Unraveling the Modification Mechanisms of Waste Bio-oils and Crumb Rubber on Asphalt Binder Based on Microscopy and Chemo-Rheology

Lei Lyu

PhD Candidate, Chang'an University
Visiting PhD student, Empa

Supervisor:
Dr. Lily Poulikakos Empa
Prof. Jianzhong Pei Chang'an University
Prof. Elham Fini Arizona State University

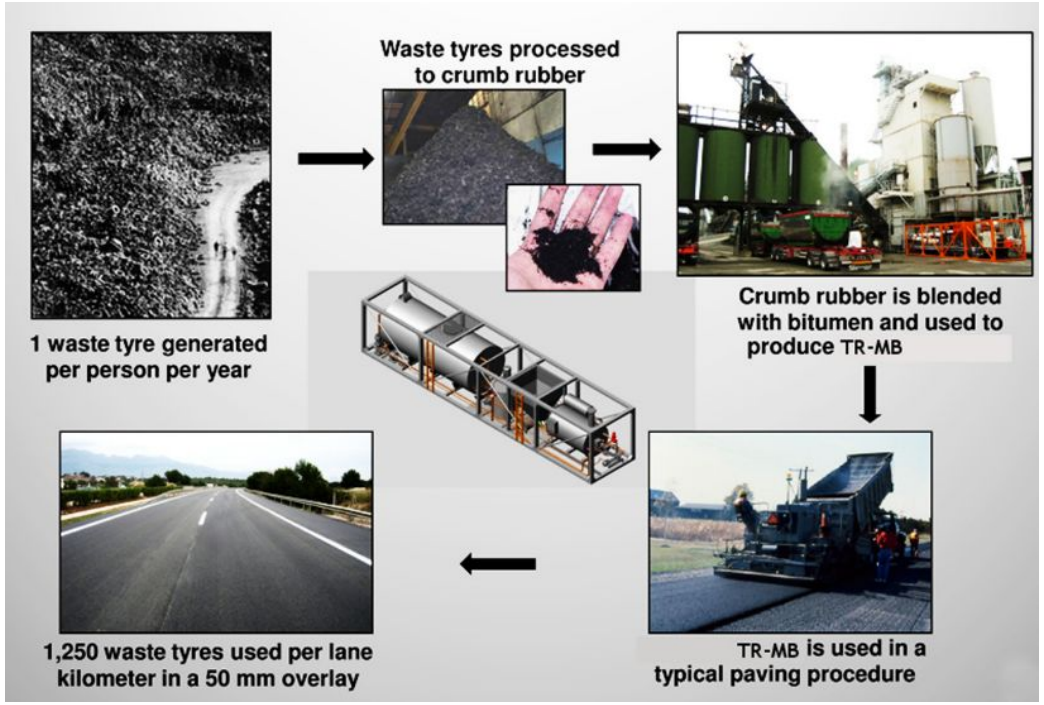
June 17, 2022

Empa
Materials Science and Technology

Backgrounds

- Crumb rubberized asphalt

Over 3 billion vehicle tires were produced worldwide every year

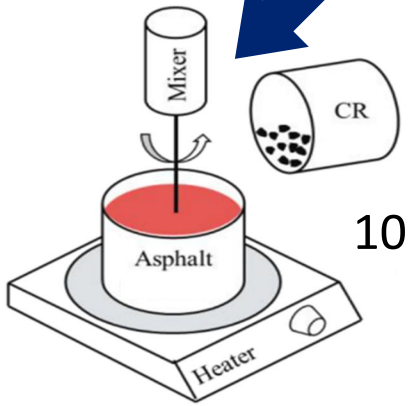


Production of crumb rubberized asphalt in practical use

End-of-Life Tires

Ambient Grinding

Crumb Rubber



10 wt% - 20 wt%

Crumb Rubberized Asphalt

Lo Presti, D., 2013. Recycled tyre rubber modified bitumens for road asphalt mixtures: A literature review. Constr. Build. Mater. 49, 863–881.

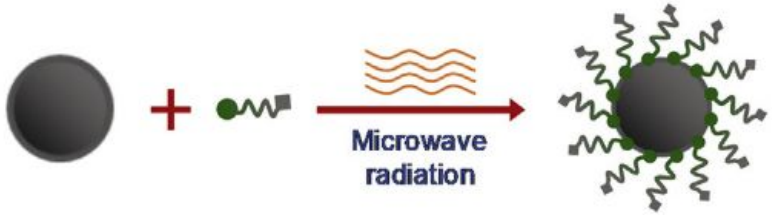
Project Overview

- Crumb rubberized asphalt

Drawbacks

- Workability
- Atmospheric emissions
- Storage stability

Bio-oils



Chemisorption method

Zhou, T., Kabir, S.F., Cao, L., Luan, H., Dong, Z., Fini, E.H., 2020. Comparing effects of physisorption and chemisorption of bio-oil onto rubber particles in asphalt. J. Clean. Prod. 273, 123112.

Experiments

Unraveling the Modification Mechanisms of Waste Bio-oils and Crumb Rubber on Asphalt Binder Based on Microscopy and Chemo-Rheology

(Published by Resources, Conservation & Recycling)

Chemical characterization

- Fourier transform infrared spectroscopy
- Thermogravimetric analysis
- Differential scanning calorimetry

Microstructural investigations

- Atomic force microscopy
- Environmental Scanning Electron Microscopy

Rheological tests

- Binder-Fast-Characterization Test
- Glover-Rowe (G-R) parameter


Contents lists available at ScienceDirect

Resources, Conservation & Recycling

journal homepage: www.elsevier.com/locate/resconrec

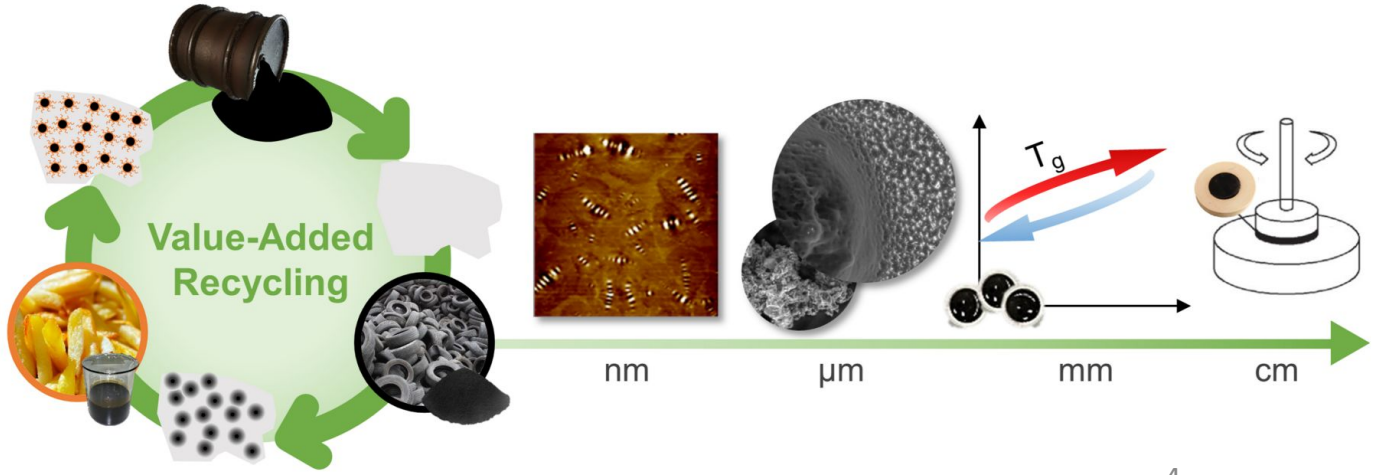
ELSEVIER

Full length article

Unraveling the modification mechanisms of waste bio-oils and crumb rubber on asphalt binder based on microscopy and chemo-rheology

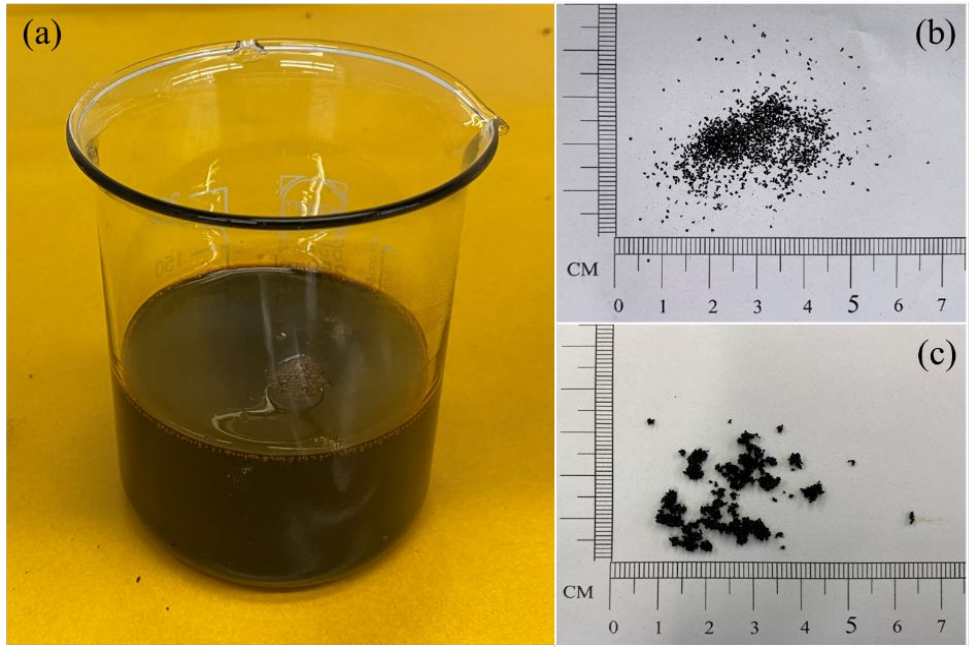
Lei Lyu [a,b], Peter Mikhailenko [b], Zhenyin Piao [b,c], Elham H. Fini [d], Jianzhong Pei [a,*], Lily D. Poulikakos [b,**]

[a] School of Highway, Chang'an University, Xi'an 710064, China
[b] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf 8600, Switzerland
[c] Institute of Environmental Engineering, ETH Zurich, Zurich 8093, Switzerland
[d] School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287, United States



Materials and samples preparation

- Raw Materials



The appearance of (a) Bio-oils, (b) crumb rubber, and (c) bio-modified crumb rubber

- Base asphalt (BA): 90 pen supplied by Donghai.

- Crumb rubber: 0.18-0.25 mm supplied by Tianjin Haitai Co., Ltd.

- Bio-oil (BO): Waste cooking oils acquired from Xuzhou Tengshun.

Table 1. Properties of base asphalt binder and bio-oil

Property	BA	Property	BO*
Penetration at 25 °C (mm)	84	Density (g/cm^3)	0.893
Softening Point (°C)	46	Acid Value (mgKOH/g)	45-55
Dynamic Viscosity at 60 °C (Pa·s)	168		

* Provide by the Xuzhou Tengshun Industry and Trade Co., Ltd.

Lyu, L., Pei, J., Hu, D., Fini, E.H., 2021. Durability of rubberized asphalt binders containing waste cooking oil under thermal and ultraviolet aging. Constr. Build. Mater. 299, 124282.

Materials and samples preparation

- Sample preparation

Microwave the mixtures of rubber particles and bio-oils

Bio-modified rubber:

1. Mix the crumb rubber and bio-oils at the weight ratio of 1:1 at 135 °C for 30 min
2. 12 h swelling at the ambient temperature
3. Microwave mixtures of crumb rubber and bio-oils at medium power for 4 min

Crumb rubberized asphalt (CRM):

15% unmodified crumb rubber (by weight of asphalt binder) was mixed with base asphalt binder using a bench-top shear mixer at 3000 rpm and a temperature of 180 °C for 30 min

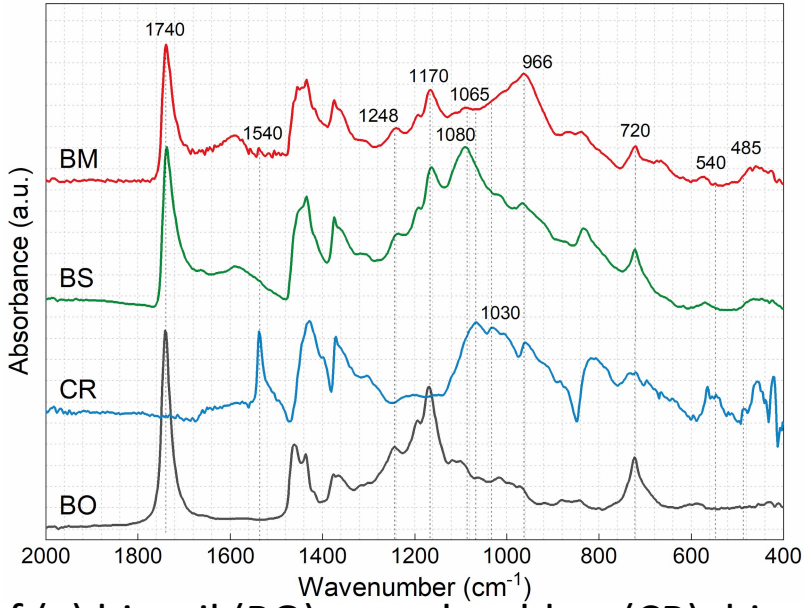
Bio-modified rubberized asphalt (BMR):

15% bio-modified rubber (by weight of asphalt binder) was mixed with base asphalt binder using a bench-top shear mixer at 3000 rpm and a temperature of 180 °C for 30 min

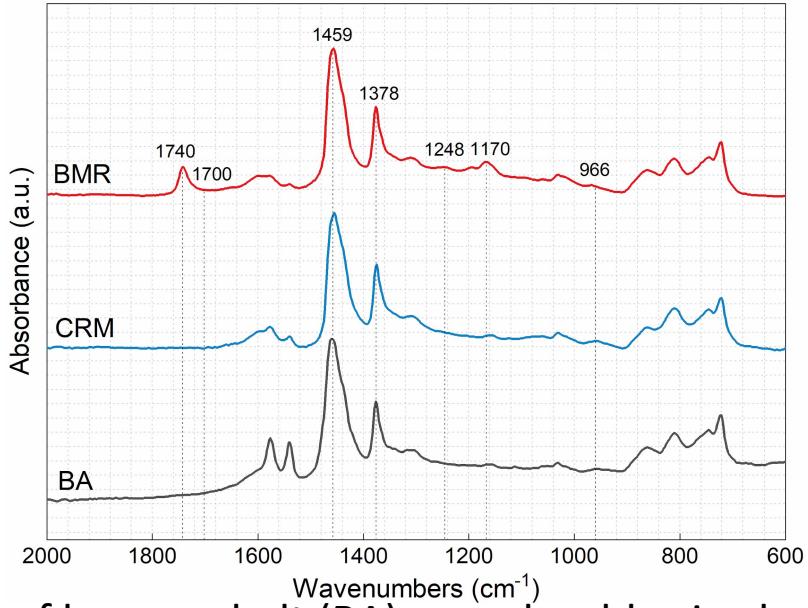
Mix the crumb rubber and base asphalt binder

Zhou, T., Kabir, S.F., Cao, L., Luan, H., Dong, Z., Fini, E.H., 2020. Comparing effects of physisorption and chemisorption of bio-oil onto rubber particles in asphalt. J. Clean. Prod. 273, 123112.

Fourier transform infrared spectroscopy



FTIR of (a) bio-oil (BO), crumb rubber (CR), bio-swelled rubber (BS), and bio-modified rubber (BM)



FTIR of base asphalt (BA), crumb rubberized asphalt (CRM), and bio-modified rubberized asphalt (BMR).

- CR, BO, and BS

1740, 1248, 1170, and 720 : Saturated fatty acids, two ethers, and alkanes [1].

Deoxidation: 1030 and 1065 [2] in CR and 1080 in BS attributes to S=O bonds, while disappear in BM

Devulcanization: Decreases at C-S bonds (540) and S-S (485) in BS and BM [3];

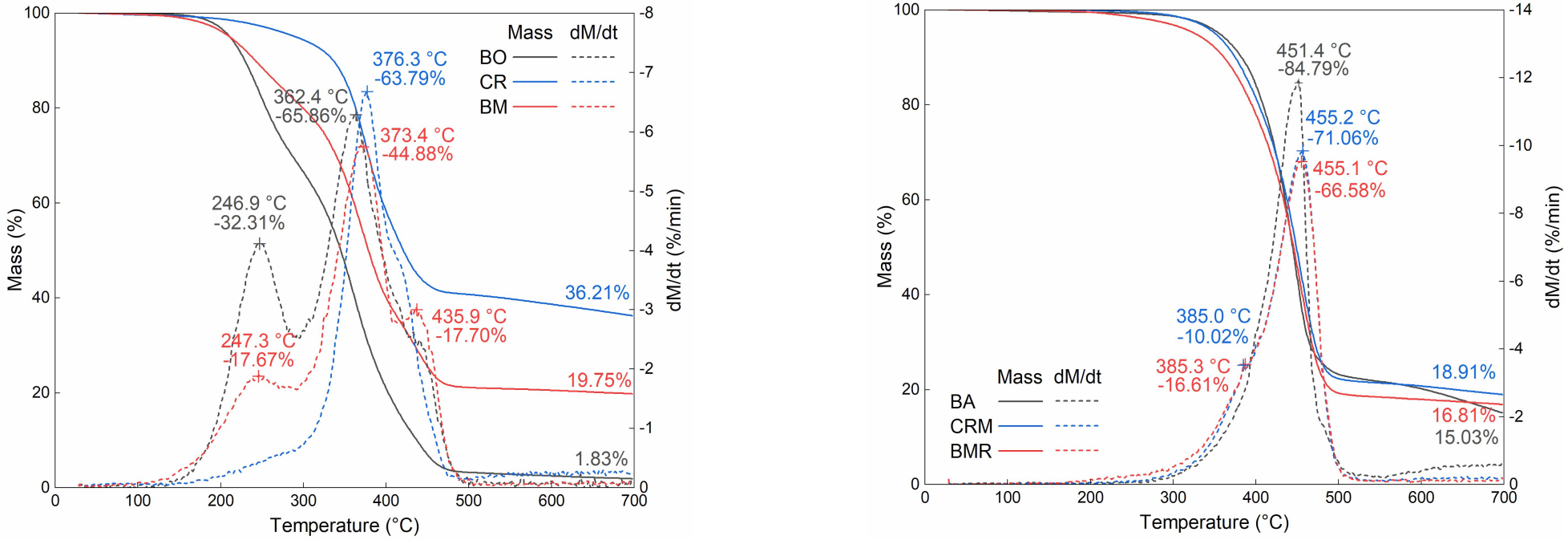
- BA, CRM, and BMR:

No strong peaks of carbonyl group at 1700 (carbonyl) - No oxidation during mixing [3].

[1] Y. Zhou, J. Chen, K. Zhang, Q. Guan, H. Guo, P. Xu, J. Wang, Study on aging performance of modified asphalt binders based on characteristic peaks and molecular weights, Construction and Building Materials. 225 (2019) 1077–1085. [2] J. Yu, Z. Ren, Z. Gao, Q. Wu, Z. Zhu, H. Yu, Recycled heavy bio oil as performance enhancer for rubberized bituminous binders, Polymers. 11 (2019) 800. [3] H. Wang, X. Liu, P. Apostolidis, M. van de Ven, S. Erkens, A. Skarpas, Effect of laboratory aging on chemistry and rheology of crumb rubber modified bitumen, Materials and Structures/Materiaux et Constructions. 53 (2020) 1–15.

Thermogravimetric analysis

Bio-oils (BO), crumb rubber (CR), and bio-modified rubber (BM);
Base asphalt (BA), rubberized asphalt (CRM), and bio-modified rubberized asphalt (BMR).



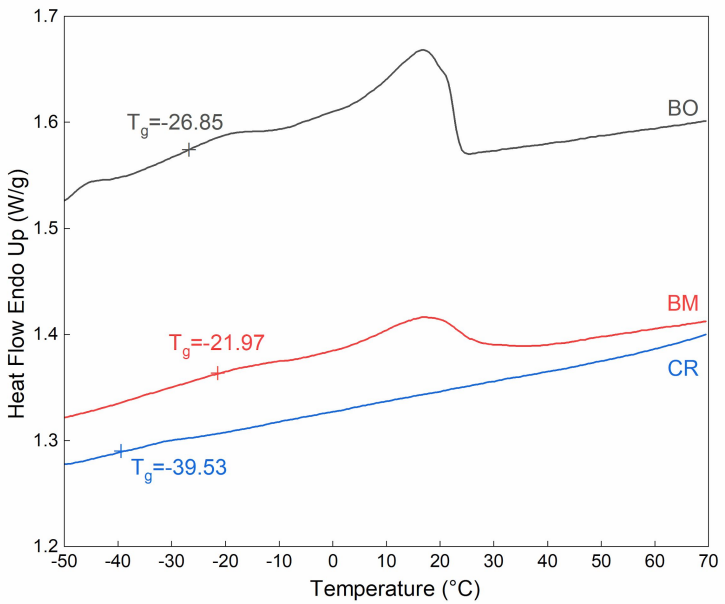
Thermogravimetric analysis (TGA) curves and its time derivative dM/dt

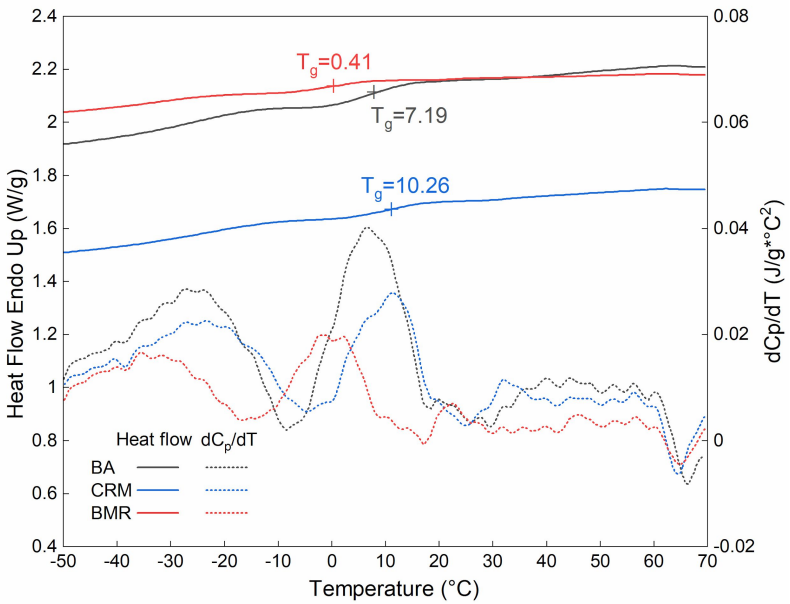
- A new peak at 435.9 °C of BM
  - Devulcanization of crumb rubber during bio-modification [1]
- CRM and BMR shift to a higher temperature than BA
  - -better thermal stability with rubber;
  - -higher decomposition temperature indicates a higher asphaltene content [2]
  - -absorption of light components by rubber [3]

[1] Colom, X., Faliq, A., Formela, K., Cañavate, J., 2016. FTIR spectroscopic and thermogravimetric characterization of ground tyre rubber devulcanized by microwave treatment. Polymer Testing 52, 200–208. [2] Al-Saffar, Z.H., Yaacob, H., Mohd Satar, M.K.I., Putra Jaya, R., Ismael, C.R., Mohamed, A., Rogo, K.U., 2021. Physical, rheological and chemical features of recycled asphalt embraced with a hybrid rejuvenating agent. International Journal of Pavement Engineering 0, 1–19. https://doi.org/10.1080/10298436.2021.1878517. [3] Li, D., Leng, Z., Zou, F., Yu, H., 2021. Effects of rubber absorption on the aging resistance of hot and warm asphalt rubber binders prepared with waste tire rubber. Journal of Cleaner Production 303, 127082. https://doi.org/10.1016/j.jclepro.2021.127082.

Differential scanning calorimetry

Bio-oils (BO), crumb rubber (CR), and bio-modified rubber (BM);
Base asphalt (BA), rubberized asphalt (CRM), and bio-modified rubberized asphalt (BMR).



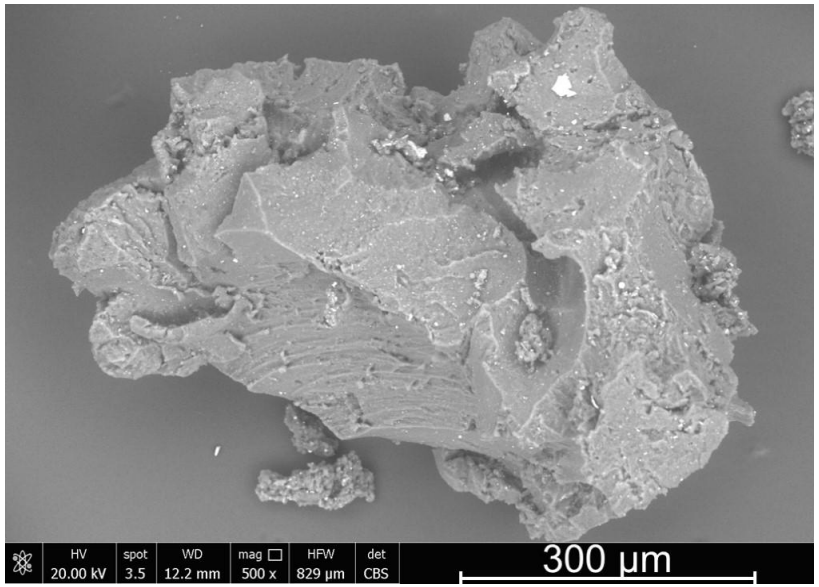


Heat flow curves and heat capacity's temperature derivative dCp/dT

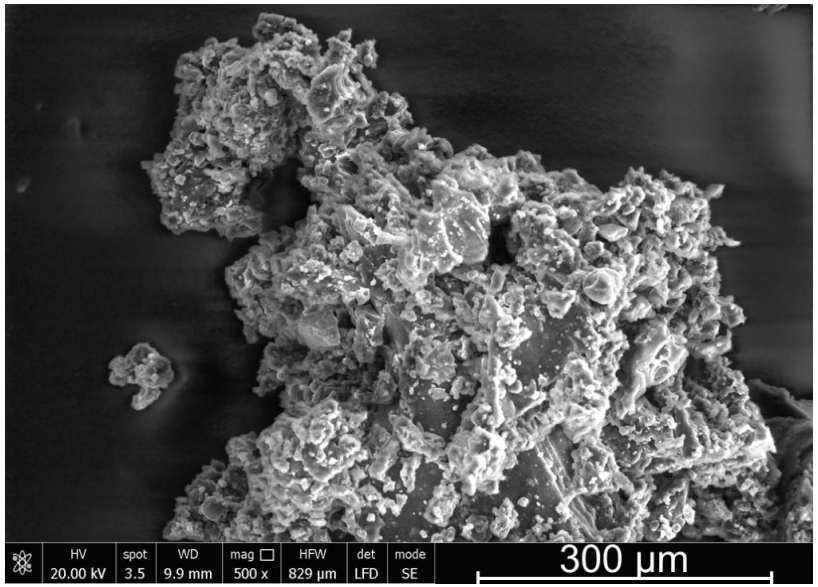
- A significant peak at 16 °C of BO and BMR due to the crystallization of the ester-based bio-oils [1]
- Tg of CRM was higher – higher asphaltenes contents [3]
- Tg of BMR was lower than BA - dilution effect of bio-oils – mitigate the physical hardening [2]

[1] Garcìa-Pérez, M., Chaala, A., Pakdel, H., Kretschmer, D., Rodrigue, D., Roy, C., 2006. Multiphase structure of bio-oils. Energy and Fuels 20, 364–375. https://doi.org/10.1021/ef050248f
[2] Qiu, Y., Ding, H., Rahman, A., Luo, H., 2019. Application of dispersant to slow down physical hardening process in asphalt binder. Materials and Structures/Materiaux et Constructions 52, 1–11. https://doi.org/10.1617/s11527-019-1320-6
[3] Li, D., Leng, Z., Zou, F., Yu, H., 2021. Effects of rubber absorption on the aging resistance of hot and warm asphalt rubber binders prepared with waste tire rubber. Journal of Cleaner Production 303, 127082. https://doi.org/10.1016/j.jclepro.2021.127082

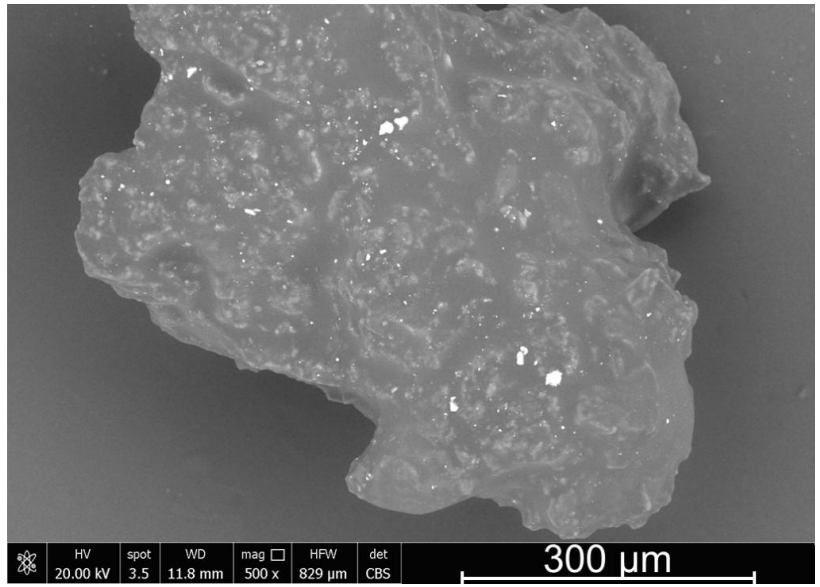
Environmental Scanning Electron Microscopy



Rubber



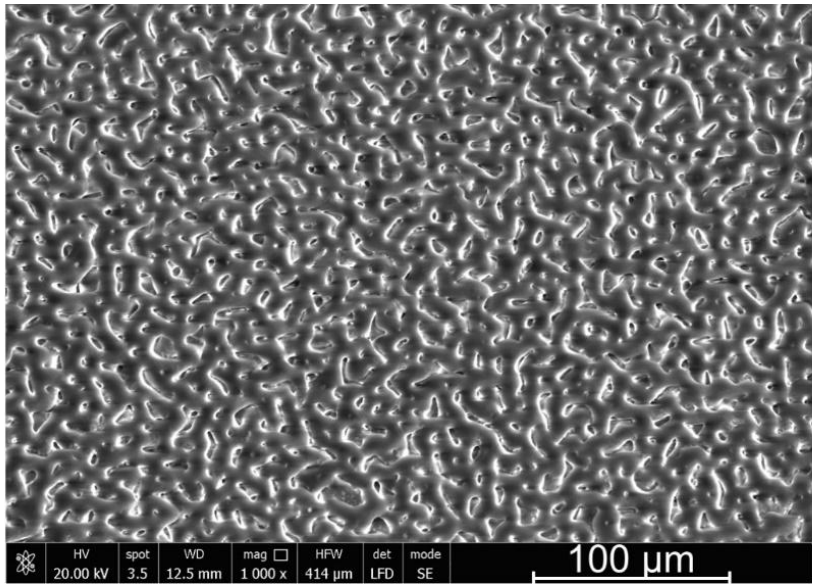
Microwaved rubber



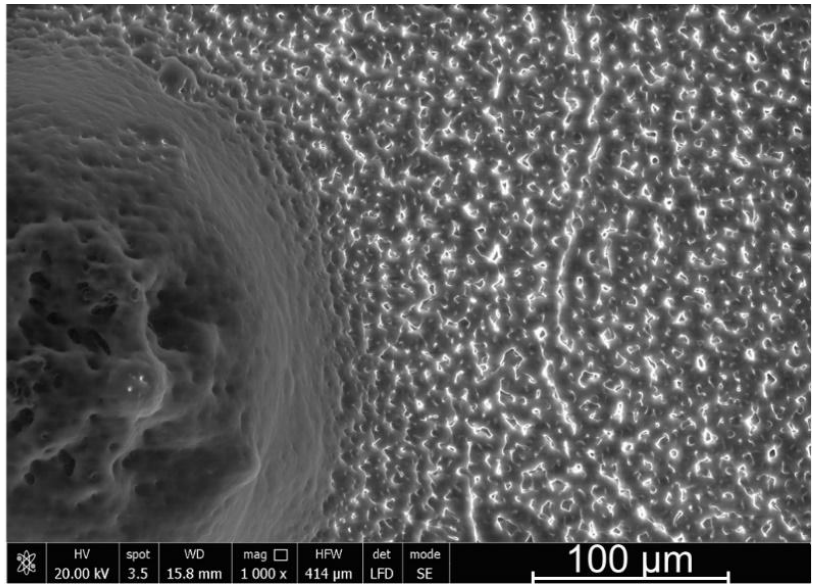
Bio-modified rubber

- Rubber: lamellar structures on the flat surface - mechanical grinding during manufacturing
- Microwaved rubber: cotton plant-like structure - improve the interaction area
- Bio-modified rubber: smooth surface with light-colored blocky structures - diffusion on the surface
- Microwave and bio-modification have minor effects on the sizes of rubber particles

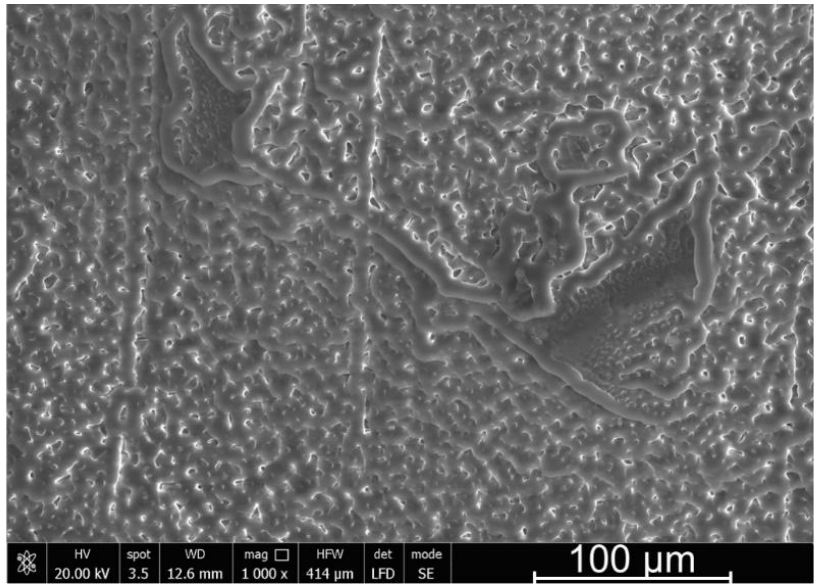
Environmental Scanning Electron Microscopy



Base asphalt



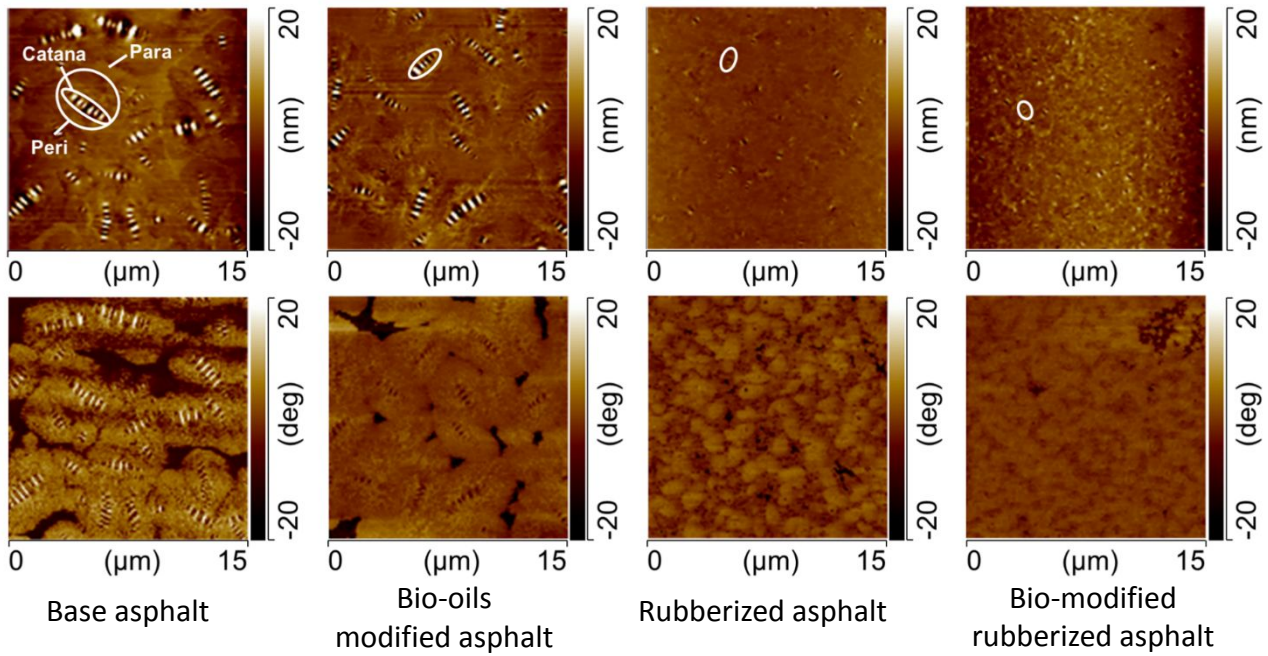
Crumb rubberized asphalt



Bio-modified rubberized asphalt

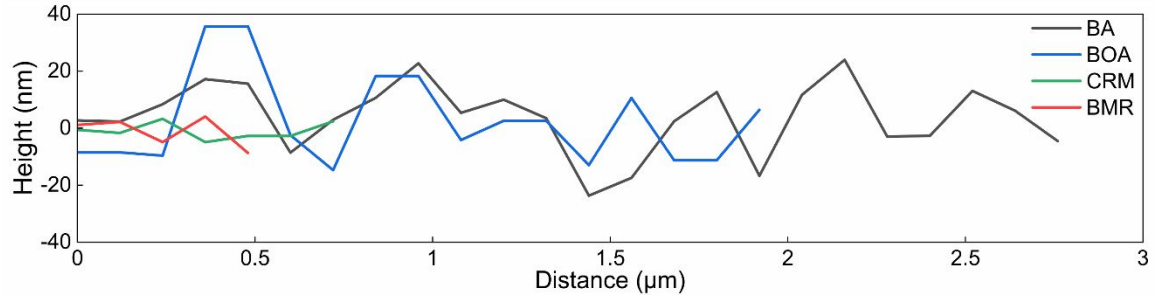
- Fibril structures was observed as a single-phase continuous structure in BA.
- Multiple phases structures are indeed existing around rubber particles in CRM.
- A dense fibril structure appeared around and even within the rubber particles of BMR.

Atomic force microscopy

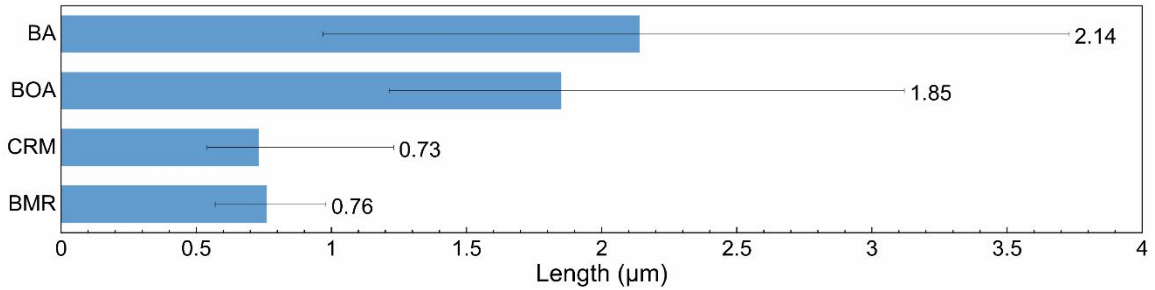


Base asphalt | Bio-oils modified asphalt | Rubberized asphalt | Bio-modified rubberized asphalt

AFM topographic images (1st row), and phase images (2nd row)



Height of the marked catana domains



The average length of catana domains

- Height and length of catana was decreased with crumb rubber.
- Stiffness difference between catana and peri was decreased with crumb rubber and bio-oils.

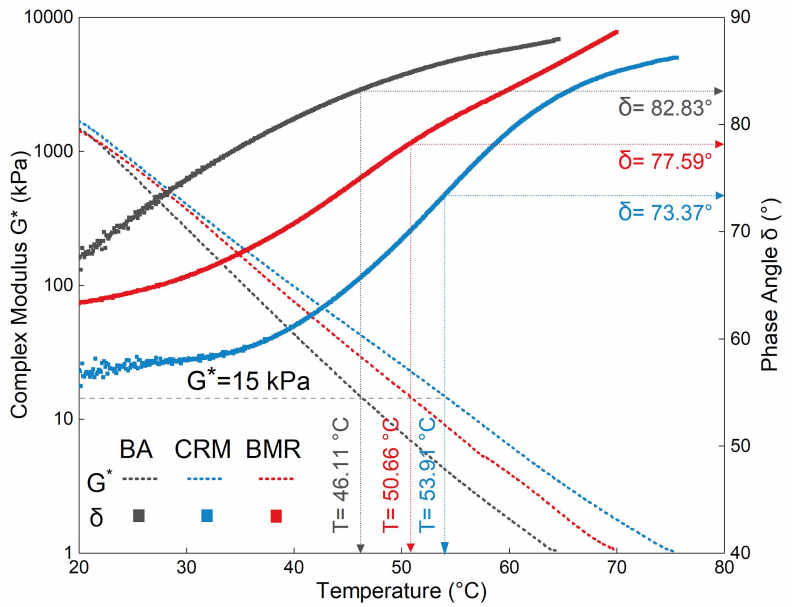
Rheological properties

- Dynamic shear rheometer (DSR)

Dynamic Shear Rheometer

|G*|: Complex shear modulus

δ: Phase angle

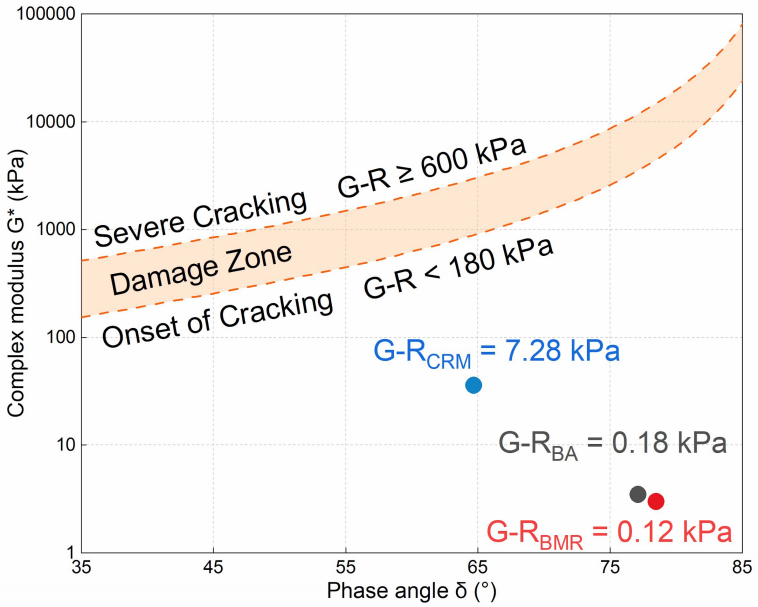


Determination of the softening temperature (T_{BTSV}) and corresponding phase angle (δ_{BTSV})

- Complex modulus of CRM and BMR are 147% and 75% higher than BA - Addition of crumb rubber
- Significant difference in high temperatures – Stiffer of CRM and BMR
- T_{BTSV}: Crumb rubberized asphalt > Bio-modified rubberized asphalt > Base asphalt

Rheological properties

- Dynamic shear rheometer



Glover-Rowe (G-R) Parameters

- G-R parameters - evaluate the susceptibility to non-load associated cracking at low temperatures

- Crumb rubberized asphalt shows the highest G-R parameters – an increased brittleness

- Bio-modified rubberized asphalt has the lowest G-R parameters – an enhanced flow behavior at low temperatures

  - Lower magnitude of physical hardening in low temperatures, which is also shown by its lower T_g in DSC results

Thanks

June 17, 2022

Empa
Materials Science and Technology