



SOLVENT-FREE AQUEOUS POLYURETHANE DISPERSIONS

Isabel Fernandes¹, Filomena Barreiro^{1*}, Mário Rui Costa²

1. LSRE – Polytechnic Institute of Bragança, Campus de Santa Apolónia, Ap 1134, 5301-857 Bragança, Portugal

2. LSRE - Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal



Introduction

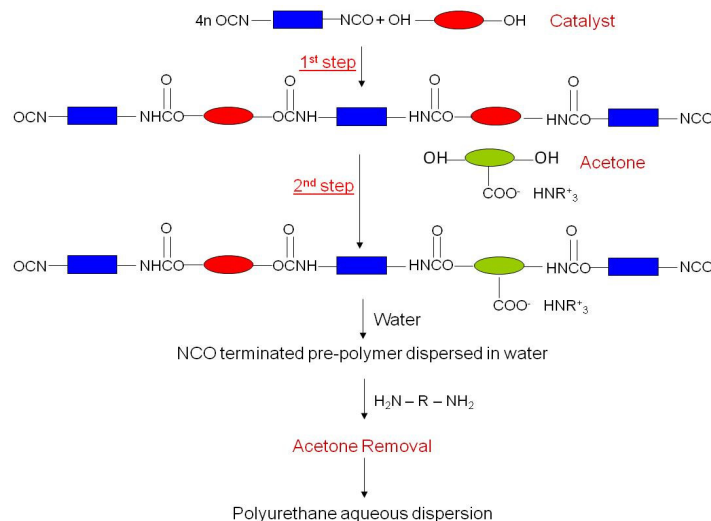
- ✓ Polyurethane aqueous dispersions (PUDs) can be produced through two main synthetic routes: the acetone process and the pre-polymer process. The pre-polymer process has one major advantage towards since it requires none or only small amounts of acetone.
- ✓ The pre-polymer process, at present, is being forced to readapt due to ongoing developments, namely 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 classified as toxic, is difficult to remove and will remain in the final product.
- ✓ The alternatives to achieve the NMP-free concept are: (1) direct NMP replacement by an equivalent solvent, (2) DMPA replacement by an equivalent hydrophilising diol but with better solubility in the reactive mixture and (3) pre-neutralization of DMPA prior to reaction with isocyanates [1, 2].

The strategy

- ✓ Using a **modified pre-polymer** process that includes the following stages: (1) Pre-polymer synthesis, (2) Pre-polymer dispersion, (3) Chain extension and (4) Co-solvent removal. The hydrophilising diol was used in its salt form, i.e., after neutralization with a tertiary amine and was introduced intermediary during the pre-polymer stage.

Formulations

- ✓ The chemical system comprises: PPG or PTMG (polyol), IPDI (isocyanate), DMPA (Hydrophilising diol), TEA (DMPA neutralizer), EDA+DETA (chain extenders). Stannous octoate was used as catalyst and acetone as the co-solvent.
- ✓ Several samples have been synthesized and compared with a base formulation produced by the conventional pre-polymer process.
- ✓ The base formulation uses a NCO/OH ratio of 1.7, a DMPA content of 5% and a chain extension degree of 40%.
- ✓ The modified pre-polymer process was optimized by varying the chain extension degree and composition (EDA+DETA).



1st step: Macrodiol + diisocyanate + catalyst → (pre-polymer)

2nd step: (pre-polymer) + pre-neutralized hydrophilising diol

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

Conclusions

- ✓ 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 product.
- ✓ The developed process was facilitated in what concerns the pre-polymer dispersion stage and chain extension effectiveness.

References

- [1].Gertzmann, R., Irle, C., Schmitt, P. (2007). Waterborne Polyurethane Coatings for Wood Floor-The Next Generation, *Bayer MaterialScience AG tech. inform.*, Leverkusen, Germany
 [2].Mestach, D., Goossen, J., (2007). New Approaches for Solvent-Free Waterborne Polyurethanes, *Polyurethane Magazine International*, 5, 313-318.

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

Process	pH	Solid Content (% (w/w))	Particle Size (nm)*	Viscosity (mPa.s)
Commercial	7.9	34.7	Volume: 1301 (m) Number: 64 (u)	183
A	8.5	30.0	Volume: 74 (b) Number: 54 (u)	17.3
B	7.1	37.1	Volume: 121 (u) Number: 116 (u)	16.4

Table 2. Dispersions properties synthesized by the modified (B) process.

Sample	GE (%)	Composition		pH	Solid Content (% (w/w))	Particle Size (nm)*	Viscosity (mPa.s)
		EDA	DETA				
1	70	30	40	7.0	40.0	Volume: 133 (u) Number: 126 (u)	15.6
2	70	50	20	8.1	40.5	Volume: 139 (m) Number: 50 (u)	26.0
3	70	35	35	7.0	32.2	Volume: 109 (u) Number: 105 (u)	32.2
4	50	40	10	6.9	31.1	Volume: 191 (m) Number: 52 (u)	31.1

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

