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Thermodynamic study of polymer blends miscibility and compatibilization through an equation of state approach

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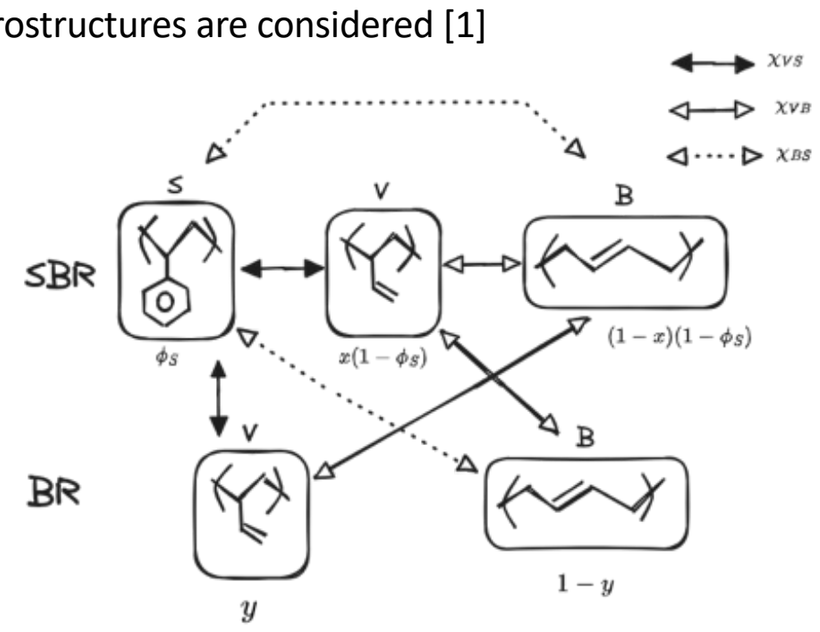
Abstract

Polymer blends can play a key role in the transition towards more sustainable material and production processes. The technological relevance of these materials is clear, but a deep understanding of their chemical physics is still lacking; phase separation and immiscibility are the rule, not the exception, for polymer blends, and gaining the ability to predict why and when this would happen opens the possibility of designing novel materials (and processes) with desired properties. Knowing the phase diagram before processing would allow precise control of the microstructure (which determines the macroscopic behaviour) of polymer blends. Phase diagrams can be determined from bulk thermodynamics, which allows to predict system miscibility conditions. The Flory-Huggins theory, which assumes incompressibility of the system, is the most common starting point for this study, both for its simplicity and capability to capture some essential features of polymer mixtures. The lattice fluid theory introduces compressibility and can naturally predict phenomena such phase separation upon heating (and the so called 'LCST', the lower critical solution temperature), moreover it gives the opportunity to link the bulk physics to the interface, that determines the compatibility of two polymer. In this work, the pressure-volume-temperature properties of different polymers are experimentally investigated and used to model their miscibility and interfacial properties with the aim of better understanding the physical-chemical processes and properties that underlie them, and to pave the way for predicting the properties that a compatibilizer should have to achieve the desired level of compatibilization for industrial applications.

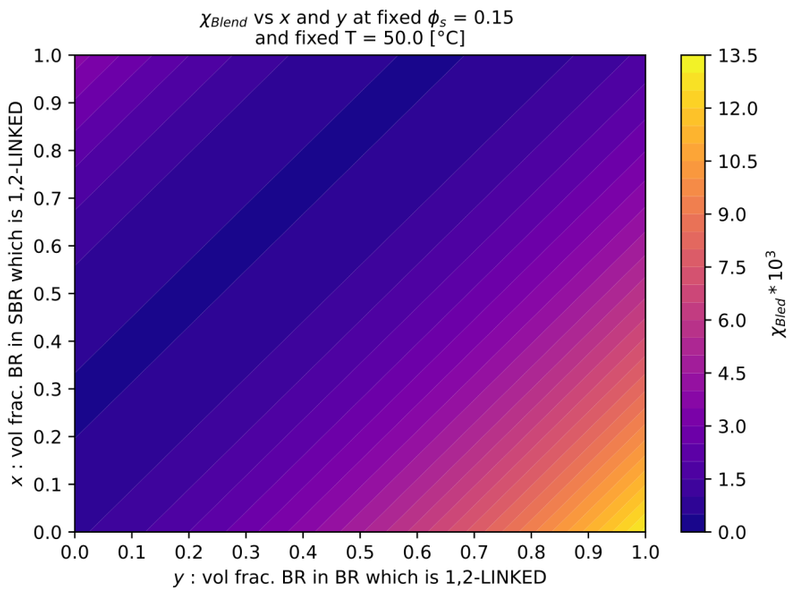
Preliminary Exploratory Results

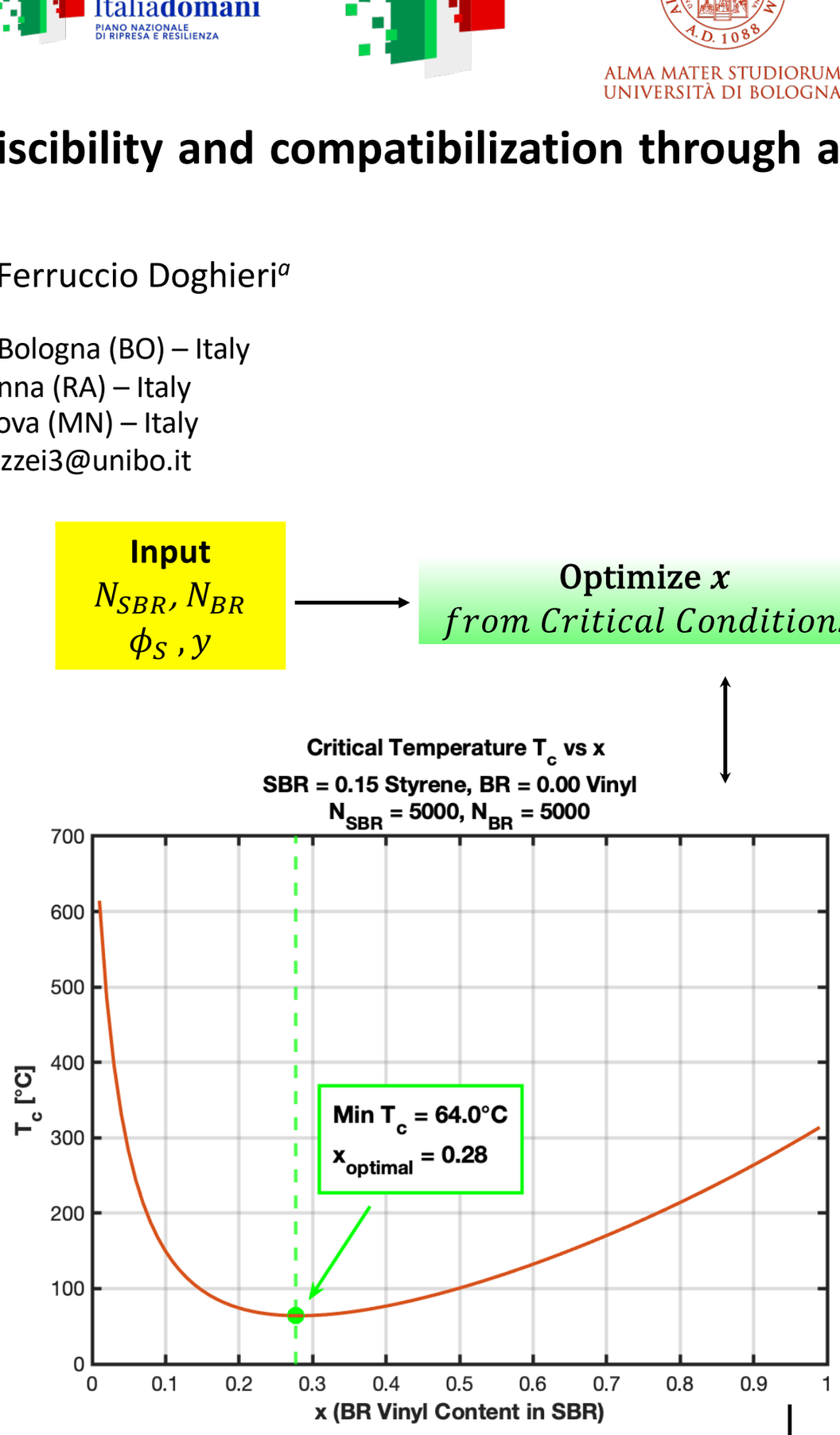
Blends of polybutadiene (BR) and styrene-butadiene copolymer are of relevant industrial interest and the miscibility of potential real systems is investigated using a Flory-Huggins framework in which the different BR microstructures are considered [1]



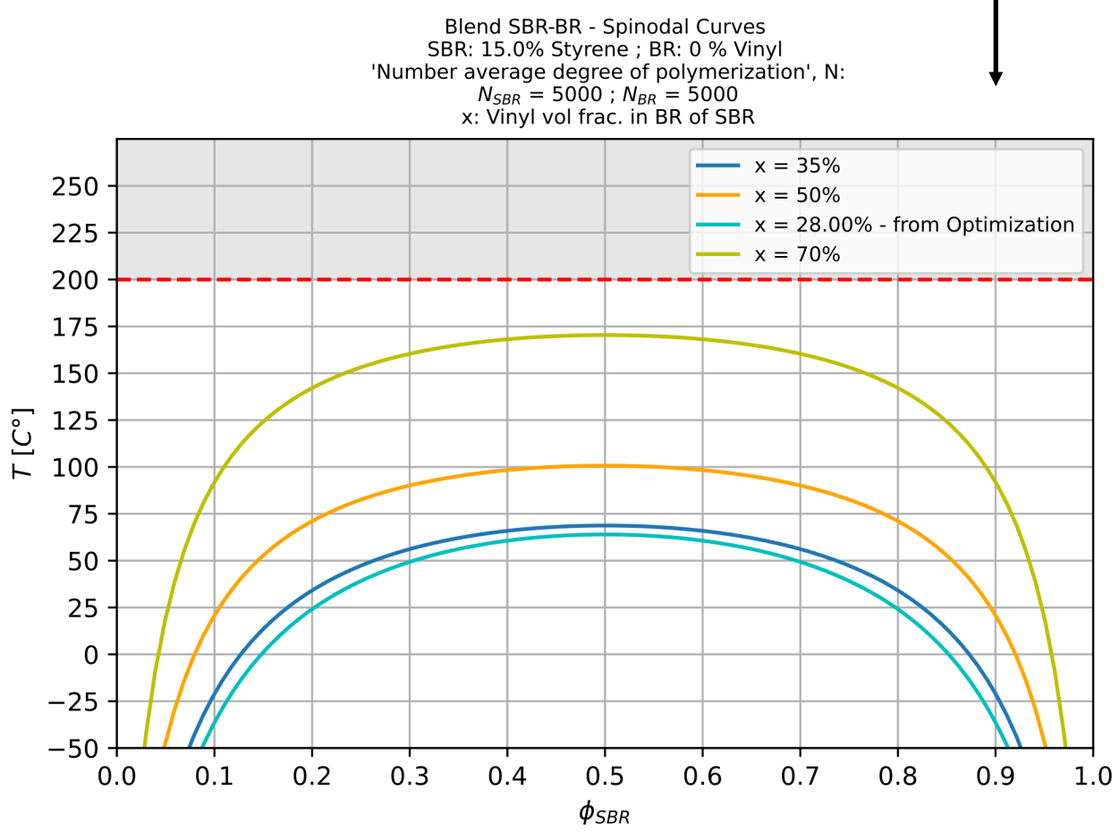
$$\chi_{Blend} = k\phi_S\chi_{VS} + (\phi_S - k)\phi_S\chi_{BS} - k(\phi_S - k)\chi_{VB}$$

$$k = y - x(1-\phi_S)$$





$$\frac{\partial^2 \Delta G_{mix}}{\partial \phi^2} = 0 = \frac{1}{N_{SBR}\phi_{SBR}} + \frac{1}{N_{BR}(1-\phi_{SBR})} - 2\chi_{Blend}$$



Conclusion and Future Perspectives

To validate the theoretical predictions, experimental investigations will be conducted. PVT (pressure–volume–temperature) characterization of the individual polymers will be used to better understand how volumetric properties affect miscibility, especially using equation of state (EOS) calculations. In future work, these EOS calculations will be extended to evaluate interfacial properties, enabling a deeper analysis of blend behavior. The calculated interfacial properties will be critically compared with the predictions of different existing thermodynamic models. Moreover, these theoretical insights will be integrated with experimental studies to explore the impact of miscibility on processes such as the functionalization of SBR–BR blends. This combined theoretical–experimental approach aims to support the development of optimized rubber materials with tailored interfacial and bulk properties.

References

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