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Review

Development of polyester binders for the production of sustainable polyurethane coatings: Technological characterization and life cycle assessment

Maria Nelly Garcia Gonzalez*, Marinella Levi, Stefano Turri

Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

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ABSTRACT

Polyurethane (PU) coatings are used in many industrial applications, like in the furniture and automotive sectors. The main objective of the present work is the re-design of polyester binder for PU coatings using a selection of monomers derived from biorefinery. A preliminary comparative evaluation of technological performances of the corresponding PU coatings is presented, showing that the introduction of biobased monomers generally leads to softer materials but it doesn't affect significantly other physical properties like wettability, adhesion and hydrolytic stability. Afterwards, the total impact of greenhouse gas emissions (GHG) and the total non-renewable energy use (NREU) are evaluated by a Life Cycle Assessment (LCA) study, following a cradle-to-factory gate approach. The ecoprofile of bio-based polyester binder is compared with other two fossil-based conventional polyesters. The results suggest that the use of bio-based monomers allows a significant reduction of the total GHG emissions of around 75% less and a reduction of around 35% less of the total NREU.

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1. Introduction

Polyurethanes (PUs) are one of the most versatile protective coating materials and they are extensively used in many

* Corresponding author.
E-mail address: marianelly.garcia@polimi.it (M.N. Garcia Gonzalez).

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manufacturing sectors such as in automotive, furniture, and heavy duty industries (Pfister et al., 2011; Szycher, 2013). Their excellent durability and mechanical properties are the main reasons that led to a successful industrial development (Zia et al., 2007). PU coatings are obtained by a stoichiometrically balanced mixture of polyols and polyisocyanates (Zhang et al., 2014) (Fig. 1). Among the polyols, mostly polyester oligomers (binders) are used, which contain both aliphatic and aromatic monomers and hydroxyl functional groups.

Currently, a large part of raw monomers for PU production is still based on petroleum sources. However, due to the foreseen decline of non-renewable feedstock, there is a growing interest in the development of monomers and macromers from renewable resources such as carbohydrates, vegetable oils, or microalgae (Pfister et al., 2011). Over the last few years, bio-based PU coatings have been proposed as sustainable alternatives due to their lower environmental impact, easy availability, biodegradability and acceptable cost (Mohanty et al., 2005; Ragauskas et al., 2006). Many works have appeared in literature about how to use these materials in a wide range of applications (Noreen et al., 2016).

The development of polyesters from renewable resources is an important topic in modern green chemistry (Vilela et al., 2014). These materials are certainly one of the most promising polymers which can be developed through biorefinery. Bio-based polyester oligomers can be used as components of paints and adhesives formulations, while high molecular weight polyester thermoplastics are promising packaging materials. There has been a certain ease of availability to obtain bio-based polyester precursors from biorefineries (Islam et al., 2014) where soybean oil-based is taking on a leading role (Miao et al., 2013; Pan and Webster, 2012), compared to, for example, isocyanates and diamines. More recently, bio-based phosgene-free routes for diisocyanate production have been described (More et al., 2013; Rajput et al., 2014). A polyisocyanate partially based on renewable carbon has been launched in the market (Bayer, 2015).

Renewable raw materials may reduce the environmental impacts compared with petroleum based counterparts. These effects can be quantified by the Life Cycle Assessment (LCA) method whose aim is to determine the environmental impacts of products and processes by the evaluation of the entire life cycle. There has been a growing use of this method since it is necessary to take measures against global climate change, and to become less dependent on petroleum sources. An example case is the study of LCA applied to the bio-based polyester polylactic acid (PLA) (Vink and Davies, 2015). In addition, an extensive number of studies have been reported where the assessment on a life-cycle basis of the different impacts of bio-based products has been compared to conventional fossil-derived products (Adom et al., 2014; Urban and Bakshi, 2009) or to other bio-based products (Cok et al., 2014).

However, bio-based resources could be involved in other environmental burdens, which can be assessed by the LCA, as it is the case of acidification, ozone depletion, land-use change, biodiversity, soil degradation, air pollution and social impacts among others.

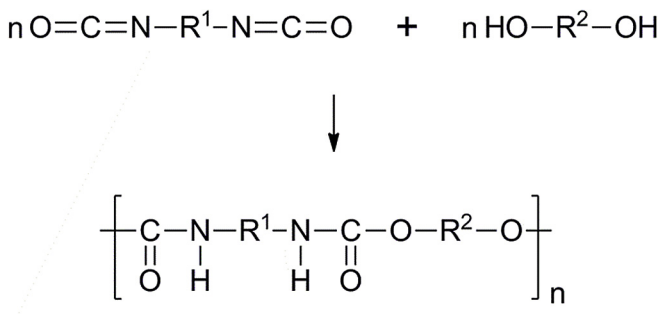

Fig. 1. Reaction of a diisocyanate with a diol to form a polyurethane.

In spite of the large number of papers describing polyurethane coatings, no specific study is reported in the literature concerning a cradle-to-gate LCA of polyester binders, which represent the larger component of the coating material. Nowadays, although the possibility of using bio-based monomers to synthesise polyester was already demonstrated, no specific evaluation of their ecoprofiles is available, being LCA studies predominantly focused on bio-based polyester as packaging materials. In the light of the above considerations, the aim of this work is to fill this specific gap in the literature. A new polyester binder for polyurethane coating was indeed re-designed through the selection of monomers derived from biorefinery. Polyester binders for coatings are complex copolymer systems made of at least 4–5 different monomers. The technological validation of the new bio-based polyester binders in comparison to fossil-based polyesters in bicomponent PU formulations was made through some preliminary experimental tests, including pull-off adhesion, indentation hardness, contact angle, and hydrolytic stability tests. The characterization of materials included the evaluation of the total impact of greenhouse gas emissions (GHG) and the total non-renewable energy use (NREU) by the Life Cycle Assessment (LCA) on the basis of a cradle-to-gate approach and considering the separated contributions of the monomer mixture composition, and of the production process of the copolyester (copolymerization).

2. Coating material

2.1. Monomer selection process

Suitable monomers were selected according to their functional role in the binder design and primary data availability in the Ecoinvent database version 3.2, and in the open literature. All the relevant information is summarized in Table 1. The data concerning succinic acid (SA) production came from the direct crystallization (SA-DC) process described by Cok et al. (2014).

2.2. Polyester binder composition

Table 2 shows the composition of the three 4-monomers copolyester binders synthesized and considered in the present study for the evaluation of their ecoprofiles, and tested experimentally in PU coating formulations. Polyesters 1 and 2 (PE1 and PE2) were designed and developed considering that all monomers are derived from fossil-based resources. The only difference between them is the change from 1,4-butanediol monomer to 1,2-propanediol monomer respectively. The latter presents a methyl side group and a secondary hydroxyl; this normally leads to a lower reactivity but at the same time it leads to the formation of sterically hindered ester groups in the polyester, which may be more stable towards hydrolysis. As for the polyester 3 (PE3), the composition was mainly based on monomers from renewable resources with the exception of the phthalic anhydride monomer. With regard to the aliphatic acids, the adipic acid has not yet a direct sustainable alternative so far. Therefore, the succinic acid was introduced as a renewable monomer (Cok et al., 2014). As the molecular structures of the two diacids are different, it is supposed that some differences between polymer Tg and hydrolytic stability may occur.

The polymerization process was the same for all the three polyesters, and consisted in a bulk polycondensation at high temperature (from 150° to 210 °C) under dry nitrogen flow to remove water as by-product. The progress of reaction was monitored by end group titration which monitored the residual acidity of