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# Toward replacement of styrene by bio-based methacrylates in unsaturated polyester resins

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## ABSTRACT

Several potentially bio-based methacrylate derivatives, namely (with mol.% of bio-based carbon), butanediol dimethacrylate (BDDMA) (33%), isobornyl methacrylate (IBOMA) (71%), lauryl methacrylate (LMA) (75%) have been evaluated as alternatives to styrene as reactive diluent of unsaturated polyester (UPR). First the compatibility of these compounds with SMC/BMC processes has been studied in terms of volatility, miscibility with UPR and viscosity. Based on these preliminary experiments, butanediol dimethacrylate (BDDMA) was selected as sole reactive diluent. The thermo-mechanical and mechanical properties of the resulting network were found to be very different from the ones of a UPR/MMA network prepared as a reference. Consequently, mixtures constituted of BDDMA and one monomethacrylate derivative (MMA, IBOMA and LMA) were then used as reactive diluents to yield networks owning a large range of mechanical behaviours.

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## 1. Introduction

Petroleum-based unsaturated polyester resins (UPRs) and vinyl ester resins (VERs) are among the most commonly used thermosetting polymers in the world [1,2]. These formulations are widely used as coatings or as constitutive matrices of chopped glass fiber-based composites such as sheet molding (SMC) and bulk molding (BMC) compounds [1,2]. The combination of good mechanical properties, low density, low cost and easy processability has made these formulations very popular in various fields such as construction, electronic and transportation. They are classically composed of petroleum-based reactive diluent (RD), such as styrene (S), in conjunction with a solid prepolymer

that is an unsaturated polyester (UP) containing fumarate groups (F) along the chain (for UPR), or the product of esterification of an epoxy monomer with methacrylic acid (for VER). Upon curing, radical (co)polymerization occurs from the unsaturations of the prepolymer and the one of the RD such that a crosslinked polymer network results. These systems are all the more appropriate for such purpose that the RD can readily homopolymerize and that the reactivity ratios for UPR (with  $r_F = 0.07$  and  $r_S = 0.30$ ) [3] or for VERs (with  $r_{MMA} = 0.50$  and  $r_S = 0.54$ ) [4] both reveal a well-pronounced tendency for alternating copolymerization. In the meantime, this copolymerization behaviour in conjunction with the conformational state of the dissolved multifunctional prepolymer leads to the development of a heterogeneous crosslinked structure [1].

However, one issue with such formulations arises from the use of styrene, which is highly volatile and has been identified as a hazardous air pollutant by the environmental protection agency [5]. Moreover, it has

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been “reasonably anticipated to be a human carcinogen” by the USA’s Department of Health and Human Services through the National Toxicology Program [6]. Furthermore, the unpredictable fluctuation of the crude oil prices and the increasing concern about the greenhouse gas emission encourage the development of bio-based chemicals derived from renewable and sustainable resources that have the same, if not better, processability and performance than the petroleum-based counterparts. For this reason, the search for a biobased RD is both industrially and fundamentally attractive. A well-suited RD should present the following requirements: low viscosity such that good processability and properties of the final material are ensured, low volatility, good compatibility with the prepolymer, and ability to homopolymerize and copolymerize with the unsaturations of the prepolymer under the given curing conditions [1,2]. It is important to have in mind that the macroscopic properties of the thermoset depend on the average number of crosslinks between chains (crosslink density) and the average length of the segments between crosslinks. On the one hand, the crosslink density depends on the structure of the prepolymer that is prepared but also on the ability of the two types of unsaturations to copolymerize. On the other hand, the average length of the crosslinks depends not only on the relative amounts of prepolymer and monomer but also on the behaviour of the radical copolymerization involving the two double bonds. Indeed, if some RD molecules remain at the end of curing, they may act as plasticizers and thus affect the global static mechanical properties such as stiffness. In the contrary, if some unsaturations of the prepolymer do not react, it will affect the crosslink density and thus the intensity of the viscoelastic relaxations. In this context, many efforts have been dedicated to replace styrene in UPRs and VERs with RDs that are derived from renewable and/or sustainable resources.

For many years, some positive alternatives have been reported for VERs especially with the use of bio-based RD presenting a methacrylate function. Indeed, the somewhat inappropriate-named VER resins bear methacrylate groups that homopolymerize very well and are thought to readily copolymerize with methacrylate-type RD. For example, fatty acids derived from triglycerides that were extracted from vegetable oils and subsequently hydrolysed, have been used to prepare methacrylated fatty acids (MFA) evaluated as RDs in VERs [7–10]. While being almost not volatile, their relatively high viscosity ( $\eta = 45\text{--}60\text{ mPa s}^{-1}$ ) and the low alpha transition temperature ( $T_{\alpha} = 70\text{--}80\text{ }^{\circ}\text{C}$ ) or low glass transition temperature  $T_g$  of the resulting cured thermosets have limited their development [7]. Wool and coworkers synthesized aromatic biobased methacrylates from vanillin, eugenol and guaiacol that are derived from lignin, the most abundant renewable aromatic polymer in nature [11–13]. These candidates are either solid (methacrylated-vanillin) or low volatile liquids but with a viscosity that is 25–40 times larger than the one of styrene, which hampers their use in SMC applications because of processing issues. Noteworthy, blends of classical vinyl esters with these candidates yielded thermosets owing  $T_g$  comparable to those of commercial VER thermosets. Other methacrylic-type candidates can be

envisioned from biobased building blocks derived from carbohydrates that can be isolated from numerous feedstocks (e.g., starch, cellulose, hemicellulose or lignin) [14]. For instance, furoic acid glycidyl methacrylate (FA-GM) or furfuryl methacrylate (FM) have been used in conjunction with commercial VE prepolymer [15]. While FA-GM is way too viscous ( $\eta = 234\text{ mPa s}^{-1}$ ), the low viscosity of FM ( $\eta = 4\text{ mPa s}^{-1}$ ) makes it suitable for substituting styrene. Dimethylitaconate diester, prepared from itaconic acid that is derived from carbohydrates fermentation, has also been used in association with dimethacrylate monomers in VERs and solely with 100%-biobased unsaturated prepolymer for UPRs [16].

Regarding UPRs, reports upon the substitution of styrene by (potentially) bio-based RD are scarce mostly because of the peculiar reactivity of fumarate groups with other double bonds. Indeed, while copolymerization of fumarate groups is well-favoured with styrene [3], the situation is much more problematic with other families of RD that may be produced using bio-based feedstocks. For example, reactivity ratios with diallylphthalate (DAP) (with  $r_F = 1.25$  and  $r_{\text{DAP}} = 0.01$ ) [17] or ethyl vinyl ether (EVE) (with  $r_F = 2.7$  and  $r_{\text{EVE}} = 0$ ) [18] attest that these systems present a tendency toward consecutive homopolymerization with fumarate groups being consumed first; while reaction proceeds, the reactive medium would thus enrich in RD that hardly (for DAP) or does not polymerize at all (EVE) through radical polymerization. These situations would lead to partially cured thermosets with a lot of residual RD. With vinyl esters such as vinyl acetate (VAc) (with  $r_F = 0.44$  and  $r_{\text{VAc}} = 0.01$ ) [19], the reactivity ratios are lower than unity attesting that both monomers are more likely to copolymerize rather than homopolymerize with a marked tendency toward alternation. As for any alternate copolymerization, there is a difference between the comonomer feed composition ( $f$ ) and the copolymer composition that is produced. It is possible to determine the instantaneous copolymer composition in RD formed from a particular feed composition ( $f_{\text{RD}}$ ) in conditions where the comonomer feed composition is relatively unchanged (low conversion generally below 5%) [20]. In the case of F-VAc system, it is found that the azeotropic monomer feed composition is around  $f_{\text{VAc}}^{\text{azeotrope}} = 0.35$ . This means that for any initial feed composition with  $f_{\text{VAc}} > 0.35$ , a situation that is encountered in UPRs for viscosity reasons, the consumption of the F units will be faster than the one of VAc, such that the feed will gradually get enriched in VAc that hardly homopolymerizes in these conditions. As a consequence, some VAc might remain in the final UPR. We recently reported on the use of vinyl levulinate (VL), derived from levulinic acid that belongs to the TOP12 list of the most promising renewable building blocks [21,22], as a RD for UPRs [23]. The reactivity ratios that were experimentally determined (with  $r_F = 0.81$  and  $r_{\text{VL}} = 0.01$ ) confirmed the previous statements: around 5.5 wt.% of unpolymers VL remained inside the prepared UPR network and acts as plasticizer. As illustrated by the two previous situations, it is of high importance that the RD readily reacts in the curing conditions (by copolymerization and/or homopolymerization) such that no residual remains in the obtained thermoset. Back in

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