A novel view of the manufacture of polyurethane-polyurea aqueous dispersions

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Over the past few decades, polyurethane-polyurea aqueous dispersions (PUDs) have developed a solid reputation for high performance applications, particularly in the field of adhesives and coatings. PUDs are mostly environmentally compatible products; they are totally devoid 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. Moreover, polyurethanes are known as “tailor-made” products with properties resulting from the wide diversity of raw-materials which can be combined in different ways during the synthesis.

The industrial production of PUDs is nowadays a well established technology. A schematic representation of the process is given in Figure 1. They are produced by several companies across the world and for various applications. There are two main synthetic routes to produce PUDs: the acetone process (a former process developed by Bayer AG) and the pre-polymer process (developed as an alternative response to the acetone process). The pre-polymer process comprises several stages briefly described as follows: a macrodiol (usually a polyester or polyether) and a hydrophilising diol (the internal emulsifier) react with an excess of diisocyanate to form an isocyanate terminated pre-polymer. After neutralizing the acid groups of the internal emulsifier, the pre-polymer is dispersed in water until phase-inversion occurs. Finally, the dispersed pre-polymer is chain extended using a short diamine. If any solvent had been added during the process, for example to suppress process viscosity restrictions, the last stage will correspond to its removal (Dieterich, 1981).

The pre-polymer process, at present, is being forced to readapt due to ongoing developments, partly motivated by process constraints, raw-materials restrictions and the need to obtain a true solvent-free product. Allied to this fact it is worthy to mention the upcoming of European REACH legislation, which is expected to have a considerable influence in the PUD industry. Most of the industrially 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. The chosen solvent must fulfil a series of criterions: dissolve DMPA, be inert towards isocyanates and be miscible in water. Additionally it must present low odour and low cost. Alternatives to the traditionally used option (methyl-2-pyrrolidone NMP) include ketones, cyclic ethers, amines and amides.

NMP has one major problem; it has a high boiling point, near 200 ºC, and thus remains in the final product. The upcoming product restrictions refer that all products containing more than 5% (w/w) of NMP will be considered toxic from June 2009 onwards (Mestach and Goossen, 2007) and at present almost all commercially available PUDs have NMP contents from 5-15 %. In this context, the NMP-free concept is gaining a

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growing importance, particularly for PUD industry which uses the pre-polymer process. Beyond this issue, the appearance of new markets for PUD, where restrictions are even more specific, such as adhesives for food contact, are justifying additional studies. In this case, besides the absence of solvents, the raw materials must be carefully chosen to avoid toxicity and noticeable smell.
Presently, there are some alternatives to achieve the NMP-free concept. Among them we may refer the direct NMP replacement by an equivalent solvent, DMPA replacement by an equivalent hydrophilising diol but with better solubility in the reactive mixture, and replacement of the macrodiol by one of the commercially available new macrodiols with incorporated ionic groups in the molecular backbone (Gertzman et al., 2007).
In recent years, our research group has been involved in the development of polyurethane-polyurea water dispersions for various applications. With this work we intend to review this theme and describe the most recent developments. Characterization of industrial dispersions (such as that shown in Table 1.) will be presented and examples of synthesis will be described. We must highlight that our experience has always been aimed at industrial applications.

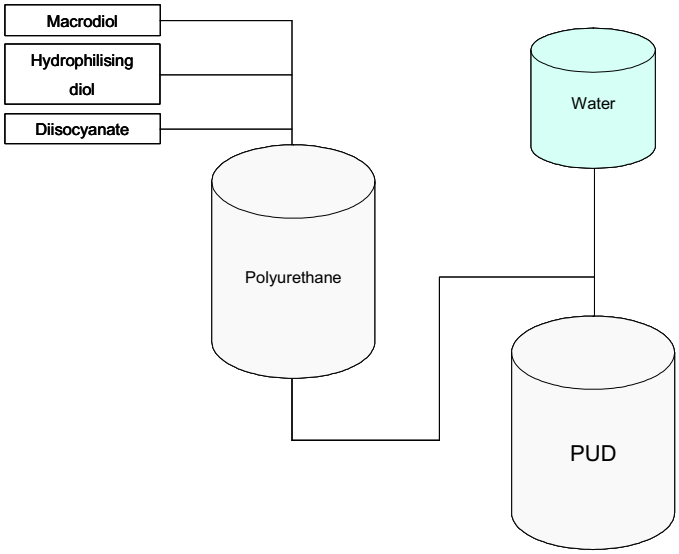

Figure 1. A process for polyurethane dispersion production (adapted from Mestach and Goossen, 2007)

Table 1. Characterization of a commercial PUD

Solid Content (%, w/w)	37.0
Viscosity (mPa.s)	40.1
pH	8.05
Mean Particle Size (nm)	
Volume distribution	114
Number distribution	109

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