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Development of new benzoxazine vitrimers based on phosphate ester exchanges

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First introduced by Leibler et al. in 2011, vitrimers offer a promising solution for materials sustainability. By combining the assets of thermoplastics and thermosets, they enable the recycling and reshaping of materials while maintaining high thermal and mechanical properties [1]. Polybenzoxazines are an emerging class of thermoset resins obtained from the ringopening polymerization (ROP) of benzoxazine monomers. They exhibit minimal shrinkage during polymerization, high char yield and excellent electrical and mechanical properties [2][3]. They can therefore be used in a wide range of applications, which makes them an interesting and promising alternative to conventional thermoset materials. However, as other thermosets, benzoxazine vitrimers suffer inherently from a lack of fire resistance, which can lead to property loss and pose a fire hazard. Strategies to tackle this primary concern have been studied for many years. Among them, the use of phosphate compounds, and especially phosphate esters, appears to be a promising approach as they are extensively used as environmental-friendly flame retardants for polymeric materials [4]. In this context, this study aims to develop a sustainable fire-retardant benzoxazine vitrimer containing phosphate ester as dynamic exchanges. It should be manufacturable by conventional tools and would be intended for interior parts within the aeronautic and transportation sectors. To this aim, the first step relies on the design of model molecules containing a phosphate ester, a benzoxazine ring, and an aliphatic -OH group to examine and understand the influence of phosphate esters on the ROP of benzoxazines and dynamic exchanges. With the knowledge gained from the first step, the following would be to design and manufacture a benzoxazine vitrimer composed of phosphorous esters as dynamic exchanges. Finally, recycling strategies will also be explored to ensure the sustainability of the materials.



Figure. Sustainable phosphate ester based benzoxazine vitrimers.

References:

[1] Montarnal, D., Capelot, M., Tournilhac, F., Leibler, L., Silica like malleable materials from permanent organic networks. Science, 2011, 334, 965–968.

[2] Ishida, H., Handbook of Benzoxazine Resins, Eds.; Elsevier: Amsterdam, 2011.

[3] Adjaoud, A., Puchot, L., Verge, P., 2023. Polybenzoxazine-based covalent adaptable networks: A mini-review. Polymer 287, 126426.

[4] Levchik, S., Weil, E., 2006. A Review of Recent Progress in Phosphorus-based Flame Retardants. Journal of Fire Sciences - J FIRE SCI 24, 345–364.