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Effect of cross-linking agent on the properties of asphalt rubber

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HIGHLIGHTS

- We investigate the high temperature and separation properties of asphalt rubber (AR) added with Trans-polyoctenamer (TOR).
- Addition of TOR in the AR can increase effectively the $G'/\sin(\delta)$ of the binders.
- Addition of TOR in AR can also decrease the phase angle of binders.
- Addition of the TOR can decrease significantly the separation of the binders.

ABSTRACT

Cross-linking agent has recently been introduced into asphalt rubber (AR) as an additive, mainly with the goal of improving workability of this material. This study was performed to investigate the high temperature properties of AR when combined with Trans-polyoctenamer (TOR) at 0%, 3% and 6% of the weight of crumb rubber. High temperature properties were evaluated using the Dynamic Shear Rheometer (DSR) and the separation properties by Tubes in conjunction with DSR method. Results showed that (1) addition of TOR in the AR can effectively increase the $G'/\sin(\delta)$ of the binders in both the original state as well as RTFO residue, with up to a 20% increase in $G'/\sin(\delta)$ found for a dose of 6% TOR; (2) addition of TOR into AR can also decrease the phase angle of the binders in the original state as well as RTFO residue; up to a 1.8% decrease in phase angle was found for a dose of 6% TOR; (3) addition of the TOR can significantly decrease the separation of AR binders, as evaluated by DSR testing. An absolute difference in failure temperatures of 20% less than the control was found for a dose of 3% TOR in PG 67-22 asphalt. The influence of TOR on the separation of AR made with PG 64-22 asphalt was less than that of AR made with PG 67-22 asphalt.

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1. Introduction

Asphalt binders modified by crumb rubber modifier (CRM) in wet process, called asphalt rubber (AR), have shown improved performance in pavements over base binders [1–4]. However, the AR is sensitive to phase separation due to non-homogeneity of the mixture [5]. Cross-linking agents, such as Trans-polyoctenamer (TOR), a double bond chemical, have been introduced into AR as additives. The primary purpose of this group of additives is the improvement of both the workability and mechanical properties of the AR mixture [6–11]. For example, Plemons [6] investigated the effect of the addition of 0.5% TOR by weight of asphalt on AR performance grading. The study used a base PG 67-22 asphalt combined with CRM of –30 and –40 mesh sizes at a rate of 10% of the weight of binder. Results indicated that 0.5% TOR increased the true high temperature grade of AR binders. However, the use of TOR was not effective in preventing settlement or the separation of the rubber during heated storage. Puga [7] characterized the effects of the TOR on the rheological properties of AR with a base asphalt of PG 46-34 and two different types of CRM. Results demonstrated that TOR does not negatively affect the final performance grading for high, intermediate, and low temperatures. Solaimanian et al. [8] evaluated the effect of TOR on AR with a virgin asphalt of PG 58-28 and CRM of –14 and –30 meshes. The study reported one grade increase in the high temperature binder grade for a combination of 5% –14 mesh CRM and 4.5% TOR (by weight of CRM). The high temperature binder grade increased by three grades at 10% –14 mesh CRM. However, the study also reported that –30 mesh CRM did not increase the binder stiffness nearly as much as –14 mesh CRM.
It was acknowledged that the TOR helps workability of asphalt mixtures, but the influence of TOR on other properties of AR, such as the separation, is not clear. In this paper, the objective is to investigate the influence of different doses of TOR on the separation and other properties of AR such as high temperature property. To this end, PG 67-22 and PG 64-22 base asphalts were mixed with three common doses of CRM. Each of these mixtures was then combined with 0%, 3%, and 6% TOR. Both Dynamic Shear Rheometer (DSR) and separation tests were used on the AR binders to evaluate the effects of TOR on the mixtures.

2. Materials used and test procedures

Ambient CRM with a size of ~30 mesh was used in the study. Table 1 presents the gradation of crumb rubber. Two base asphalt binders (PG 67-22 and PG 64-22), three doses of crumb rubber (8%, 10%, and 12% of the weight of binder), and three doses of TOR (0%, 3%, and 6% of the weight of binder) were used to produce AR binders for the study. Per NCAT Report 12-09, the target mixing temperature of the CRM and binder was 163°C, and the blender was set to 900 RPM for a mixing time of 45 min. To ensure that each blend received the same style of blending, the blender propeller was placed at a depth to ensure a one-inch vortex (Fig. 1) during blending.

The accelerated aging processes of standard RTFO (163°C for 85 min) was used to generate RTFO aged binders. The high temperature rheological properties of AR binders were measured using DSR testing according to AASHTO T315. In this research project, a one-millimeter gap was utilized for each AR binder. The complex shear modulus ($G'$) and phase angle ($\delta$) of each binder were measured at 76°C. The separation tube test is performed to determine the tendency of crumb rubber to separate during static heated storage. Testing was conducted in accordance with ASTM D7173-11, Standard Practice for Determining the Separation Tendency of Polymer from Polymer Modified Asphalt. In the separation tube testing, 50 ± 0.5 g of the hot AR binder with TOR was poured into a cylindrical aluminum tube, and the tube was closed on one end to prevent air from reaching the sample. The tubes were placed in an oven at 163 ± 5°C and allowed to condition for 48 ± 1 h. After conditioning, the tubes were removed from the oven and placed in a freezer at 10 ± 1°C for at least 4 h to solidify the binder. The frozen material was then cut into three equal portions. The middle portion was discarded while the top and bottom thirds were used for comparison. Fig. 2 showed the combination of the experimental design used in this study.

3. Results and discussions

3.1. Influence on high temperature properties

In order to evaluate the performance of the AR added with TOR at high service temperatures, a complex shear modulus ($G'$) and a phase angle ($\delta$) were measured using the DSR on the AR binders in both original state and RTFO residue. The values of $G'$/$\sin(\delta)$ and phase angle ($\delta$) at 76°C obtained for the binders tested are shown in Figs. 3–6. A general trend is observed that the $G'$/$\sin(\delta)$ of the binders in original state (unaged) increased as the dose of TOR increased from 0% to 6% regardless the dose of the CRM added and the grade of base binder (see Fig. 3a and b). The values of $G'$/$\sin(\delta)$ also increased as the dose of CRM increased from 8% to 12% regardless of the dose of the TOR added and the grade of the base binder (see Fig. 3a and b).

In many previous lab and field studies, it has been shown that modified binders with CRM generally appear to have a higher value of the $G'$/$\sin(\delta)$ than base asphalts. The presence of TOR in the binders did not change the trend, i.e., the content of CRM is still effective to increase the $G'$/$\sin(\delta)$ of the AR added with TOR. The addition of TOR in the AR appeared to provide additional increases in the value of $G'$/$\sin(\delta)$ of the AR binders tested. Although TOR is not added with the primary goal of increasing the $G'$/$\sin(\delta)$ value of AR, the study shows that the addition of TOR can significantly raise the $G'$/$\sin(\delta)$ of AR as a secondary benefit.

With a PG 67-22 base asphalt and 8% CRM, the $G'$/$\sin(\delta)$ of the binders tested with 3% and 6% TOR were 8.5% and 0.9% higher than those without TOR (the controls), respectively. For AR with 10% CRM, the $G'$/$\sin(\delta)$ of the binders tested with 3% and 6% TOR were 17.4% and 23.0% higher than the controls, respectively. For AR with 12% CRM, the $G'$/$\sin(\delta)$ of the binders tested with 3% and 6% TOR were 15.8% and 35.8% higher than the controls, respectively. An average increase of 14% and 20% in the $G'$/$\sin(\delta)$ was found when a dose of 3% and 6% of TOR was added, respectively.

For the PG 64-22 base binder, an average increase of 4.3% and 6.7% in the $G'$/$\sin(\delta)$ was found when a dose of 3% and 6% of TOR was added, respectively. It is obvious that the TOR had a greater influence on values of $G'$/$\sin(\delta)$ when a higher percentage of CRM and a high temperature grade base binder was used.

In order to determine if TOR has significant influence on $G'$/$\sin(\delta)$ of AR, the results were statistically analyzed with a 5% level of significance. An analysis of variance was performed to statistically analyze the data. Table 2 indicates that TOR has no significant influence on $G'$/$\sin(\delta)$ of all AR with PG 64-22, but TOR has significant influence on $G'$/$\sin(\delta)$ of AR with PG 67-22 and higher rubber content (10% and 12%).

### Table 1

| Sieve (mm) | No. 16 | No. 30 | No. 40 | No. 50 | No. 100 |
|------------|--------|--------|--------|--------|--------|
| Percentage passing (%) | 100    | 99.0   | 88.4   | 40.4   | 7.7    |

**Fig. 1.** Sample vortex.

**Fig. 2.** Flowchart of experimental design.
Fig. 3. $G'/\sin(\delta)$ of original binders at 76°C: (a) asphalt binder of PG 67-22, and (b) asphalt binder of PG 64-22.

Fig. 4. Phase angle of original binders at 76°C: (a) asphalt binder of PG 67-22, and (b) asphalt binder of PG 64-22.

Fig. 5. $G'/\sin(\delta)$ of RTFO residuals at 76°C: (a) asphalt binder of PG 67-22, and (b) asphalt binder of PG 64-22.

Fig. 6. Phase angle of RTFO residuals at 76°C: (a) asphalt binder of PG 67-22, and (b) asphalt binder of PG 64-22.
The phase angle of the AR binders in original state (unaged) decreased as the dose of TOR increased from 0% to 6%, regardless of the dose of the CRM added and the grade of the base asphalts used. Phase angle also increased as the dose of CRM increased from 8% to 12%, regardless of the dose of the TOR added and the grade of the base binders (see Fig. 4a and b).

It has been established in prior studies that modified binders containing CRM generally have a lower phase angle than base asphalt. However, the presence of TOR in the AR makes it more effective in decreasing the phase angle of the binder. Again, although the purpose of adding TOR is not to decrease the value of phase angle, it can be shown in the study that the addition of TOR can beneficially lower the value of the phase angle of AR binders.

When PG 67-22 was used as base asphalt, for unaged AR with 8% CRM, the phase angle of the binders tested with 3% and 6% TOR were 1.5% and 1.0% lower than the controls, respectively. For 10% CRM, the phase angle of the binders tested with 3% and 6% TOR were 0.5% and 0.7% lower than the control, respectively. For 12% CRM, the phase angle of the binders tested with 3% and 6% TOR were 2.7% and 3.8% lower than the controls, respectively. An average decrease in phase angle of 1.6% and 1.8% was found for a dose of 3% and 6% of TOR, respectively.

When PG 64-22 base binder was used, an average decrease in phase angle of 0.5% and 0.8% was found for a dose of 3% and 6% of TOR, respectively. It is obvious that the TOR had a greater effect on phase angle when a higher percentage of CRM was used. The grade of the base binder did not affect the sensitivity of the phase angle to the percentage of TOR in the mixture.

In order to determine if TOR has significant influence on phase angle of AR, the results were statistically analyzed with a 5% level of significance. An analysis of variance was performed to statistically analyze the data. Table 3 indicates that TOR has no significant influence on phase angle of all AR with PG 64-22, but TOR has significant influence on phase angle of AR with PG 67-22 and 12% crumb rubber.

### Table 3

| TOR 0%–TOR 3% | TOR 0%–TOR 6% | TOR 3%–TOR 6% |
|---------------|---------------|---------------|
| Virgin binder: PG 67-22 |               |               |
| Rubber 8%     | N             | N             |
| Rubber 10%    | N             | N             |
| Rubber 12%    | N             | N             |
| Virgin binder: PG 64-22 |               |               |
| Rubber 8%     | N             | Y             |
| Rubber 10%    | N             | N             |
| Rubber 12%    | Y             | Y             |

Note: Y: P-value < 0.05 (significant difference); N: P-value > 0.05 (no significant difference).

The RTFO residue showed a similar trend to unaged binders in that the $G'/\sin(\delta)$ of all the RTFO residue increased as the dose of TOR increased from 0% to 6%, regardless the dose of CRM (Fig. 5).

For RTFO aged AR consisting of a PG 67-22 base binder and 8% CRM, the $G'/\sin(\delta)$ of the binders tested with 3% and 6% TOR were 1.9% and 5.6% higher than the controls, respectively. For 10% CRM, the $G'/\sin(\delta)$ of the binders tested with 3% and 6% TOR were 17.5% and 13.3% higher than the controls, respectively. For 12% CRM, the $G'/\sin(\delta)$ of the binders tested with 3% and 6% TOR were 2.2% and 5.6% higher than the controls, respectively. An average increase of 6.8% and 8.0% in the $G'/\sin(\delta)$ was found when a dose of 3% and 6% TOR was added, respectively.

When PG 64-22 was used, an average increase of 8.3% and 10.0% in the $G'/\sin(\delta)$ was found when a dose of 3% and 6% TOR was added, respectively.

The phase angle of the RTFO aged AR binder showed a similar trend to unaged binders in that the phase angle decreased as the dose of TOR increased from 0% to 6% regardless of the dose of the CRM and the grade of the base binder. The phase angle also increased as the dose of CRM increased from 8% to 12% regardless of the dose of the TOR and the grade of the base binder (Fig. 6a and b).

For RTFO aged AR consisting of a PG 67-22 base binder and 8% CRM, the phase angles of the binders tested with 3% and 6% TOR were 0.2% and 0.5% lower than the controls, respectively. For 10% CRM, the phase angles of the binders tested with 3% and 6% TOR were 2.9% and 3.5% lower than the controls, respectively. For 12% CRM, the phase angles of the binders tested with 3% and 6% TOR were 2.5% and 5.5% lower than the controls, respectively. An average decrease in phase angle of 1.6% and 3.1% was found for a dose of 3% and 6% of TOR, respectively.

When PG 64-22 base binder was used, an average decrease in phase angle of 0.2% and 1.1% was found for a dose of 3% and 6% of TOR, respectively. It is obvious that the TOR had a greater effect on the decrease in phase angle for higher percentages of CRM. The grade of the base binder did not affect the sensitivity of the change in phase angle to the percentage of TOR.

### 3.2. Separation test results

Separation tubes were used in conjunction with the DSR to determine if CRM and TOR can prevent the overall separation of the CRM particles from the asphalt binder. This is especially important for the AR mixtures produced in plants. Separation tube test can indicate how much the crumb rubber particles settle from the top of the mixture. This settling causes a difference in the properties of the binders in top of the container from those in the bottom. The degree of separation was quantified by taking the difference in the failure temperature between the top and bottom third of the separation tube. The failure temperature is the DSR test temperature that the RTFOT binder from the separation tube decreased. This indicates that TOR may serve to lessen the degree of separation of AR binders to some extent.

For AR consisting of a PG 67-22 base binder and 8% CRM, the absolute difference in the failure temperature between the top and bottom part of the binders tested with 3% and 6% TOR increased from 0% to 6%, regardless the dose of CRM (Fig. 7).
were 13.6% and 16.0% lower than the controls, respectively. For 10% CRM, the absolute difference in the failure temperature of the binders tested with 3% and 6% TOR were 18.8% and 15.8% lower than the controls, respectively. An average absolute difference in the failure temperature of 19% and 17% lower than the controls was found for a dose of 3% and 6% of TOR added in the asphalt rubber binders.

When a PG 64-22 base binder was used, an average absolute difference in the failure temperature of 4% and 6% lower than the controls was found for a dose of 3% and 6% of TOR, respectively. The influence of TOR on the separation of AR with PG 64-22 asphalt was less than that with PG 67-22. Therefore, the influence of TOR on the separation of AR may depend on the type of base asphalt binder.

4. Summary and conclusions

TOR, as a cross-linking agent, was added in AR to improve the properties of asphalt rubber. In the study, two base asphalt binders (PG 67-22 and PG 64-22), three doses of crumb rubber (8%, 10%, and 12% of the weight of binder), and three doses of TOR (0%, 3%, and 6% of the weight of binder) were used to produce AR binders for the study. High temperature properties were evaluated using the DSR, and the stability was evaluated by the Tube method in conjunction with DSR tests. Here are the conclusions that can be drawn from the testing results:

(1) An increase of 14% and 20% in the $G'/\sin(\delta)$ of asphalt rubber binders in original state was found when a dose of 3% and 6% of TOR was added, respectively. A lower rate of increase was found for RTFO aged residue. The addition of TOR in the AR increased the high temperature properties of the binders.

(2) The phase angle of asphalt rubber binders decreased up to 1.8% when TOR was added increasingly at the doses used for the study. This is true for the unaged binders and RTFO residue. The addition of TOR in the AR improved the elastic properties.

(3) The absolute difference in failure temperatures for the binders taken from the top and bottom of a tube was about 20% less than the controls when a dose of 3% TOR was added into PG 67-22 asphalt. Further increase of the dose of the TOR did not decrease the absolute difference in the failure temperatures.

(4) The influence of TOR on the separation of AR with PG 64-22 asphalt is less than that with PG 67-22. Therefore, the influence of TOR on the separation of AR may depend on the types of base asphalt binders.

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