White Paper on

The Effects of Digesting Crumb Rubber in Modified Binders (MB)

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By

The University of Wisconsin-Madison
Asphalt Research Group

In Collaboration with the
Recycled Materials Resource Center
Executive Summary

With the advent of new processes for incorporating varying amounts of scrap tire rubber (TR) into binders for hot mix asphalt and seal coats, there appears to be a lack of clarity about the best method of using TR. There is also a lack of clarity in the identification of the products produced using various methods. One of the basic core variables of incorporating TR into asphalt binder is the level of digestion of the crumb rubber into the binder. The range in methods is from the extreme of full digestion of the TR in binder to the dry mixing of TR with aggregates with minimal digestion. The two extremes have their advantages and disadvantages. The partial digestion method (the TR is partially digested in the binder to create a gel-like composition through a specific time temperature reaction), which is the more established process, is called Asphalt-Rubber (AR). Asphalt-Rubber is clearly defined in the ASTM and other widely used standards (See footnote (1) below). In recent years claims regarding the value of higher level of digestion have resulted in new products. Also, the test of solubility, to ensure the higher level of digestion, has been instituted in specifications.

The purpose of this paper is to summarize the results of important past studies evidencing that the complete digestion of TR in an asphalt binder does not necessarily improve the binder characteristics. The data collected from these studies convincingly demonstrates that there is a high risk in too much digestion, as it can virtually eliminate the stiffening and elastic influence of the TR on binder properties.

It has also been claimed that the need for full digestion is to allow use of the current PG binder testing system for these binders. This study, however, shows that Asphalt-Rubber binders (with partial digestion) have been successfully tested utilizing existing equipment for binder performance grading (PG) with or without minor modification of test geometries.

The data presented in this study indicates that there is no performance related benefits that merit requiring solubility testing, which is a test method required only to distinguish asphalt products with a high level of digestion from the more conventional asphalt rubber products.

The study recommends the appropriate use of the PG grading system for products such as Asphalt-Rubber. Such testing will allow performance based comparison of these different products, leading to better practice and more choices for designers and policy makers responsible for long lasting pavements and effective recycling of TR.

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Background and Need for this Paper

The binder specification currently utilized by Caltrans for modified binders (MB) also known as Terminal Blend in Hot Applied Chip Seal applications is shown in Table 1. The table shows that the MB produced with polymers and MB produced with tire rubber (TR) meet the same testing criteria, with the exception of minimum solubility.

This report is written to discuss the merits of the solubility requirement and document examples of studies conducted to evaluate consequences of dissolving the TR virtually completely in the asphalt binder. TR is shown in a number of studies to be the most effective in modifying asphalt binders when it is not completely dissolved, but swelled and adequately reacted with the binder (the fundamental basic concept of Asphalt-Rubber). It is also recognized that solubility is not a performance related property and many two-phase binders can be very effective in providing enhanced performance.

There is also a contradiction between the attempt to advance the practice of implementing performance related concepts, such as PG grading, and the insertion of a solubility limit that does not appear to be justified for product performance. There is no published research to date that proves a lower solubility will lead to inferior performance. On the contrary, Asphalt-Rubber, has been produced and applied with 20% minimum TR content and has been very successful in providing extended service life of hot applied chip seals and hot mix asphalt, such as Asphalt-Rubber Composite Layering Systems (ARCLS).

The other significant issue contained in the current MB specification is the lack of verification concerning the TR content. This lack of a control test opens the opportunity for not using rubber at all, or adding just a small amount that will pass the solubility requirement. Most MB specifications state minimum TR content requirements ranging from 8-10 percent. In fact, the solubility requirement discourages using rubber.

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(2) Asphalt-Rubber Composite Layering Systems (ARCLS) refers to a multiple layering system utilized in overlay strategies typically consisting of cold planning, a conventional leveling course, an Asphalt-Rubber Aggregate Membrane Interlayer (ARAMI) followed by final cap of Asphalt-Rubber Hot Mix (ARHM). The system ranges in total thickness from 2 inches to 3 inches depending upon if a leveling course is incorporated into the layering design.
One of the unique advantages of Asphalt-Rubber is it allows recycling of a waste product, and effectively saving the environment from accumulation of this solid waste by improving paving asphalts. The lack of specific requirements for tire rubber amount used defeats this important recycling advantage, and in fact discourages producers from using more rubber. This could put the solid recycling programs in California at risk of diminishing.

In recent years proprietary technologies have been developed which claimed that TR can be included in asphalts at higher concentrations but with using heat and shear it can be de-vulcanized to perform similar to polymer modified binders. Research however has shown that this is a risky proposition since TR could lose its effectiveness if it is highly de-vulcanized. It is suspected that in these newer products, which can meet the PG 76-22 TR specification of Caltrans, either lesser rubber is being included, or polymers are added to substitute for the lost effects of the rubber due to de-vulcanization. In either case it seems to be counterproductive because either very little TR rubber is recycled, or significant energy is wasted in de-vulcanizing and using virgin, high cost materials such as virgin polymers (e.g. SBS).

This report is prepared to shed some light on the subject of tire de-vulcanization and the consequences of dissolving tire rubber on critical properties of binders. It is based on a critical review of literature in which the effect of de-vulcanization, also called de-polymerization, has been carefully studied using rheological measurements similar to those used in the Caltrans specifications, as well as others.
### Table 1. Modified Binder Specification for Hot Applied Chip Seal Applications

<table>
<thead>
<tr>
<th>Property</th>
<th>AASHTO Test Method</th>
<th>Grade</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PG 76-22 PM</td>
<td>PG 76-22 TR&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Original Binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash Point, Minimum °C</td>
<td>T 48</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Solubility, Minimum %&lt;sup&gt;c&lt;/sup&gt;</td>
<td>T 44&lt;sup&gt;a&lt;/sup&gt;</td>
<td>98.5</td>
<td>97.5&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Viscosity at 135°C, Maximum, Pa's</td>
<td>T 316</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Dynamic Shear, Test Temp. at 10 rad/s, °C</td>
<td>T 315</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>Minimum G*/sin(delta), kPa</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>RTFO Test, Mass Loss, Maximum, %</td>
<td>T 240</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>RTFO Test Aged Binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic Shear, Test Temp. at 10 rad/s, °C</td>
<td>T 315</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>Minimum G*/sin(delta), kPa</td>
<td></td>
<td>2.20</td>
<td>2.20</td>
</tr>
<tr>
<td>Elastic Recovery&lt;sup&gt;e&lt;/sup&gt;, Test Temp., °C</td>
<td>T 301</td>
<td>Note f</td>
<td>Note f</td>
</tr>
<tr>
<td>Minimum recovery, %</td>
<td></td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>PAV&lt;sup&gt;h&lt;/sup&gt; Aging, Temperature, °C</td>
<td>R 28</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td><strong>RTFO Test and PAV Aged Binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic Shear, Test Temp. at 10 rad/s, °C</td>
<td>T 315</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Maximum G*/sin(delta), kPa</td>
<td></td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>Creep Stiffness, Test Temperature, °C</td>
<td>T 313</td>
<td>-12</td>
<td>-12</td>
</tr>
<tr>
<td>Maximum S-value, MPa</td>
<td></td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Minimum M-value</td>
<td></td>
<td>0.300</td>
<td>0.300</td>
</tr>
</tbody>
</table>

**Notes:**

a. Do not modify binder using acid modification.

b. Supplier is required to certify 10% minimum scrap tire rubber modifier in binder.

c. The Department allows ASTM D 5546 instead of AASHTO T 44

d. For hot applied chip seal applications the solubility for field blended material will be a minimum of 93% and a binder profile at the temperature utilized for field production is required for suppliers,

e. 

f. Test temperature is the temperature at which G*/sin(delta) is 2.2 kPa. A graph of log G*/sin(delta) plotted against temperature may be used to determine the test temperature when G*/sin(delta) is 2.2 kPa. A graph of (delta) versus temperature may be used to determine delta at the temperature when G*/sin(delta) is 2.2 kPa. The Engineer also accepts direct measurement of (delta) at the temperature when G*/sin(delta) is 2.2 kPa.

g. Tests without a force ductility clamp may be performed.

h. "PAV" means Pressurized Aging Vessel.
Studies on De-polymerization of Ground Tire Rubber in Asphalt Binder

The existing technologies of using scrap tires in asphalt pavements are recognized to be of two types: the dry and the wet technologies. In both cases the rubber is intended to be used as elastomeric filler. In the dry process, the rubber is assumed to form part of the aggregate component. In the wet process, which is used in Asphalt-Rubber, however, some of the three dimensional network of the vulcanized rubber is expected to de-polymerize or dissolve in asphalt. Most of the rubber remains intact with a somewhat loosened rubber matrix, swollen by the asphalts’ oils. It is also known that the crumb rubber/asphalt mixtures have to be prepared under controlled conditions such that the danger of complete de-polymerization will not lead to the CRM’s total digestion into the binder. There is, therefore, an optimum blending time and process during which rubber is incorporated effectively in a binder. Producers of Asphalt-Rubber binders today are very skillful in optimizing the use of high rubber amounts and incorporating it in asphalt binders for effective modification of performance properties of asphalts.

Another process for recycling rubber in asphalts that has been studied is called rubber pyrolysis. This process is used in terminal blend binders. In this process, heat and shear are used for the decomposition of vulcanized rubber to carbon black, gas, and unsaturated oils. This decomposition destroys the elastomeric behavior that is critical for the modification of asphalt binders. This destruction of the rubber has been shown to deteriorate the performance properties of binders in a few important studies that covered a wide range of mixing conditions and types of binders (Zanzotto and Kennepohl 1996, Bullin et al. 1996, and Glove et al., 2000). In one of these studies, authors also reported on attempts to at least partially re-polymerize the oils resulting from tire rubber pyrolysis in laboratories in order to recover some of the elastic effects needed, but indicated that such attempts could not achieve any success (Zanzotto and Kennepohl 1996).

In the following sections some of the critical data from these reports are shown and analyzed. The full citations of these reports are as follows:


There could be a number of other studies that have covered this subject; these three selected reports appear to give sufficient information about the consequences of over reacting the rubber in asphalts and explain some of the risks involved in attempting to dissolve virtually all of the tire rubber.

**Important Data Collected and Analysis**

**Study by Zanzotto and Kennepohl**

In this study three forms of tire rubber (60 mesh, 20 mesh, and buffed rubber) were subjected to different combinations of heat and high shear for various times to study the effects of de-polymerization on rheological properties. The properties measured included creep and recovery, viscosity, and some conventional tests. In addition, the amount of un-reacted rubber and tendency to separation during the hot storage were also tested.

Figure 1 is an example of the results reported in which the trend of deteriorating high temperature properties is clearly shown in terms of softening point as a function of increasing temperature of reaction for standard time of 2 hours. It is important to note that the softening point of the base asphalt is 36 deg C. As shown in Figure 1, at 260 C (500 F) the effect of 25 % tire rubber of 60 mesh is almost completely eliminated. The effect of de-polymerization shown could have significant un-favorable effects on high temperature performance, in particular the possible loss of resistance to rutting.
Figure 2 taken from the same study explains what is causing this reduction in softening point. As shown there is a similar trend of decreasing amount of un-reacted rubber, in other words, the increase in dissolved rubber due to de-polymerization causes the softening point reduction.

(After Zanzotto and Kennephol, 96)

FIGURE 1  Effect of reaction temperature on softening point R&B of rubber/asphalt mixture (25 percent CRM 60 minus mesh), reacted for 2 hr.

(After Zanzotto and Kennephol, 96)

FIGURE 2  Amount of unreacted rubber in rubber/asphalt mixture (25 percent CRM 60 minus mesh) after 2 hr reaction (unsolubles after reaction at 280°C, 3 hr subtracted from each value).

(After Zanzotto and Kennephol, 96)
The study by Zanzotto and Kennepohl suggests that there is an opportunity to optimize Asphalt-Rubber binders. If none of the rubber is “cured” in the sense of swelling and partial depolymerization, then viscosity could be very high and thus workability is a challenge. In addition, insufficient curing (defined as a time/temperature reaction of the binder) of the rubber could cause phase separation. However, curing (prolonged high temperature reaction causing virtually the complete depolymerization of the TR) too much could eliminate the benefits of rubber and causes loss of the properties as was shown in Figure 1. (Loss of the properties = reduction of the softening point).

**Bullin et al study**

The study by Bullin and co-workers followed a similar path to the first study in the sense of measuring amount of dissolved rubber as a function of time, temperature and heat. Figure 3 is an example of such results which shows that as time of curing is extended, more rubber is lost, particularly at higher shearing rate. At 375 F, which is relatively a low temperature for production of Asphalt-Rubber, 30 to 40 % of the rubber is lost in 2 days at low agitation of 500 rpm and in less than 4 hours if high agitation (1500 RPM) is used. One can speculate that at higher temperatures and high shear rates, typical of conditions used in production of Asphalt-Rubber today, a significant amount of rubber can be lost in a few hours.

![Figure 3. Amount of tire rubber dissolved as function of curing time at 2 different shearing rates.](After Bullin et al, 1996)

Bullin and co-workers concluded that the extent to which tire rubber dissolves into the asphalt is very dependent upon the curing environment. Under the curing conditions studied, dissolving the rubber could improve the properties of a binder by improving stability and reducing viscosity during construction. However, more work should to be done to look at the effect on
performance properties, since it is doubtful that complete destruction of the rubber molecules, and thus its elasticity, is desirable. That is, the optimization of binder properties is very dependent on the extent to which the rubber particle is de-vulcanized and/or de-polymerized.

Bullin’s group also concluded that the chemical composition of the asphalt, the rubber mesh size, and the rubber content are important variables as they influence the interaction of asphalt with rubber and the de-polymerization of the latter.

**Glover et al study**

The work that was started by Bullin at Texas Transportation Institute was followed by a more comprehensive study by one of his Co-workers (Dr. Charles Glover). Glover’s study looked at the changes in performance grading with curing. Figure 4 below taken from Glover et al reports shows the changes in the rutting parameter (G*/sinδ) with curing at 400 and 450 F, typical of terminal blending, where G* is the complex modulus and δ is the phase angle. It is clear that after 3.5 hours at 450 F the values of G*/sinδ reduced to almost the level of the base binder. These results confirm earlier studies and indicate that too much curing could eliminate the benefits of rubber modification.

![Figure 4](image)

*Figure 4  G*/sin(δ) of Original Binders After First Curing at Different Curing Conditions.*

*(After Glover et al, 2000)*
Glover’s group also looked at low temperature properties. The low temperature changes (as measured by Bending Beam Rheometer, BBR, stiffness) are shown in Figure 5 taken from Glover’s study. It can be seen that there are better values (lower stiffness) initially, but as curing temperature is increased, these benefits are partially lost.

![Figure 5: Stiffness of Binders After First Curing at Different Curing Conditions.](image)

(After Glover et al, 2000)

Glover’s group also paid special attention to changes in elasticity. They measured the changes in elasticity using the phase angle since it is known that as elasticity improves a reduction in the value of the phase angle is observed. Figure 6 is taken from one of the studies of this group and it shows a dramatic increase in phase angle, indicating loss of elasticity, as a function of curing time. The loss in elasticity (increase in phase angle) is seen for all three blends tested.
Glover concluded that shear mixing and higher temperature can break down the rubber particles and digest the long polymer chains and crosslink structures. He indicated that the viscosity of modified binder decreases with additional curing, but remains elevated above that of the base asphalt material. He speculated that although a particle phase continues to coexist with the binder at longer curing time, its size distribution rapidly declines as shortened polymer chains are integrated into the binder phase, which yields a lower viscosity at hot-mix installation. However, it certainly is possible to cure too far. Materials produced at the highest level of curing indicate severe polymer degradation. These binders produced with long curing times and/or higher shearing have wider PG span, but do not always yield improvement on a PG specification basis.
Summary of Main findings from the Literature and Concluding Remarks

Multiple studies have been conducted to evaluate the impact of digesting TR in asphalts. The studies lead to similar findings that could be summarized in the following points:

1. High shear mixing and high temperatures can break down the TR particles and result in a rubber-reinforced binder with reduced viscosities at the time of the hot mix asphalt installation. The mixing and heating can be controlled to optimize viscosity. Optimized viscosities have already been established for Asphalt-Rubber binders allowing for pumpability in a Hot Mix Asphalt (HMA) production facility. The PG requirement of 3.0 Pa-s is most widely recognized as a requirement for “pumping” in a production facility and it can be achieved easily using current conventional Asphalt-Rubber production methods.

2. The studies reviewed clearly show it is possible to cure rubber for too long a period at high temperatures. Materials produced at the highest level of curing indicate severe rubber degradation. This high level of curing can widen the PG span only incrementally and does not always yield improvements on specification basis required for a specific traffic condition.

3. The studies reviewed, and others cited in these studies, that have used the PG grading testing system for Asphalt-Rubber binders, seem to indicate no concerns regarding the results when the geometry and sample preparation is done carefully. The perception that Asphalt-Rubbers cannot be tested using the standard PG grading system is not confirmed in the studies reviewed.

4. The PG grading system includes testing with 4 different types of testing equipment, 5 geometries, at 4 temperatures. As shown in the schematic referenced as Attachment A, the equipment includes the rotational viscometer to be used at mixing and compaction temperature (135 C), DSR at high (~ 60 C) and intermediate (~ 20 C) temperatures, and the BBR and Direct Tension (DT) at low pavement temperatures (~-20 C). Asphalt-Rubber can, and has been, tested with all these types of equipment successfully. Table shown in Attachment A is from a study conducted as part of the Recycled Materials Resource Center (RMRC) and depicts the comparison of the PG high grade for rubber reacted for various times, with the effect of SBS and a high-digestion TR asphalt (PG-TR). As shown in the table the results confirm that partial digestion is the best approach to achieve high PG grade. The only exceptions that need modification for Asphalt-Rubber are testing at high pavement temperature using the parallel plate geometry with one millimeter gap and the aging in the RTFO when a high percent of rubber is used. For the parallel plate geometry at high pavement temperature, a simple modification by increasing the gap to 2.0 mm, instead of the 1.0 mm used currently, can solve the problem, of size of rubber particles and allow grading of the Asphalt-Rubber with rubber particles as large as 0.5 mm. For the RTFO problems, which, is in fact a problem for not only Asphalt-Rubber, but also other highly elastic polymer modified binders, the TFOT aging procedure can be used. The TFOT is a test
that is known to compare well to RTFO, is a standard test, and is still used in many parts of the world as an acceptable short term aging procedure. These 2 modifications could make it possible to PG grade most of the Asphalt-Rubber binders used today.

5. The studies reviewed have reported simple methods of separating un-dissolved rubber using common solvents and simple centrifuge. It is expected that one of these tests could be standardized and used as a requirement to ensure sufficient rubber has been added to make an Asphalt-Rubber binder.

6. The solubility requirement in the current Caltrans specification is not justified and studies reviewed do not include any indication that such a test is necessary to ensure performance. The current specifications could jeopardize the solid waste recycling program for used tires. It favors producing binders with reduced amount of TR, with highly digested TR, and/or more virgin polymers without a performance advantage. The experience and advancement in incorporating rubber in asphalt is very mature and cannot be used to justify this specification.

### ATTACHMENT A – Table Taken from Study #54 of RMRC

<table>
<thead>
<tr>
<th>Binder- React</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Average</th>
<th>Std. Dev</th>
<th>COV</th>
<th>PG Grade</th>
<th>Bump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valero Neat</td>
<td>67.4</td>
<td>67.2</td>
<td>67.3</td>
<td>0.141</td>
<td>0.2%</td>
<td>64</td>
<td>0</td>
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<td>10GTR_45min</td>
<td>85.1</td>
<td>83.9</td>
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<td>0.849</td>
<td>1.0%</td>
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<td>83.9</td>
<td>84.3</td>
<td>0.566</td>
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<td>3</td>
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<td>84.0</td>
<td>83.7</td>
<td>0.424</td>
<td>0.5%</td>
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<td>10GTR_360min</td>
<td>82.3</td>
<td>81.4</td>
<td>81.9</td>
<td>0.636</td>
<td>0.8%</td>
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</tr>
<tr>
<td>PG -10TR</td>
<td>78.7</td>
<td>78.8</td>
<td>78.8</td>
<td>0.071</td>
<td>0.1%</td>
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<tr>
<td>Valero + 2% SBS</td>
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<td>73.0</td>
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<td>0.071</td>
<td>0.1%</td>
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<tr>
<td>2% SBS + XL</td>
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<td>75.4</td>
<td>75.4</td>
<td>0.000</td>
<td>0.0%</td>
<td>70</td>
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