Non-isocyanate routes to Polyurethanes: some recent investigations

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Polyurethanes (PU) represent a very important class of materials with numerous applications as foams, adhesives, elastomers, etc. With the current regulatory constraints on the use of toxic isocyanates and the ambitious goals to increase the renewable content of plastics, isocyanate-free formulations are needed for more sustainable PU in the future.[1] Among all the possible routes to isocyanate-free PUs, aminolysis of cyclic carbonates, leading to polyhydroxyurethanes (PHUs) is one of the most promising pathways. In this presentation, a first part will focus on the design of bio-based PHU exhibiting original features. The synthesis of such materials in comparison to classical PU will be discussed in terms of polymerization kinetics, processes and PHU molar masses and mechanical properties.[2-6] A second part of the presentation will be dedicated to the elaboration of self-blown PHU and PU foams through different routes. First, various abundant waste streams-sourced biofillers (proteins, lignin derivatives, and polysaccharides) were incorporated into isocyanate-free PHU formulations composed of CO_2-based poly(cyclic carbonate)s, diamines and a catalyst. The formulations containing up to 30 wt.% of biofillers were foamed at 100 °C without adding any external foaming agent. Moisture naturally present in the biofillers partially hydrolyses the cyclic carbonates, which generates the blowing agent (CO_2).[7-8] Second, the step-growth polymerization of *in situ* generated polyisocyanates through the decarboxylation of polyoxamic acids, in the presence of phenyliodine diacetate (PIDA), and polyols was considered. The CO_2 produced during the reaction allowed the access to self-blown polyurethane foams through an endogenous chemical blowing. The acetic acid released from ligand exchange at the iodine center was also shown to accelerate the polymerization reaction, avoiding the recourse to an additional catalyst. Changing simple parameters during the production process allowed us to access flexible PU foams with a wide range of properties.[9]

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