머개질아스팔트, 노화, 산화, GPC, LDPE, SBS, HP-GPC, RTFO, PAV

Abstract

Oxidation causes increment of the quantity of large molecular size or LMS in asphalt and is a major reason for hardening of asphalt binder. An extended service life of pavement on a road is expected by reducing oxidation of binder. Oxidation of binder occurs during hot mixing with aggregates before placement on road and then during in-service after the asphalt pavement is constructed. Quantitative increase of LMS as result of aging after RTFO and PAV was analyzed

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based on the data from high-pressure gel-permeation chromatography (HP-GPC). Polymer modified asphalt (PMA) after RTFO procedure showed 20-30% increment in LMS and then after PAV procedure more than twice, although the percentage of increment was different according to asphalt brand and grade. The PMAs containing LDPE or SBS, which showed a great mechanical property improvement in previous studies, were selected for characterizing PMA aging in this study. Considerably reduced increment of LMS was observed from the PMA containing LDPE after RTFO and PAV procedures. The GPC result showing the binder with less LMS increment means that the asphalt while being mixed with LDPE was aged less during the aging treatment. The dispersed particle of LDPE in asphalt cement seems to disturb oxidative aging reaction and evaporation.

INTRODUCTION

Polymer modifiers are being used in an effort of reducing early pavement distress and to extend service life by enhancing the binder's adhesion, cohesion and elasticity. The idea of adding polymer to asphalt to improve its property dates back to beginning of the 1960s (Laboratoire... 1963). Addition of polymer(s) alters the rheological properties of asphalt allowing softer asphalt to be used without causing adverse performance at higher service temperatures and improves properties such as resistance to cracking (Lee and Hesp 1994).

Although an interest has mainly focused at the effect of polymer on binder rheology change and mixture property change, the effect of polymer on the aging of binder has not been recognized. In a previous polymer modified asphalt (PMA) study (Kim 1996, Kim et al. 1997), the fact that some polymers had something to do with delaying aging has been recognized and led authors' deep attention to the analysis of the effect of polymers on aging.

Asphalt is made from crude petroleum and composed of carbon and hydrogen about 90 to 95 percentage by weight. The remaining portion consists of metals and heteroatoms such as nitrogen, oxygen, and sulfur. In addition, cyclic rings in naphthene or aromatic molecules are opened and combined with oxygen to form carbonyl groups. These carbonyl groups actually increase aging viscosity instead of the oxidized sulfur. Oxidation is the primary part of the overall asphalt aging process; evaporation (volatilization) and degradation associated with light (photo-degradation) also slightly contribute. Oxidation changes the structure and composition of asphalt molecules, resulting in increased quantities of high-molecular weight molecules, generating the term oxidative hardening or age hardening.

In practice, a considerable amount of oxidative hardening occurs before the asphalt is placed. At the hot mixing facility, asphalt binder is added to the hot aggregate and the mixture is maintained at elevated temperatures for an hour or two at least. The Superpave specification uses the rolling thin film oven (RTFO) procedures to simulate this form of aging. After the asphalt pavement is constructed, aging continues. The Superpave specification uses the pressure aging vessel (PAV) procedure to simulate in-service aging (Superpave... 1995).

High-pressure Gel permeation chromatography

(HP-GPC) is a useful technique for examining molecular size distribution of asphalt binder. Many researchers showed GPC was a relatively accurate method for evaluating aging of normal asphalt (Kim and Burati 1993, Byrum and Traxler 1970, Price 1988) and PMA (Asi et al. 1997, Al-Abdul Washhab et al. 1999). Oxidation of asphalt results in increased quantities of high-molecular-weight molecules (large size molecules or LMS). Thus, aging of asphalt is defined in terms of relative quantity of LMS in the GPC profile.

Objective of this sturdy is to compare the molecular size distribution of selected PMAs and to characterize aging of the PMAs in terms of molecular size distribution change. Since the significance of aging is defined by quantity of LMS, a focus was brought into comparison of LMS quantities to see if any noticeable difference exists between normal asphalt and PMA after aging.

MATERIALS AND METHODS

Materials

Four base asphalts were collected from three different refineries in Korea, and designated as H-AP3, L-AP3, S-AP3, and S-AP5. The penetration grade of the AP3 asphalt is 85-100 and that of AP5 asphalt is 60-70. Polymers used in this study were LDPE (low-density polyethylene) and SBS (styrene-butadiene-styrene block copolymers). These polymers were originally selected as the best performing modifiers from several choices for reducing rutting and improving tensile properties of asphalt mixture in previous studies (Kim 1996, Kim et al 1998). Each polymer (powder type) was added to a pre-heated asphalt at 180℃ while mixing with a high-shear

Table 1. Binder designation and its description

Binder	Description
Fresh	Fresh asphalt without any aging process
NA	Normal asphalt without polymer
L3	PMA with 3% LDPE by weight of asphalt
L4	PMA with 4% LDPE by weight of asphalt
L5	PMA with 5% LDPE by weight of asphalt
L6	PMA with 6% LDPE by weight of asphalt
S3	PMA with 3% SBS by weight of asphalt
S4	PMA with 4% SBS by weight of asphalt
S5	PMA with 5% SBS by weight of asphalt

homogenizer.

Contents of LDPE were 4, 5 and 6% by weight of binder for AP3 and 3, 4 and 5% for AP5. Contents of SBS were 3, 4 and 5% for all asphalts. These contents were determined based on the result of mechanical property testing on PMA mixtures in previous studies (Kim 1996, Kim et al 1998).

Table 1 shows each binder designation and its description. Fundamental properties of each binder are shown in Table 2. Absolute viscosity (AVS), kinematic viscosity (KVS) and penetration (PEN) were measured by ASTM D2170, ASTM D2171 and ASTM D5, respectively. High-temperature and low-temperature performance grade (PG) were measured by Strategic Highway Research Program (SHRP) method using dynamic shear rheometer (DSR) and bending beam rheometer (BBR), respectively.

Methods

The chromatogram profile explains how much asphalt contains quantities of high, medium and low molecular weight molecules. A Waters GPC equipment with computerized data-acquisition software was used for the chromatographic analysis of the asphalt binders. A differential refractive index meter (Waters 410 RI detector) was used as a detector.

Table 2. Fundamental properties of asphalts binders before aging

Asphalt	Polymer	Penetation (0.1mm)	Absolute Viscosity(ps)	Kinematic viscosity(cps)	PG
H-AP3	NA	99	827	278	58-16
	L4	69	2598	650	64-10
	L5	63	3063	856	70-10
	L6	65	3938	975	70-10
	S3	72	4533	700	64-16
	S4	60	5864	850	64-10
	S5	64	8207	1105	70-10
L-AP3	NA	94	1387	296	58-16
	L4	71	2612	883	70-10
	L5	59	3748	1078	70-10
	L6	54	5086	1325	76-10
	S3	83	3549	750	64-10
	S4	66	5308	1033	70-10
	S5	60	18817	1458	70-10
S-AP3	NA	95	951	285	58-16
	L4	66	2400	636	64-16
	L5	48	3369	783	64-16
	L6	63	5229	1046	70-10
	S3	81	2901	580	64-16
	S4	67	4708	805	64-16
	S5	62	6966	1048	70-16
S-AP5	NA	60	1865	432	64-10
	L3	50	3813	786	70-10
	L4	42	4934	953	10-10
	L5	41	5620	1143	76-10
	S3	50	5496	932	70-10
	S4	40	11818	1455	76-10
	S5	40	11807	1680	76-10

A series of two styragel columns (Waters HR 4E and HR 3) was used for separating constituents of asphalt by molecular size. For testing the sample at a constant temperature, the columns were kept at 35℃ throughout the test in a column oven. The mobile phase was tetrahydrofuran (THF) flowing at a rate of 1 ml/min. A test sample was dissolved into THF and filtered through a 0.45-μm syringe filter prior to injection into a 50 ml injection module. The concentration of sample was 1/200 or 0.5% by wt, and three test were conducted for a sample.

The filtered-out asphalt solution was injected into GPC system for analysis after 15min, 60 min, 180 min and 240 min incubation in the room temperature (25 ℃). A fresh binder (S-AP3) and binders after RTFO and PAV treatment were used for comparison of association intensity by incubation time. The LDPE which is non soluble in THF solvent and larger than 0.45-μm was also filtered out. Therefore, only asphalt molecule in the sample of LDPE PMA was eluted (detected), without LDPE molecule, through columns.

Figure 1 illustrates a typical chromatogram of an asphalt in fresh and after PAV-treated conditions. Elution of asphalt started at approximately 11 min and ended at around 20 min from injection. The area under a curve represents 100% of the asphalt molecules
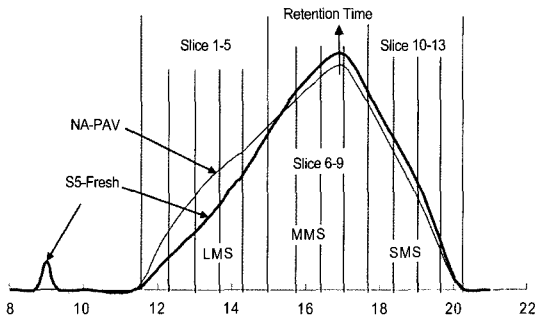
Figure 1. Typical chromatograms of fresh S5 and PAV-treated NA asphalts and illustration of 3 molecular groups and 13 slices.

injected into the column except for SBS PMA. Some of smaller SBS molecules which were not screened out by 0.45μm filter were eluted at around 9 min, showing a small peak as shown in the figure.

Investigators classified asphalt constituents into several groups, such as 3, 8, 10, 12 and 30 by elution time or by average area (Garrick and Wood 1994, Kim and Burati 1993, Price 1988, Kim et al 1995, 1997, Wahhab et al 1999). In this study a chromatogram was partitioned into 13 slices and three molecular groups, large molecular size (LMS: slice 1 to 5 from left), medium molecular size (MMS: slice 6 to 9) and small molecular size (SMS: slice 10 to 13) as shown in Figure 1.

Defining LMS portion as front 5 slices was verified in the previous study (Kim et al 1995), in which LMS of normal asphalt was defined as the area under a curve from elution start to the elution time slightly past 1/3 of total elution time. Among quantitative data (%) of the chromatograph, the front part or LMS value was only used for evaluation of binder aging.

However, in calculation of LMS, the initial peak of SBS PMA, shown in Figure 1, was disregarded, because the peak is not the response of asphalt. The peak is a response of SBS molecules smaller than pore size of 0.45um filter, but much greater than largest

asphalt molecule.

Each binder was conditioned by RTFO aging procedure for short term asphalt aging. The RTFO conditioned binders were used for penetration, viscosity tests and chromatographic analysis. The binder in PAV were removed after 20 hours of exposition to a high pressure (2070 kPa) at 90℃ and was placed in a 163℃ oven for 30 min and then transferred to a storage container for further testing.

To determine content of asphaltene, the bitumen was dissolved in n-heptane (0.5g/20 ml) and followed by 5 minutes of ebullition. The warm solution was then filtered through a 0.45-μm membrane. The precipitate and the membrane were dried at 100℃ until constant weight. Three tests were conducted for each sample and range value was reported.

RESULT AND DISCUSSION

Association of asphalt

Although LMS gradually increased by time up to 180 min as shown in Figure 2, LMS did not increase any further after that time. The gradual LMS increase is related with the association of asphaltene as colloidal particles in THF solution with asphalt 0.5wt% (Figure 3), because asphaltene is considered to associate in most solvent.

The LMS area % of the fresh asphalt was only approximately 9% but those in the asphalts after RTFO and PAV became greater as shown in Figure 2. The highest amount of LMS after PAV indicates that the binder became rich with high- molecular-weight molecules due to aging.

The increment in LMS (%) according to incubation time was minor for fresh asphalt. However, for the asphalt after PAV, the increments according to
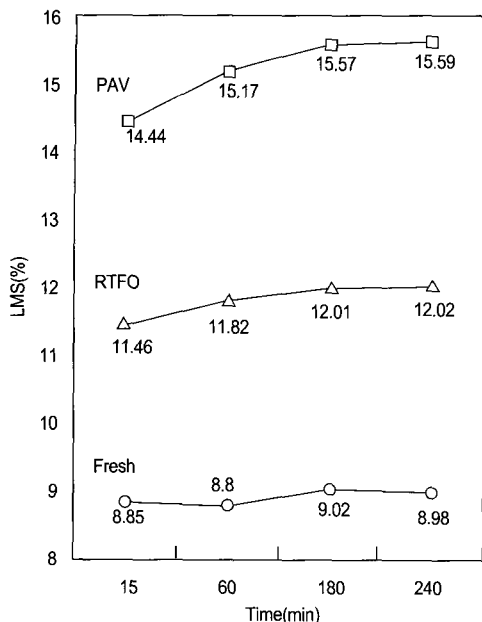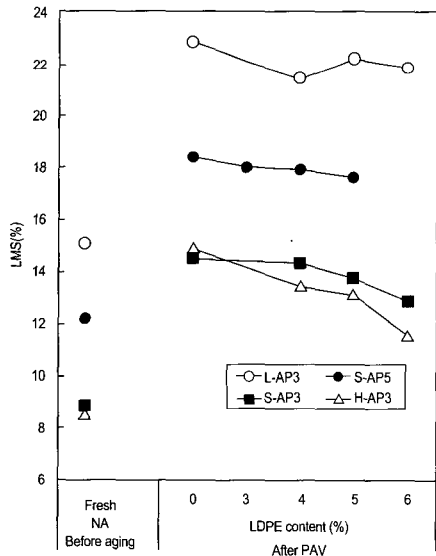
Figure 2. Change of LMS(%) by incubation time

Figure 3. LMS in each asphalt by LDPE content after PAV.

incubation time became greater than any other conditioning. This indicates that the degree of association depends on the initial amount of high-molecular-weight molecules in the binder because the higher content of asphaltene creates the more association among molecules.

Therefore, since LMS does change by incubation time, the GPC data from 3-hour incubation were used for analysis in this study. It is recommended that three-hour incubation or approximately the same incubation time should be used throughout the study to obtain more consistent test results from GPC analysis.

Effect of LDPE on asphalt aging

Although the effect of polymer in PMA on aging of the base asphalt has not draw much attention in asphalt industry, this study detected a sign of delaying or retarding aging of the asphalt in LDPE PMA. The major evidence of this finding is that LDPE PMA had less amount of LMS than normal asphalt after PAV as shown in Table 3. To clarify this effect of LDPE by content, binders containing different amount of LDPE was evaluated. Polymer content was found to be an important factor in formation of LMS shown in Figures 3. On the other hand, other polymer as shown in Figure 4 did not show the same pattern of the phenomenon.

It was observed after PAV that the higher the LDPE content, the lower the LMS increment. This phenomenon was more clearly evidenced in H-AP3 and S-AP3 asphalts (Figure 3). The lower LMS increment ratio in PMA containing LDPE after artificial aging may be due to a certain retarding effect of LDPE against molercular association of aged asphalts. Although the GPC test evaluated LDPE PMA, the sample injected into GPC was only the solution of asphalt cement out of the PMA after filtering the LDPE particle out.

Therefore, the GPC profile represents the aging characteristics of base asphalt cement in the PMA, which was mixed with LDPE. The GPC result

Table 3. Area % change in LMS after RTFO and PAV

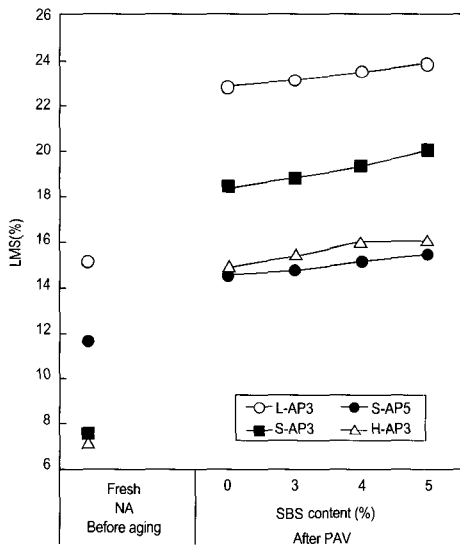| Asphalt	Polymer	Aging treatment							
		Fresh		RTFO			PAV		
		LMS (%) 1	LMS (%) 2	Increment		LMS (%) 4	Increment		
				Amount 2-1=3	Ratio(%) 3/1 × 100		Amount 4-1=5	Ratio(%) 5/1 × 100	
H-AP3	NA	8.66	12.13	3.47	40.1	14.59	5.93	68.5	
	LDPE	8.82	11.56	2.74	31.1	12.50	3.68	41.7	
	SBS	8.67	11.22	2.55	29.4	15.59	6.92	79.8	
L-AP3	NA	15.11	18.50	3.39	22.4	22.14	7.03	46.5	
	LDPE	15.22	18.71	3.49	22.9	21.84	6.62	43.5	
	SBS	15.14	17.71	2.57	17.0	23.42	8.28	54.7	
S-AP3	NA	8.85	11.59	2.74	31.0	14.53	5.63	63.3	
	LDPE	8.86	11.05	2.19	24.7	13.75	4.89	55.2	
	SBS	8.88	10.85	1.97	22.2	14.85	5.97	67.3	
S-AP5	NA	12.22	14.77	2.55	20.9	18.42	6.20	50.7	
	LDPE	12.28	13.82	1.54	12.5	17.26	4.98	40.6	
	SBS	12.49	14.75	2.26	18.1	19.88	7.39	59.2	

Figure 4. LMS in each asphalt by SBS content after PAV.

showing the binder being in less aging condition means that the asphalt mixed with LDPE was aged less during the aging treatment. When LDPE is mixed into an asphalt, LDPE particles are being dispersed in the asphalt. The dispersed particle of LDPE in asphalt cement seems to disturb aging reaction and evaporation.

Comparison of the LMS area (%) among base asphalts

A comparison of each slice area (%) of 4 base asphalts in fresh condition is shown in Figure 5. S-AP3 and H-AP3 displayed similar LMS quantities as shown in Table 4. But L-AP3, penetration grade of which is the same as S-AP3 and H-AP3, had much higher quantity of LMS. This asphalt also showed a

Table 4. Comparion of LMS quantity of base asphalts

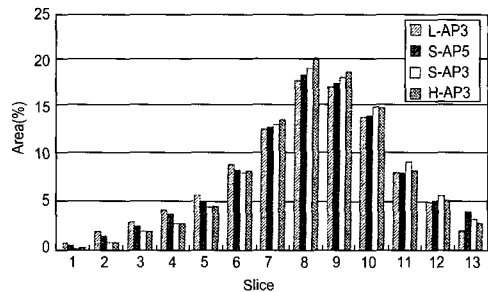| Asphalt	H-AP3	L-AP3	S-AP3	S-AP5
LMS(%)	8.66	15.11	8.85	12.22

Figure 5. Comparison of slice area(%) of fresh asphalts

higher absolute viscosity(Table 2) than any other same-grade asphalts.

It is widely known that LMS quantity has a good correlation with performance of asphalt pavement in the field (Jennings 1980, Jennings and Prabanic 1985, Kim and Burati 1993, Kim et al 1995, Price 1988). The result about L-AP3 suggests that the asphalt should have different property from other AP3 asphalts even though it has the same penetration grade. This is an evidence that if the grade of binder for the pavement in a certain environmental condition is selected by penetration only, there is a high chance for the asphalt to perform unexpectedly in the field.

The higher amount of LMS was expected in S-AP5 than in S-AP3 because of its lower penetration grade and the result confirmed that the binder with a lower penetration have a higher macromolecule content.

RTFO-aged binders

Table 3 shows average LMS values for each aging treatment for each PMA. After RTFO procedure, LMS increased approximately 1.5-3.5% points or 12.5 - 40.1% in ratio in all binders. This result indicates that the aging occurred in asphalt molecules by reacting with oxygen at high temperature.

Each cell value of LDPE and SBS in Table 3 is the mean of 9 samples (3 polymer contents x 3 replicates), respectively, except for SBS-modified L-AP3 after PAV. The data of Table 3 showed that amounts of LMS in most of PMAs with LDPE or SBS were less than those of normal asphalt after RTFO procedure. This suggests that the polymer has something to do with preventing aging of asphalt.

PAV-aged Binders

The chromatogram analysis results of PAV-aged binder were presented in Table 3. Area (%) of LMS increased up to 80% after PAV procedure (through RTFO). After PAV procedures, the LMS of normal asphalt considerably increased, while PMA containing LDPE showed the least increase in all asphalts. Especially in two LDPE-modified asphalts (H-AP3 and S-AP3), the lower LMS quantities were observed than the other two. Therefore, it is expected that using LDPE as modifier of asphalt binder will give somewhat favorable effect on retarding aging of asphalt.

Although L-AP3 and S-AP5 have the higher content of LMS at fresh state, it was observed that the ratio of LMS increment after PAV showed no meaningful difference from others containing smaller amount of LMS initially. This is an indication of the fact that the increment of LMS by aging is not related with the amount of high-molecular-weight molecules existing originally in binder.

The polymerization of asphalt molecules by condensation reaction is activated by air oxygen or sulfur at high temperature. The molecules that contain -OH, -SH, -NH also favor the formation of high-molecular-weight molecules (Yen and Chilingarian 1994). Therefore, the binders used in this study are considered to consist of a similar chemical composition about aging.

Asphaltene and LMS

Asphaltene is characterized by high polarity and high-molecular weight in asphalt and is known to associate in many solvents (Srorm and Sheu 1994).

In order to find out the association characteristics of asphaltene in THF (tetrahydrofuran), which was used as solvent of asphalt for GPC test, binder was dissolved in THF for 0.5 wt% solution which was determined as a suitable concentration for RI detector

Table 5. Comparison of asphaltene content(%) of base asphalts

Aging	Asphaltene content(%)			
	H-AP3	L-AP3	S-AP3	S-AP5
Fresh	9-10	15-16	8-9	12-13
RTFO	-	17-18	11-12	16-18
PAV	17-19	23-24	16-17	20-23

used in this GPC system. Asphaltene characterized with high mass is considered to exist mainly in LMS and asphaltene content of base asphalt increased by artificial aging as shown in Table 5.

The area (%) of slices 1 to 5 (LMS) among 13 slices mainly increased after artificial aging with corresponding reduction in the other parts (MMS and/or SMS). The LMS occupied approximately front 35~38% of total elution time in a chromatogram. The values of asphaltene in base asphalt in Table 5 are similar to the values of LMS in Tables 3 and 4. Therefore, it is valid that the area % of LMS was used as a variable for comparison of the association of asphaltene.

FINDINGS AND CONCLUSIONS

High-molecular-weight molecules or large molecular size (LMS) were produced due to an artificial aging process. However, the PMA containing LDPE or SBS showed less increment in LMS than normal asphalt after RTFO procedure. After PAV, however, only LDPE PMA showed less increment in LMS than normal asphalt.

The major finding of this study is that the base asphalt in LDPE PMA showed less amounts of LMS than normal asphalt after PAV and that LDPE was found to have favorable effect on retardation of asphalt aging. It was also detected that the higher the LDPE content, the lower the LMS increment after aging treatment. According to the current results, it is

concluded that the base asphalt in LDPE modified-binder existed with being less oxidized.

It was found that the increment of LMS by aging was not related with the amount of high-molecular-weight molecules existing originally in binder. However, the degree of association, resulting in increment of LMS, in THF solution was related with the amount of high-molecular-weight molecules in the binder, depending upon incubation time. Therefore, the incubation time is important and incubation for three hours should be applied or the same incubation time should be used throughout the study to obtain consistent test results from GPC analysis.

This is a just beginning of this type of work. Since the conclusion drawn in this study is based on limited number of GPC evaluation, further studies are needed using other properties with various asphalts for more generalized conclusion.

Acknowledgement

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