



Louisiana Transportation Research Center

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TECHNICAL SUMMARY

Summary of Report Number 291

CHARACTERIZATION OF ASPHALT CEMENTS MODIFIED WITH CRUMBED RUBBER FROM DISCARDED TIRES

INTRODUCTION

To enforce the recycling of scrap tire rubber in asphalt the Congress passed in 1991 the Intermodal Surface Transportation Efficiency Act (ISTEA) [4]. Section 1038(d) of ISTEA sets minimum utilization levels for the use of recycled rubber (and/or other selected reclaimed material, such as reclaimed asphalt pavement, known as RAP) beginning in 1994 (5%) and increasing by 5% each year through 1997, where it levels off at 20%. In 1994, the minimum utilization requirement in ISTEA called for states to use 5% recycled rubber as a percentage of total tons of asphalt laid in projects receiving federal-aid funding.

A moratorium, as approved by Congress in the FY94 transportation appropriation bill, delayed implementation of the requirement in ISTEA Section 1038(d), giving states one year to further study the performance, costs, and environmental impact associated with hot mix asphalt pavement containing crumb rubber. A second moratorium delaying funding enforcement of Section 1038(d) until Fiscal 1996 has just been announced [5]. The moratoria were enacted at the request of 49 state transportation departments to allow time for the requirement mandating crumb rubber incorporation to be modified to allow a wider selection of rubber additives and mix designs based upon recommendations from state departments of transportation.

One of the areas of performance requiring additional study is the compatibility of asphalt cement and rubber blends. This study concentrates on the rheological behavior of asphalt cement and rubber blends with respect to the Superpave specifications for asphalt cements developed in the Strategic

Highway Research Program. In addition to the incorporation of crumb and powdered rubber, focus is also placed on the use of other polymeric waste materials consuming landfill space, such as polyolefins (especially polyethylene) and ethylene-propylene rubbers, as additives for asphalt cements.

OBJECTIVES AND SCOPE

- To prepare a series of crumb and powdered rubber blends with Louisiana asphalts and assess the compatibility and stability of each blend.
- To evaluate the potential for applying dynamic testing techniques to asphalt/rubber blends. The survey includes determination of rheological parameters, high temperature viscosity, and creep.
- To subject the rubber asphalt blends to both TFOT and PAV aging to determine the hardening characteristics and compatibility of the blends during accelerated aging.

Blends of crumb rubber with one AC5, seven AC10, one AC20, and 10AC30 asphalts using two differential mixing protocols were prepared. Corresponding blends of powdered rubber with one AC5, three AC10 and one AC20 asphalts were also prepared using the favored mixing protocol.

Dynamic mechanical testing procedures were employed to characterize the rubber/asphalt blends. The tank asphalts and rubber/asphalt blends were subjected to aging by thin film oven testing followed

by pressure aging and recharacterized using dynamic mechanical testing procedures.

RESEARCH APPROACH

Materials

Tank asphalts provided by Louisiana refineries were used for the preparation of rubber/asphalt mixtures. Sample rubber blends were prepared using grades (number of sources) AC-5 (1), AC-10 (7), AC-20 (2) and AC-30 (10), and two different types of rubber particles. The distribution of components in selected samples was determined by solution NMR in perdeuterotetrachloroethane. A relaxation agent, $\text{Cr}(\text{acac})_3$, 12 mg/ml, was added to the ^{13}C NMR samples. The relative crystallinity of the asphalts as measured by DSC is also reported.

Rubber from ground tires was used as received from the suppliers as crumbs (Baker Rubber Inc., Southbend, IN) or fine powder (Rouse Rubber Industries, Inc., Vicksburg, MS). The crumb rubber, CR, had a maximum particle size of 1.2 mm and contained residual polyester fiber particles; 25.7% of the particles did not pass a #20 mesh sieve ($>0.84\text{ mm}$) and 3.5% were retained on the #16 mesh ($>1.19\text{ mm}$). The powder rubber, PR, was a fine 200 mesh (0.074 mm) ground rubber.

One of the styrene(S)-butadiene(B) copolymers investigated as an additional asphalt additive was Kraton D1101 (Shell), which is a linear SBS triblock copolymer of medium molecular weight containing 31% styrene. The block copolymer rubber was coded as BCR. It was mixed with asphalt cements with or without PR. A devulcanized rubber asphalt mix (Ecoflex, The Bitumar Group, Montreal, Canada) was a material completely soluble in aromatic hydrocarbons. No high molecular material could be isolated by precipitating fractionation using benzene as solvent and methanol as nonsolvent. The insoluble fraction in petroleum ether, i.e. the nonpolar components, amounted to 24.2%. It was mixed with PR and asphalt cements according to the protocol described for PRAC blends.

A virgin styrene-butadiene copolymer, i.e., not vulcanized, was separated by precipitation with methanol as small crumbs (0.5 - 1 mm) from Ultrapave SBR latex (Goodyear-Textile Rubber & Chemical Co.). The dried crumbs were then used in combination with CR to obtain blends according to the protocol described for CR/AC blending. The SBR containing blend was coded CoPolyR.

Novophalt^R modified asphalt cement -- a bi-phase binder system containing 4-6% polyolefin additives and paving grade asphalt cements -- was our reference material, especially for isochronal representations and creep measurements. Novophalt,

introduced to this country in 1976, is used in place of conventional binders to improve the performance of asphalt concrete. Reducing of permanent deformation, particularly at elevated temperatures, the increase of the resistance to fatigue and the improving of the resilient modulus are the primary benefits of Novophalt modified asphalt cements. It was coded Novophalt AC-10 or Novophalt AC-30, depending on the grade of the base asphalt used (Marathon AC-10 or AC-30).

Test Methods

The relative crystallinity of a given asphalt was measured by DSC. A Seiko DSC 220°C calibrated for temperature and enthalpy with indium was employed to estimate the relative volume of the crystalline phase in each of the asphalt samples. The DSC was conducted on $\approx 10\text{ mg}$ samples sealed in an aluminum sample pan using an empty aluminum sample pan with cap as a reference. Initially each sample was cooled at $3^\circ\text{C}/\text{min}$ to -45°C and then heated at $3^\circ\text{C}/\text{min}$. The percent crystallinity was estimated from this data by assuming that completely crystallized hydrocarbons in an asphalt matrix exhibit an average enthalpy of 200 J/g . The glass transition temperatures, T_g , of the neat asphalts, and of blends containing BCR, Ecoflex, PR or CR were estimated by differential scanning calorimetry, DSC, using a seiko dsc 220 at a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition was observed after the sample had been subjected to one heating/cooling cycle ($\text{RT} \rightarrow 150^\circ\text{C} \rightarrow -30^\circ\text{C}$).

A Brookfield viscometer (Spindle # 3) was used to evaluate the change in consistency of binders at high temperatures. Viscosity variations based upon both the amount of rubber added and the blending/storage times were measured. Bohlin CS and VOR rheometers and a Seiko DMS110 dynamic mechanical spectrometer were used to investigate the rheological behavior of both polymer modified asphalt cements, PMAC, and rubber-asphalt cements, RAC. Initial rheological measurements were made using a Bohlin CS rheometer, the measurements were made with a 4° cone and plate with a diameter of 20 mm; the minimum gap was set at 0.15 mm. The Bohlin VOR measurements were made using 8 mm parallel plates at a gap of 2 mm. The Seiko DMS employs a vertical parallel square plate system; the contact area of the plates was 100 mm^2 and a gap varying from 0.7 to 1.5 mm. A constant stress creep test was run at 35°C with the Bohlin CS rheometer; the stress applied was 590 Pa. Creep recovery was measured after stressing the sample for 10, 100 and 1000 sec.

To generate a master representation of DMA data, multiple frequency determinations (Bohlin CS, $f = 1, 5, 10, 20, 30$; VOR; $f = 1, 2, 5, 10, 20, 50$ and 100 Hz)

were used in the present study. The reference temperature was taken as $T = 64^{\circ}\text{C}$ to comply with the performance graded asphalt binder specification particularized for the hot climate typical of Louisiana. Using the WLF equation to estimate the shift factor, the best grouping of data was obtained when the values of C_1 and C_2 were 17 and 60, respectively.

Representative asphalt and asphalt/rubber blend (both crumb rubber and powder rubber as described above) specimens were selected for RTFO and PAV aging. RTFO bottles loaded with $35 \pm 0.5\text{g}$ material were subjected to aging in the oven at 163°C for 85 min under an air jet positioned to blow air (flow rate: $4,000\text{ mL/min}$) into each sample bottle at its lowest travel position while being circulated in the carriage (rotation rate of the carriage: $15^{\circ}/\text{min}$). Pure asphalt samples were RTFO aged without any difficulties and were submitted to the next aging step in the PAV. Asphalt/rubber blends, containing especially crumb rubber, foamed excessively. Therefore, the RTFO test was discontinued and replaced with the thin film oven test (TFOT). New samples were prepared ($50 \pm 0.5\text{g}$ material) which were aged in the TFOT oven at 163°C for 5 hr under a continuous air flow. A gross phase separation was noted in the case of certain asphalt/crumb rubber blends. All RTFO pure asphalt specimens and TFOT asphalt/rubber blend samples ($50 \pm 0.5\text{g}$ each) were subjected to PAV aging at 100°C and 300 psi for 20 hr.

The bending beam rheometer (Applied Test System, Butler, NC) was used to measure the low-temperature creep response of PAV aged tank asphalts and rubber/AC blends. The data, which were collected at six loading times (8, 15, 30, 60, 120, and 240 sec) for a load on the beam of $100 \pm 5\text{ g}$, allowed the calculation of the creep stiffness, $S(t)$, and the creep rate of the sample under load, m , as the absolute value of the slope of the log stiffness versus log time curve. The required calculations were performed by a software program supplied with the rheometer.

CONCLUSIONS

The chemical composition of the asphalt is a very important parameter in determining the physical properties of RACs. Asphalts with high aliphatic contents can induce excessive swelling of the rubber particles with a corresponding order of magnitude increase in the rheological properties.

Blends of vulcanized rubber particles can be analyzed using dynamic mechanical rheological techniques if the particle size is less than 1/10 of the gap between the plates of the rheometer. This was demonstrated by evaluation of powdered rubber blends. If the

average particle size approaches the width of the gap, anomalous results may be obtained.

Addition of ground rubber particles to asphalt affects the performance related properties of the rubber-asphalt cement as follows:

- The stiffness of the blend as reflected by $G^*/\sin \delta$ can be enhanced several fold depending upon the concentration of rubber added. This should improve the rutting resistance of the RAC's.
- The increase in the loss modulus is parallel to the increase in stiffness. If the maximum value for G'' is considered 3000 Pa @ 64°C for example, the concentration of rubber which may be added to a given asphalt is limited to approximately 10%.
- The high temperature viscosity increases significantly when the rubber content exceeds 10%. The ability to prepare RACs with 15% rubber that exhibit η @ 135°C less than 3.0 Pa depends upon the chemical composition of the asphalt and the rubber particle size.
- Creep and creep recovery (resiliency) of RACs are directly dependent upon the rubber content. These tests may be the most effective method for assessing the rubber/asphalt interactions.
- PAV aging of asphalt/crumb rubber blends reveals that these blends will exhibit long term incompatibility. Asphalt/powdered rubber blends appear to be more compatible even after PAV aging and the low temperature properties of these blends suggest that the rubber imparts improved cracking resistance.

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