

Solvent-free aqueous polyurethane dispersions

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Introduction

The industrial production of aqueous polyurethane dispersions (PUDs) is nowadays a well established technology. 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 patented acetone process). Comparatively to the acetone process, the pre-polymer process has one major advantage since it requires none or only small amounts of acetone.

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 worth mentioning the European REACH legislation, which is having a considerable influence on 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, usually N-methyl-2-pyrrolidone (NMP). NMP is difficult to remove and will remain in the final product.

There are some alternatives to achieve the NMP-free concept. Among them we can refer the direct NMP replacement by an equivalent solvent, the DMPA replacement by an equivalent hydrophilising diol but with better solubility in the reactive mixture and the pre-neutralization of DMPA prior to reaction with isocyanates [1, 2].

Materials and methods

In this work we present a modified pre-polymer process that includes four main stages: (1) Pre-polymer synthesis, (2) Pre-polymer dispersion, (3) Chain extension and (4) Co-solvent removal, as described in Figure 1. Comparatively to the conventional pre-polymer process the hydrophilising diol was used in its salt form, i.e., after neutralization with a tertiary amine. The chemical system comprises a polyetherdiol (polytetramethylene glycol (PTMG) or polypropylene glycol (PPG)), an isocyanate (isophorone diisocyanate (IPDI)), a hydrophilising diol (DMPA), a neutralizing amine (triethylamine (TEA)), a chain extension agent (ethylenediamina (EDA) diethylenetriamine (DETA) or hydrazine monohydrate (HYD)), a catalyst (stannous octoate – SO) and acetone as the co-solvent for the DMPA salt solubilisation.

The obtained dispersions have been characterized in terms of pH, viscosity, solid content, particle size and stability (thermal and electrolyte presence).

Several samples have been synthesized and compared with a base formulation produced by the conventional pre-polymer process.

Results and conclusions

In this work it has been shown that the use of DMPA in its salt form can provide a way to readapt, with minor modifications, the conventional pre-polymer process to

produce dispersions in accordance with the present PUD market requirements (NMP-free). By substituting DMPA through its salt form, NMP can be directly replaced by acetone that provides the possibility to obtain solvent free dispersions since acetone will be easily removed at the end of the synthesis and could be further recycled and reused in the process. Additionally, the developed process was facilitated in what concerns the pre-polymer dispersion stage and chain extension effectiveness. Table 1 shows the comparison between samples produced by the two processes.

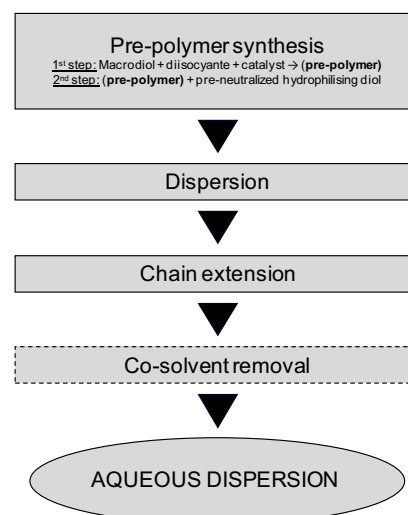


Figure 1. Schematic drawing of the modified pre-polymer process.

Table 1. Dispersion properties obtained by the conventional (A) and the modified (B) processes.

Process	pH	Solid content %(w/w)	Particle size ^(*) (nm)	Viscosity (mPa.s)
A	8.5	30.0	Volume: 74.0 (m) Number: 54.0 (u)	17.3
B	8.1	40.5	Volume: 139 (m) Number: 50.2 (u)	26.0

(*) Multimodal (m) and unimodal (u) distributions

References

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