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

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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.

Dyspersje wodne poli(uretanowo-mocznikowe) w świetle wymagań prawodawstwa Unii Europejskiej

Streszczenie: Omówiono metody syntezy dyspersji wodnych poli(uretanowo-mocznikowych) (PUD), które znajdują coraz szersze zastosowanie, szczególnie w produkcji klejów i powłok. PUD są na ogół produktami bezpiecznymi dla środowiska, ze względu na brak lub małą zawartość lotnych związków organicznych (VOC), co jest ważne w świetle obecnej polityki ochrony środowiska. Przedstawione w pracy metody syntezy PUD uwzględniają wymagania wynikające z prawodawstwa Unii Europejskiej w zakresie spełniania surowych ograniczeń środowiskowych.

Słowa kluczowe: poli(uretano-mocznik), dyspersja wodna, prawodawstwo Unii Europejskiej, produkty wolne od *N*-metylo-pirolidonu.

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

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*) Material presented at the conference „Polyurethanes 2015 — cooperation for innovation", September 9—11, 2015, Cracow, Poland.

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strongly limited, or even banned. This is an issue of great concern for PUD industry since some of the traditionally used raw materials are presently subjected to severe restrictions. These include co-solvents such as *N*-methyl-2-pyrrolidone (NMP)] [3] and tin-base catalysts, such as dibutyltin dilaurate (DBTDL) [4].

This paper presents an overview of the recent developments deriving from the adaptation of the EU legislation with impact on the synthesis of PUD.

PUD SYNTHESIS PROCESSES

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 dispersion and the ketamine/ketazine processes [5—7].

In a general way, the described production processes comprise the following three main stages:

— 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].

The acetone process

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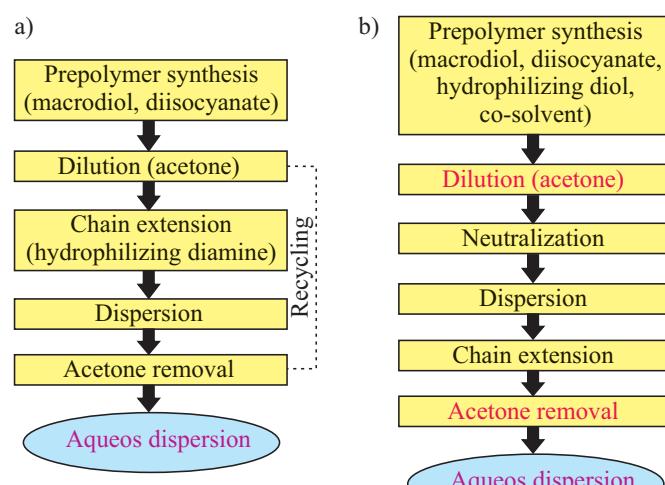

Fig. 1. Schematic drawing of: a) the acetone process, b) the prepolymer processes

— 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 α,ω-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].

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 (aliphatic), a macrodiol (usually a polyester or polyether α,ω-diols) and a hydrophilizing diol (since the hydrophilizing diol is not soluble, neither in the prepolymer mixture nor in acetone, it requires other co-solvents which are in general highly polar and low volatility components — in general, the co-solvent will remain in the final product);

— neutralization of the internal emulsifier acid groups using a tertiary amine;

— dispersion (phase inversion is promoted by adding water to the previously produced prepolymer);

— chain extension, usually using a short diamine.

If viscosity constraints are encountered during the process, acetone is added to dilute the medium. In this case, the last stage will correspond to its removal. These steps (dilution and acetone removal) can be viewed as optional and are directly related to the chemical system used. As an example, polyester based formulations have higher viscosity than the counterpart polyether based formulations.

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 α,ω-diols), 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 dimethylol 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 dimethylol 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 Bayhydrol™ UH 2342 that contains less than 5 wt % of NMP. Alberdingk Boley has the U series line of NMP-free PUD, while

T a b l e 1. PUD component limitations according to EU directive 2008/39/CE ([30]) and FDA positive list 21CFR 175.105 ([29])

Component		Directive 2008/38/CE	FDA
Diisocyanate	dicyclohexylmethane diisocyanate	$QM(T) = 1$ mg/kg (free NCO)	21CFR 175.105
	isophorone diisocyanate		21CFR 176.170[a], 21CFR 175.105[b]
	tetramethylxylilene diisocyanate		
Polyol	polycaprolactone	NR	without limitations
	polypropylene glycol	21CFR 175.105	
	polyethylene glycol		
	polytetramethylene ether glycol		
Catalyst	dibutyltin dilaurate	NR	NR
	stannous 2-ethylhaxanoate	21CFR 175.105	NR
Internal Emulsifier	dimethylol propionic acid (DMPA)	21CFR 175.105	$QM(A) = 0.05$ mg/6 dm^2 (free DMPA)
	dimethylol butanoic acid	21CFR 175.105	NR
Neutralizing Agent	triethylamine (TEA)	21CFR 175.105	NR
Chain Extender	diethylenetriamine	21CFR 175.105	$LME = 5$ mg/kg
	hydrazine monohydrate	NR	NR
	ethylenediamine	21CFR 175.105	$LME = 12$ mg/kg
Co-Solvent	*N*-ethyl-2-pyrrolidone	NR	NR
	dimethyl sulfoxide	NR	NR
	acetone	21CFR 175.105	without limitations
	N-methyl-2-pyrrolidone (NMP)	NR	NR

NR — not referred to, $QM(T)$ — maximum total amount, $QM(A)$ — maximum amount allowed, LME — specific migration limit.
[a] FDA positive list where PUDs are referred to as anionic polyurethanes.
[b] FDA positive list where PUDs are referred to as polyurethane resins.

the Lubrizol Corporation has the NMP-free PUD Sancure™ 20041 [22—24].

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.

Some specific markets for PUD, where restrictions are even more specific, such as adhesives for food contact, also justify additional studies. In this case, besides the absence of solvents, the raw materials must be carefully chosen to avoid toxicity, component migration and noticeable smell. Moreover, there is a lack of protocols to characterize these issues [28]. In the USA, Food and Drug Administration (FDA) [29] regulates the allowed reac-

tants through the elaboration of positive lists. Reactants allowed to be incorporated in the synthesis of PUD adhesives for indirect food contact are catalogued in the 21CFR 175.105 positive list. In the EU context, since 1989 the legislation has been harmonized and the main restrictions were assembled in the directive 2008/39/CE [30]. It is worth to mention that adhesives are not yet treated as an individually regulated group [28]. A summary of the existing limitations considering PUD production in general using the EU directive 2008/39/CE and FDA positive list 21CFR 175.105 is shown in Table 1.

CONCLUSIONS

The industrial production of PUDs is nowadays a well-established technology and the number of applications using this type of products is increasing. Two main synthetic routes are used: the acetone process (a former process developed by Bayer AG) and the prepolymer process (developed as an alternative response to the patented acetone process).

PUD industry in general and the prepolymer process in particular, are facing some challenges due to the emerging new markets and environmental restrictions. According to EU legislation, substitutes for some of the traditionally used raw materials need to be found and implemented. In this context, some companies start already to offer products that fulfil the imposed restric-

tions, namely limitations concerning NMP contents in PUD.

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