Water-based poly(urethane-urea) dispersions — meeting the European Union legislation

Isabel P. Fernandes¹, Mário Rui P.F.N. Costa², Maria José Ferreira³, Maria Filomena Barreiro⁴, ⁵

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Abstract: This article discusses the synthesis methods of water-based poly(urethane-urea) dispersions (PUD), which over the past few decades have developed a solid reputation for high performance applications, particularly in the field of adhesives and coatings. PUDs are mostly environmentally compatible products since they do not contain or contain only low amounts of volatile organic compounds (VOC). This is an important feature in view of the present environmental policies, where governments and internal agencies are placing emphasis on developing sustainable processes, improving work conditions and reducing emissions of toxic and polluting substances into the atmosphere. In this context, this paper will discuss the main approaches applied to PUD synthesis in order to meet severe environmental restrictions resulting from the EU legislation.

Keywords: poly(urethane-urea), water-based dispersion, European Union legislation, N-methyl-pyrrolidone free products.

Over the past few decades, water-based poly(urethane-urea) dispersions (PUD) have developed a solid reputation for high performance applications, particularly in the field of adhesives and coatings. PUDs have good film-forming ability at low temperatures and the films produced from PUDs show excellent properties, such as good chemical resistance, high flexibility and good adhesion to a broad class of substrates.

The ascribed importance of this type of products is reflected by a significant number of registered patents that reached more than 1300 since 1990. Some of these patents deal with the process development itself, but most of them refer to final product formulation, which attests the versatility of these products in a wide range of applications. However, only 253 research and technical papers were registered in the same time period, according to the performed survey on the database Web of Knowledge using the keywords “water based polyurethane dispersions”.

European Union (EU) is committed to reducing emissions of toxic and polluting substances into the atmosphere, and therefore improving production processes sustainability and work conditions [1]. The toxicity of several substances was evaluated by the European Chemicals Agency (ECHA), which proposed to the European Commission modifications of their classification [2]. Consequently, the use of several substances in chemical preparations, mixtures and final products became

¹) Polytechnic Institute of Bragança, Associate Laboratory LSRE/LCM, Laboratory of Separation and Reaction Engineering (LSRE), Campus Santa Apolónia Ap. 1134, 5301-857 Bragança, Portugal.
²) University of Porto, Faculty of Engineering, Department of Chemical Engineering, Associate Laboratory LSRE/LCM, Laboratory of Separation and Reaction Engineering (LSRE), Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
³) Portuguese Footwear Technological Centre (CTCP), Rua de Fundões — Devesa Velha, 3700-121 S. João-da-Madeira, Portugal.
⁵) Author for correspondence; e-mail: barreiro@ipb.pt
Prepolymer synthesis developments deriving from the adaptation of the EU legislation with impact on the synthesis of PUD.

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The industrial production of PUD is nowadays a well-established technology. There are two main synthetic routes to produce PUD: the acetone process (a former process developed by Bayer AG) and the prepolymer process (developed as an alternative response to the patented acetone process). A schematic representation of the two processes, highlighting their similarities and differences, is shown in Fig. 1. Other used processes, but with more modest industrial implementation are the melt polymer process developed by Bayer AG) and the prepolymer process yielding final products with good performance. The main drawback of this process is related to the associated costs. Due to the use of large amounts of acetone, it requires a high reactor volume and, in general, explosion-proof equipment. Moreover, acetone needs to be distilled and dried before recycling [5, 6].

The acetone process

The acetone process, presented in Fig. 1a, can be described as comprising five main stages [6, 7, 11, 12]:

- synthesis of an isocyanate (NCO)-terminated prepolymer,
- dispersion of the prepolymer in water,
- chain extension.

Depending on the selected route, the chain extension can take place either during the first step (before the dispersion stage, i.e., in homogeneous medium) or after the second step (subsequently to the dispersion stage, i.e., in heterogeneous medium) [1, 5—10].

Fig. 1. Schematic drawing of: a) the acetone process, b) the prepolymer processes

The prepolymer process

The prepolymer process (Fig. 1b) can be described as comprising the following four main stages [13—15]:

- formation, in bulk, of an isocyanate terminated prepolymer from the reaction of a diisocyanate (aromatic or aliphatic) and a macrodiol (usually a polyester or polyether \( \alpha, \omega \)-diols);
- prepolymer dilution in acetone in order to suppress any viscosity constraints and also to dissolve the hydrophilic diamine;
- chain extension (in this step, the hydrophilizing diamine assumes a double role, i.e., it acts simultaneously as an internal emulsifier and as a chain extender);
- dispersion (phase inversion is promoted by adding water to the previously generated polymer in acetone solution);
- acetone removal to achieve a solvent-free product.

The described acetone process presents some advantages. It avoids viscosity constraints through the dilution of the polymer with a low boiling temperature solvent acetone, which will be easily removed at the end of the synthesis and can be further recycled and reused in the process [10]. Moreover, it is described as a reproducible process yielding final products with good performance. The main drawback of this process is related to the associated costs. Due to the use of large amounts of acetone, it requires a high reactor volume and, in general, explosion-proof equipment. Moreover, acetone needs to be distilled and dried before recycling [5, 6].

Comparatively to the acetone process, the prepolymer process has one major advantage, i.e. it requires none or only small amounts of acetone. As main disadvantages, it uses other co-solvents that might be difficult to remove and will remain in the final product. Chain extension is...
carried out in heterogeneous medium in opposition to the acetone process that uses a homogeneous medium (acetone solution before dispersion). This could lead to incomplete isocyanate conversion (inaccessible isocyanates entrapped inside polymer particles) and consequently to a lower final molecular weight of the polymer [7]. The chemical system associated to the prepolymer process is rather complex and involves polyols (mainly polyester or polyether, [8]), aliphatic diisocyanates to hinder isocyanate consumption due to water reactivity, hydrophilizing diols that will act as internal emulsifiers, co-solvents to dissolve the hydrophilizing diol and suppress process viscosity constraints, neutralizing agents to activate the ionic groups present in the internal emulsifier, chain extenders (mainly di- or triamines) to increase the molecular weight. Moreover catalysts are also needed during the prepolymer synthesis. A typical formulation uses a NCO/OH molar ratio of 1.7, a degree of neutralization of 100 % and a chain extension degree of 100 %. Typical process temperature conditions are: 70—90 °C during the prepolymer synthesis, 35—50 °C during the neutralization stage and 25—35 °C during the inversion phase. The extension reaction is usually performed at the room temperature (around 25 °C).

CONSIDERATIONS CONCERNING THE PREPOLYMER PROCESS IN THE CONTEXT OF THE RECENT EU LEGISLATION

In recent years, the former prepolymer process was re-adapted due to legislation developments that comprise process constraints, raw materials restrictions and the requirement to obtain a true solvent-free product. According to the European Commission Regulation No 1272/2008 [3], the N-methyl-2-pyrrolidone (NMP) is now classified as carcinogenic, mutagenic and toxic for reproduction (CMR). Moreover, the established restrictions for the EU market require that, after June 2015, the products incorporating NMP contents higher than 5 wt % needed to be labelled as toxic, while products containing less than 5 wt % will be labelled as irritant. In this context, the NMP-free concept gained a growing importance for the PUD industry using the prepolymer process, where the majority of the produced PUDs use dimethyl propionic acid (DMPA) as the internal emulsifier. DMPA is sparingly soluble in the reactive mixture and needs to be previously dissolved in an organic solvent being NMP the more generalized choice. NMP has a high boiling temperature, near 200 °C, and thus remains in the final product [16].

CHALLENGES TO OBTAIN NMP-FREE PUD

Three approaches leading to NMP-free PUD have been taken so far [16, 17]:

— the direct replacement of NMP by an equivalent solvent (the chosen solvent must fulfil a series of criteria: dissolve DMPA, be inert towards isocyanates, be miscible with water, have low odor and low cost),
— DMPA replacement with an equivalent hydrophilizing diol but with better solubility in the reactive mixture,
— replacement of the macrodiol with a counterpart diol incorporating ionic groups in the molecular backbone.

Direct replacement of NMP

For direct NMP replacement some alternatives can be envisaged, namely, the use of dimethylsulfoxide (DMSO) or N-ethyl-2-pyrrolidone (NEP). DMSO has one major disadvantage related to the strong odor that intensifies as a result of exothermic decomposition (formation of dimethylsulfide). NEP was commercially announced as a directly obvious alternative to NMP. Nevertheless this relatively new product is at present too expensive and insufficiently studied. Other possible NMP substitutes are ketones, i.e. acetone or methyl ethyl ketone (MEK). Ketones have an additional benefit: their low boiling temperature allows an easy removal by vacuum distillation from the final product [18—20]. However, the solubility of DMPA in ketones requires large amounts of a solvent or pre-neutralization. As a reference, the dissolution of 2.3 g of DMPA needs 100 g of acetone while 100 g of NMP are enough to solubilize 41 g of DMPA [21].

Direct replacement of DMPA

This alternative comprises the direct replacement of DMPA by an equivalent hydrophilizing diol but with better solubility in the reactive mixture, as is the case of dimethyl butanoic acid (DMBA). Comparatively with DMPA, DMBA is more soluble in acetone and in the used macrodiols [17].

Utilization of macrodiols with incorporated ionic groups

It is also feasible to replace DMPA by macrodiols with incorporated ionic groups in the molecular backbone [16]. These products are already available on the market, e.g., DMPA polyol HA series from GEO Specialty Chemicals [21]. However, two major disadvantages are inherent to the use of this solution: high viscosity and high cost.

Brief overview of the current PUD industry panorama

Following the need to fulfil the imposed directives, some companies have already in their portfolio of products PUD based on DMPA that meet the latest NMP restrictions. Bayer Material Science has the NMP-free Bayhydrol™ UH 25 product series and the Bayhydro® UH 2342 that contains less than 5 wt % of NMP. Alberdingk Boley has the U series line of NMP-free PUD, while
Another important issue in the PUD industry is the changing hazard classifications of tin catalysts, e.g. DBTDL from “harmful” to “toxic”. According to the European Commission Regulation No 276/2010 [4], di-substituted tin compounds shall not be used in articles and mixtures at tin contents above 0.1 wt %. DBTDL is used worldwide mainly because it presents excellent catalytic effect and selectivity towards hydroxyl-isocyanate reaction (urethane group formation). A direct alternative is the use of amines, but the recently established restrictions also impose limits to these compounds. Other viable substitutes include zinc and bismuth carboxylates and zirconium complexes. Some studies indicate the ability of zirconium compounds to selectively catalyze the isocyanate-hydroxyl reaction; however the specific use of these catalysts in PUD synthesis requires further studies [8, 25—27]. Moreover, as compared to the presently used catalysts, they are rather expensive.

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tions, namely limitations concerning NMP contents in PUD.

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