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Abstract

Bituminous sealants used in the maintenance of roadways are installed hot and heated to 150°C-200°C during installation. High temperatures can degrade polymers in sealants, but there is no standard method to account for this possible degradation. In an attempt to find such a method, the aging of two sealants in large kettles during field applications was compared to that obtained in the laboratory by heating in a small kettle. The results indicate that 4h of small kettle aging (SKA) at the highest suggested sealant application temperature (HiSAT), or about 2h at HiSAT + 10°C, provided as much copolymer aging as that found in sealants sampled midway through installation.

Keywords: Aging; Asphalt; Bitumen; Crack sealing; Degradation; Gel Permeation Chromatography; Polymer; Sealant; Styrene-Butadiene-Styrene.

1. Introduction

Bituminous, hot-poured, sealants are used in the preventive maintenance of pavements, where they help reduce the infiltration of water, brine and grit in the substructure, thus delaying degradation and extending pavement service life. During installation, sealants are heated to temperatures between 150°C and 200°C for several hours. Early laboratory studies demonstrated that sealants can degrade when they are heated to excessive temperatures or maintained at suggested installation temperatures for too long (Masson *et al*. 1998). Sealant degradation during installation has been substantiated by field studies (Oba and Partl 1996) that showed that the extent of aging varies in the course of installation (Masson *et al. 2007)*.

There is no standard method to reproduce the aging of sealants during installation. The sealant specification ASTM D6690 does not account for the aging of sealants at high temperatures as it states "…(increase) the sealant's temperature to manufacturer's recommended maximum heating temperature within the required 1 hour of time… Immediately upon reaching the maximum heating temperature, pour samples for testing…". Hugener and Hean (1996) compared the aging of four sealants sampled at one time during installation to that obtained by five methods of oxidative aging, including the rolling thin film oven test (RTFOT) at 180°C. No method could be said to mimic the aging of all the sealants during their application. In retrospect, these results are not surprising because the aging of sealants during installation was more recently found to be non-oxidative (Masson *et al.* 2007).

The goal of this study was to determine if the heating of sealants in the laboratory in a vessel immersed in hot oil, a small-scale representation of double-walled kettles used in the field, could simulate the aging of sealants during installation. To this effect, the aging of two sealants were compared in the course of their field installations to the non-oxidative aging obtained in the laboratory during 5h of heating at 185°C, 200°C and 210°C. Given that the sealant copolymer governs sealant rheology (Masson et al. 2007), the aging was assessed by the extent of copolymer degradation in the sealant as obtained by gel permeation chromatography (GPC). It was found that small kettle aging in the laboratory could suitably reproduce sealant aging during installation.

2. Background

2.1 Polymers in sealants

Bituminous sealants often contain a styrene-butadiene (SB) copolymer (Masson *et al.* 2002). These copolymers contain a polystyrene (PS) and a polybutadiene (PB) block, thus the name SB-diblock. These diblocks can be linked to $(SB)_n$, where n is most often 2 to 4. A most common copolymer is the SBS triblock copolymer, where $n=2$, $(SB)_2 \equiv$ SB-BS $\equiv$ SBS. With $n > 2$, the structure is that of an n-arm star. Figure 1 provides an illustration of these structures. Given that these polymers have different sizes, they can be separated by GPC.

[insert Figure 1 about here]

2.2 Gel permeation chromatography (GPC)

GPC separates molecules according to their size by eluting a solution of a mixture through a column filled with a gel. The process is reminiscent of the separation of aggregates passing through several sieves of different sizes. In GPC, the larger

molecules exit the column first and the smallest molecules exit last. The typical GPC result is an intensity-time plot, the column exit time being inversely proportional to the logarithm of the molecular size. Figure 2 shows results for a bitumen, an SBS copolymer and a bituminous sealant (the raw materials in figure 2 are not those in the sealant). Due to its high molecular mass, from about 1.5 Mg/mol to 100 kg/mol, the copolymer in Figure 2 shows a peak at earlier times than bitumen. A small shoulder on the right side of the SBS (labelled as Polymer) peak shows a residual content of SB diblock. Bitumen, which shows as a broad and intense peak at longer times, has molecular masses of about 300 to 1200 g/mol. Its molecular mass is thus 100 to >1M times lower than that of the copolymer. For the sealant in Figure 2, the GPC results show, from left to right, peaks for $(SB)_3$, $(SB)_2$ and bitumen.

[insert Figure 2 about here]

Given that GPC allows for measuring molecular sizes, the method helps to determine the nature of the aging that affects the copolymer in bituminous sealants. Figure 3 illustrates, for instance, the effect of scission and cross-linking on the size and length of a copolymer chain. Figure 4 shows how these degradation pathways can be differentiated by GPC. Copolymer degradation is first visible as a decrease in the intensity of the main copolymer peak. As the copolymer chains break down into smaller fragments, there is a rise in the background on the right side (low molecular mass side) of the main copolymer peak. When there is cross-linking, the rise in molecular mass is visible as an increase in the background on the left side of the main copolymer peak.

With the above background on copolymers in sealants and their analysis by GPC, the effect of field or laboratory aging on the copolymer in a sealant can be presented.

[insert Figures 3 and 4 about here]

3. Procedure

3.1 *Sealants*

Two sealants were studied. Sealants N and Q were hot-pour polymer modified bitumens purported to meet ASTM D6690, type IV sealants. The sealant suggested application temperature range was 185-200°C for sealant N, and 193°C for sealant Q.

3.2 Field aging

The sealants were installed by contractors as part of regular pavement maintenance. Both sealants were heated in kettles of 1500L capacity. The thermal history and the temperature variations and control during the sealant installations were noted. We have reported earlier on the temperature variation (Masson *et al.* 2005).

Prior to installation, sealant N was heated for several hours due to warm-up times in the morning, and because the contractor had a nearly full kettle at the end of the previous day of operation, the sealant was also hot during a cool-down time. The contractor of sealant Q had less sealant in the kettle. Table 1 provides a summary of the thermal history for the sealants *prior* to the beginning of installation: V is the percent volume of sealant in the kettle with respect to full capacity when heating started at 5 to 7AM; R is the percent content of reheated sealant in the kettle when the first crack was sealed in the morning; T^R is the average sealant temperature during warm-up and cool-down for the reheated sealant; and t^R is the total estimated time for warm-up and cool-down based on V. Values for T^R and t^R were estimated from on-site inspection and discussions with the contractors.

Sealant N was heated in a kettle with a rocking bed agitator where the rocking period was about 10s. Sealant Q was heated in a kettle equipped with a circumferential agitator turning with a period of about 20s, or 3 rpm. During installation, sealant N was heated to 187°C, with a standard deviation (sd) of 15°C, whereas sealant Q was heated to 170°C, with an sd of 10°C (Masson *et al.* 2005).

[insert Table 1 about here]

3.3 Field sampling

A box of virgin (unaged) sealant was retrieved, along with heated sealant poured into cracks. About 1 kg of heated sealant was collected every hour from 0 to 5-6h after the contractor had started the work. The virgin material was labelled Nv (or Nvh after remixing in accordance with ASTM D5167). The samples collected in the field during installation were labelled Nk0 to Nk6, where k stood for "kettled" and the 0 to 6 for the time in hours after the start of installation. The same labels were used for sealant Q.

3.4 Small kettle aging

In the laboratory, about 500g of sealant were slowly stirred in a 1L aluminum can bathed in oil maintained at 185°C, 200°C and 210°C. The method is essentially that in ASTM D5167. Sealant heat-up times were typically 30 min and once the sealant had reached the oil temperature, as measured in the bulk of the sealant with a thermocouple, samples were retrieved after 0 to 5 h of heating. The samples were labeled Nb0 to Nb5 (b for "bathed in oil"), or Qb0 to Qb5, before they were analyzed by GPC.

3.5 GPC

GPC was performed on a Waters chromatograph equipped with four Styragel columns (HR-1, -3, -4, and -5). These columns covered a molecular mass range of about 100 g/mol to 2 Mg/mol The reported signal is the ultraviolet absorbance intensity of a 2% (w/v) sealant solution in tetrahydrofuran (THF) as obtained from a UV detector set at 210 nm. The sealants were left to dissolve for 1h in THF before they were passed through a 0.45 µm pore size filter and injected in the chromatograph.

4. Results and Discussion

4.1 Sealant N

4.1.1 Field aging

Figure 5 illustrates the effect of installation on the copolymer in sealant N as obtained by GPC. The bitumen signal, which was not affected by installation, is not shown, and not to overcrowd the view, figure 5 only shows the control (Nv) and two field samples, Nk0 and Nk5. The unaged Nv contained a mixture of three SB copolymers, identified as A, B and C. Each of these copolymers degraded during sealant installation, as seen by the loss of intensities for A, B and C in going from Nv to the Nk samples. The degradation led to shorter copolymer chains that gave rise to an increase in background at D in figure 5. The nature of this field degradation was thus a scission that produced (shorter) polymer chains of lower molecular weight (figure 3). Details of this degradation and its effect on sealant rheology are found elsewhere (Masson *et al.* 2007).

A different perspective on the degradation of sealant N during its installation is provided in figure 6. It shows the percent change of copolymers A to D over time. With

copolymer A, for instance, the change was calculated from $(I^Ak - I^Av)/I^Av \times 100$, where I is the maximum intensity of the signal at peaks A to D in Figure 5. Figure 6 shows that the concentrations of copolymers A, B and C increased as the installation progressed, which is why figure 6 shows the control sample Nv on the right, at a fictive 6h of installation, and not on the left, prior to the start of installation. The trend for the copolymer degradation by-products (D) is the reverse of those for A, B and C. It decreased throughout the day. As described in detail elsewhere (Masson *et al.* 2007), these results indicate that sealant N was already degraded early in the morning and that throughout the day, as the sealant in the kettle was replenished with fresh and unaged sealant, the overall concentration of degraded sealant in the kettle decreased over the course of installation.

[insert Figure 6 about here]

4.1.2 Small kettle aging (SKA)

In an attempt to reproduce in the laboratory the effect of field installation, sealant N was first heated in the small kettle for up to 5h at 185°C. This temperature was the lowest suggested application temperature for this sealant and it was close to the average sealant heating temperature measured in the field, 187°C (Masson *et al.* 2005). The effect of the SKA on the sealant copolymers is shown in figure 7 as the percent change over time. Aging caused a 10% decrease in copolymer A, the highest molecular mass copolymer, and an increase in D, the shorter polymer by-products. Aging had little effect on copolymers B, in contrast to field aging. The concentration in copolymer C varies as a result of competing degradation mechanisms, details of which are beyond the scope of this paper. Based on the results for copolymers A and B in figure 7, it may be concluded

that the SKA of sealant N at its lowest suggested application temperature of 185°C led to degradation, but that this degradation was not as extensive as that caused by field installation.

[insert Figure 7 about here]

In field applications, sealants can be heated for several hours before the contractor begins to pour sealant into cracks (Masson *et al.* 2005). The extended heating leads to sealant degradation (Masson et al., 2007). The SKA reproduces this premature degradation, and because no fresh sealant was added to the small kettle (in contrast to the field kettle), the trends in Figures 6 and 7 are reversed. That is to say, the apparent decrease in sealant degradation in the field over time is due to the pumping out of degraded sealant, which is replaced with fresh undegraded material. In the laboratory, degraded material was not replaced with fresh sealant, so a net polymer degradation was monitored.

To reflect the extended heating in the field, SKA times at 185°C could be extended beyond the 5h of Figure 7. However, given that SKA is labour intensive, aging beyond 5h renders the method unsuitable for rapid quality control (QC). Sealant N was therefore heated to 200°C, its highest suggested application temperatures (as advocated in ASTM D6690), and to 210°C, the average of the highest measured field application temperatures of 207°C and 214°C (Masson *et al.* 2005). Based on the exponential relationship between temperature and chemical reactions (Atkins 1982), shorter aging times are expected at higher temperatures.

The effect of SKA at 200°C and 210°C on sealant N is shown in figure 8. The trends for copolymers A, B and C were similar at these temperatures, hence only the changes to copolymer A are shown in Figure 8, along with its change at 185°C. After 3 to 5h at

185°C, 10% of copolymer A had been lost. After 4h at 200°C and 210°C, the loss had exceeded 20%. At shorter times, the loss was faster at 210°C than at 200°C, as expected. Never was the degradation as extensive as that observed for the most degraded field sample, Nk0, with a loss of copolymer A near 35%.

[insert Figure 8 about here]

The best correspondence between SKA samples of sealant N and field samples was observed with samples collected midway through installation, when an intermediate level of degraded copolymer was measured. This was the level shown by the SKA sealants heated about 2.5h at 210°C or 4h at 200°C, as indicated by the dotted box in figure 8.

The highest suggested application temperature (HiSAT) of sealant N was 200°C. Four hours of heating at this temperature were needed to consider the average effect of installation on this sealant. In contrast, ASTM D6690 only requires that sealants be heated for 1h at their HiSAT. Thus, the standard specification does not properly account for installation, but it would if sealants were heated 4h at the HiSAT. The results in Figure 8, also indicate that this time could be halved if the temperature was increased by 10°C, which is consistent with the doubling of the rate of chemical reactions with each increase of 10°C (Atkins 1982).

4.2 Sealant Q

4.2.1 Field aging

This sealant had a low volume of reheated material in the kettle when installation began and a short thermal history (table 1). Notwithstanding this careful sealant preparation, the heating of sealant Q in the field also resulted in the application of a sealant with

degraded copolymer (figure 9). The degradation was the greatest for the high molecular mass copolymer A, which levelled after a loss close to 35% (figure 10). The change in copolymer B, which only showed as a shoulder in figure 9, was not tracked. The copolymer with the greatest concentration, copolymer C, showed a loss near 10%. As expected, copolymer degradation led to by-products of low molecular mass that raised the background at D in figure 9.

The trend in the degradation of sealant Q in figure 10 is significantly different from that for sealant N in figure 6. Sealant Q degraded while it was heated and applied, whereas sealant N had degraded before it was applied. This highlights the importance of minimizing sealant volume and heating time prior to the start of the crack sealing work.

4.2.2 Small kettle aging

Given that the field aging of sealant N was suitably and most quickly mimicked at 210°C, sealant Q was also aged at this temperature. The results of SKA on copolymer A in this sealant are shown in figure 11. A similar trend was obtained with copolymer C. The copolymer was quickly degraded to a constant level that matched that for the field samples. One hour at 210°C was sufficient to attain the level obtained after 3 to 6h in the field. SKA was thus a convenient method to accelerate the aging of sealant Q.

As indicated earlier, every 10°C increase in temperature doubles the rate of a chemical reaction (Atkins 1992). This, of course, also affects copolymer degradation. The results in figure 11 are consistent with such acceleration. Based on the time it took for degradation to be completed, 3h in the field and 1h in the laboratory at 210°C, the field application temperature was estimated to be near 190°C, which fits very nicely with the

maximum sealant temperature of 191°C measured in the field (Masson *et al.* 2005). This correspondence highlights the important effect of temperature on sealants. Despite an average application temperature near 170°C (Masson *et al.* 2005), sealant Q was seemingly affected to the greatest extent by its highest application temperature.

5. Conclusions

The goal of this study was to determine if sealant degradation during regular crack sealing work could be simulated in the laboratory by small kettle aging (SKA). Based on the GPC measurement of copolymer degradation in two sealants that were aged both in the field and in the laboratory, it is concluded that it is indeed the case. Four hours of SKA at the highest suggested sealant application temperature (HiSAT) provided as much copolymer aging as that found in sealants sampled midway through their installation. Given the accelerating effect of increased temperatures on degradation, it was also found that about 2h of aging at HiSAT + 10°C provided near identical, but faster aging than 4h at HiSAT. These aging conditions could be used in the future to rapidly determine the effect of installation, or sealant degradation, on sealant properties.

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Table 1. Thermal history of sealants

Sealant	$V,\%$	$R,\%$	$T^R,°C$	t^R, h
N	80	100	130	4
Q	30	40	130	2

SB-diblock

$(SB)_2 \equiv SBS$

$(SB)_3 \equiv$ tri-arm star-SBS

$(SB)_4 \equiv$ four-arm star SBS
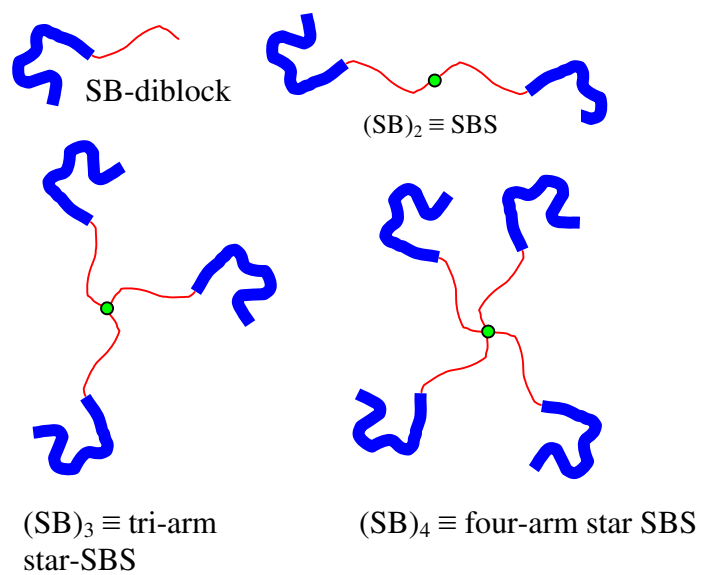
Figure 1. Illustration of the structure of SB-type copolymers.
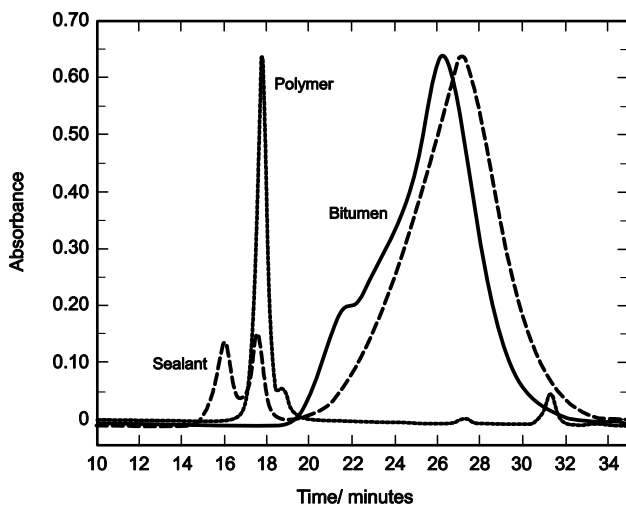
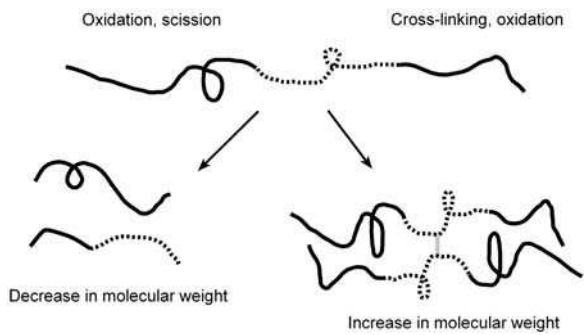Figure 2. Typical GPC results for bitumen, an SBS copolymer and a sealant. Molecular size and mass increase from right to left.

Figure 3. Illustration of the effect of scission and cross-linking on the size of the copolymer.
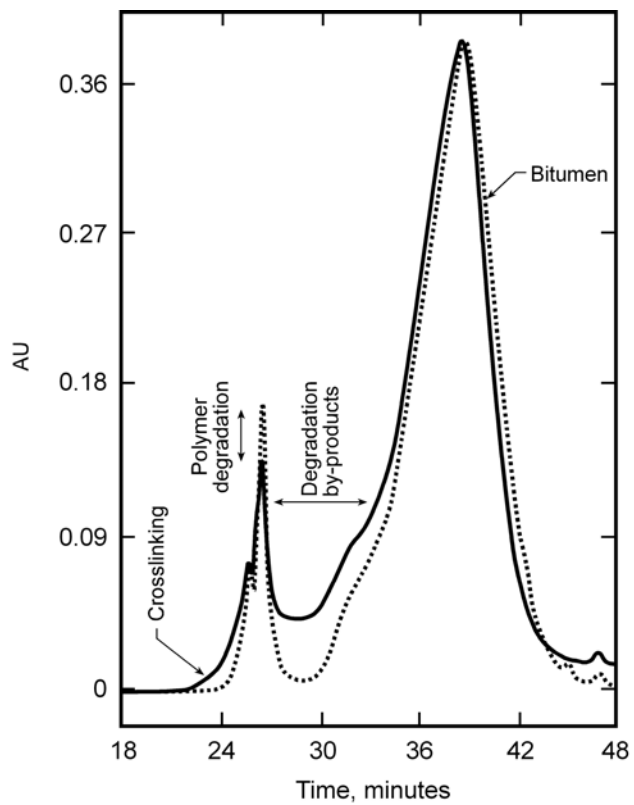
Figure 4. Illustration of the effect of cross-linking and scission on the copolymer on a sealant as obtained by GPC. The sealant is not the same as that in Figure 2, nor as that in later figures.
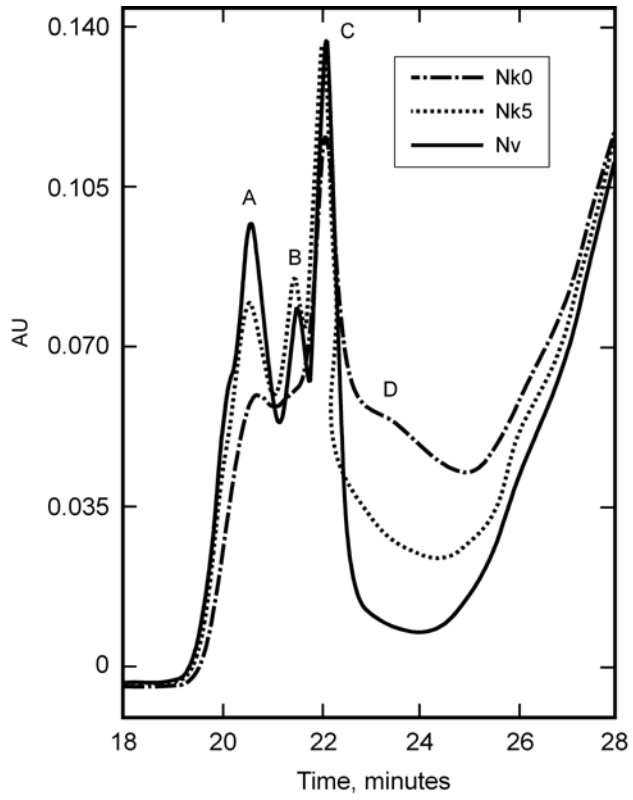
Figure 5. GPC results for sealant N aged in the field.
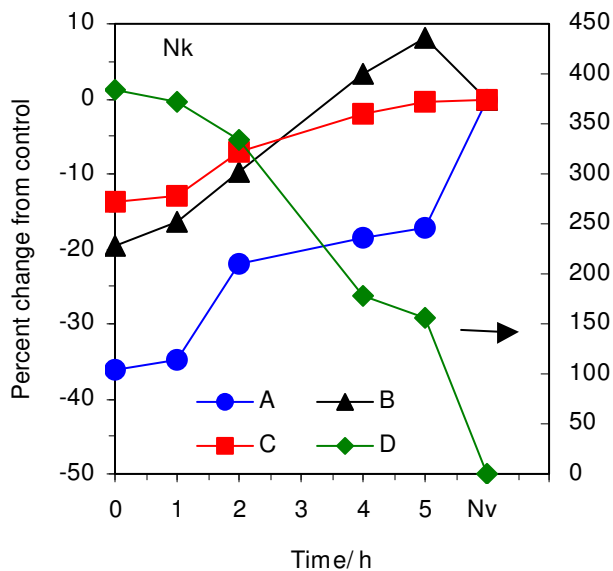
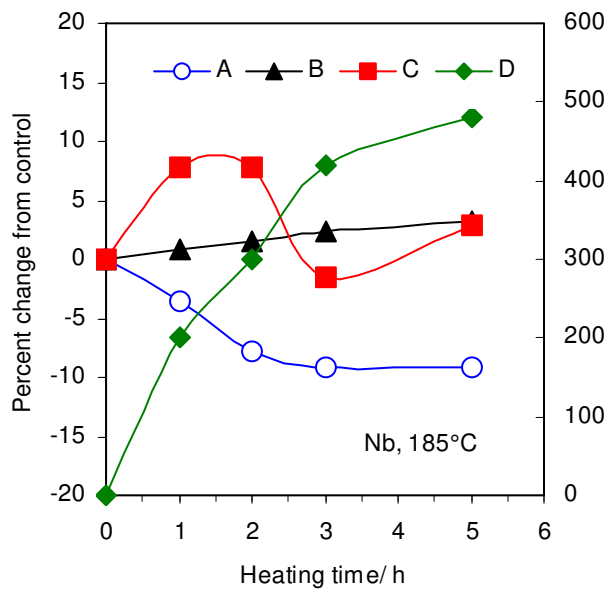Figure 6. Effect of sealant installation on the GPC polymer peaks in sealant N. The percent change in the background (D) is shown on the right ordinate.

Figure 7. Effect of laboratory heating at 185°C on the GPC polymer peaks in sealant N. The percent change in the background (D) is shown on the right ordinate.
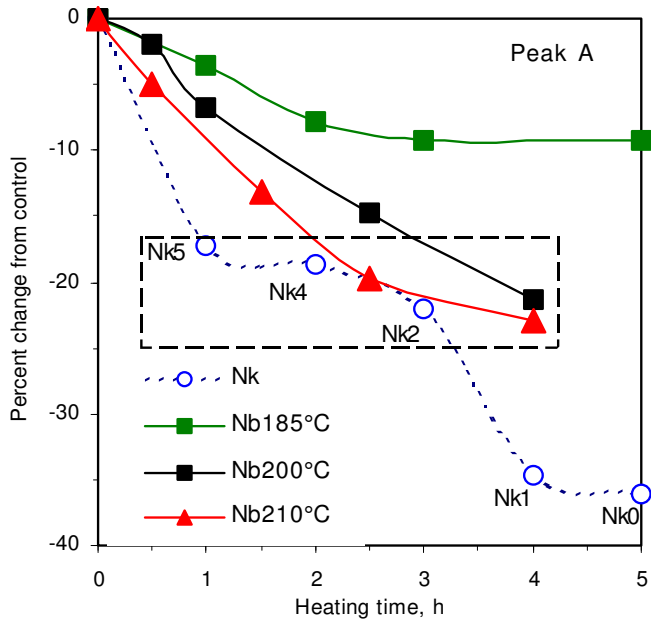
Figure 8. Polymer degradation measured by the decrease in the GPC polymer/bitumen peak ratio.
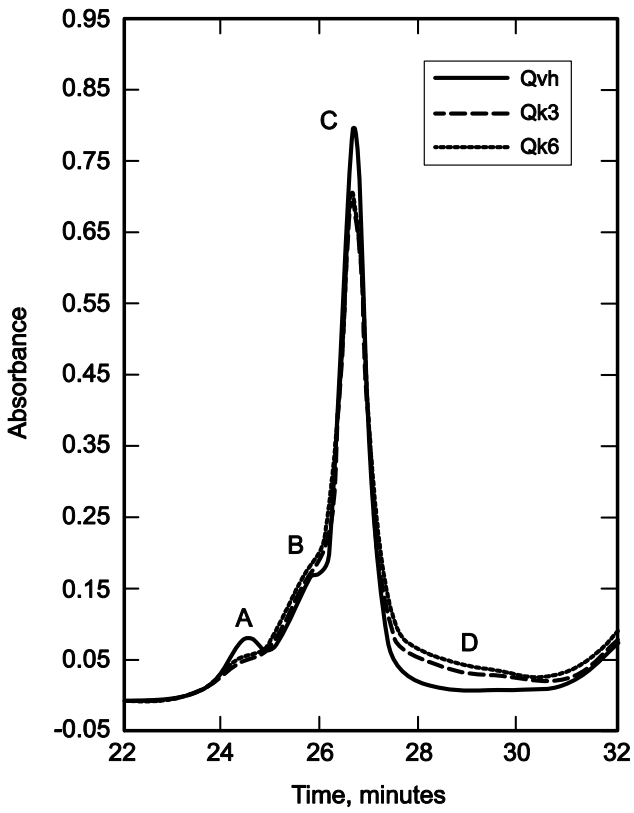

Figure 9. GPC results for the polymer in sealant Q aged in the field. The bitumen portion, unaffected by installation, is not shown.
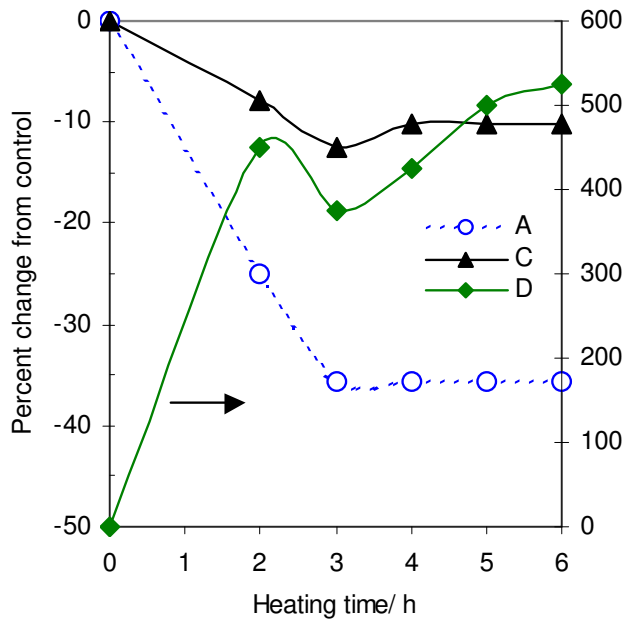
Figure 10. Effect of sealant installation on the polymers in sealant Q. The percent change in the background (D) is shown on the right ordinate.
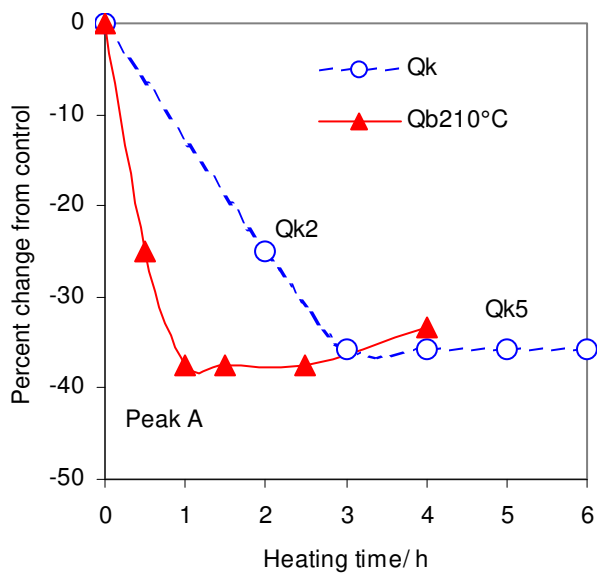

Figure 11. Polymer degradation measured by the decrease in the GPC polymer/bitumen peak ratio in sealant Q.