

# Waterborne Polyurethane Coatings for Wood Floors – The Next Generation

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New pathways were explored to make aqueous polyurethane dispersions without the co-solvent n-methylpyrrolidone (NMP). This includes methods to process these materials with alternate co-solvents as well as with co-solvents that can be removed from the product during processing. Chemical modifications of the polyurethane were investigated in order to use these alternative processes.

New co-solvent free polyurethane dispersions, useful as coatings for wood floors, have been developed using an alternative process. These materials have outstanding properties, are low odor, and free of NMP.

## **Introduction**

NMP has been the solvent of choice for the widely used prepolymer mixing process (PMP) for aqueous polyurethane dispersion (PUD) synthesis. This solvent reduces the prepolymer viscosity during the production steps to enabling smooth handling and dispersing of the prepolymer. This is due to the good solubilizing characteristics of NMP for organic materials and its water solubility. Furthermore NMP supports the coalescence of the dispersion particles when the dispersion is applied to a substrate. [1]

NMP is a suspected fetotoxin. Recent studies on NMP have persuaded the *EU Commission Working Group on the Classification and Labeling of Dangerous Substances* to label NMP as toxic. According to a recent decision, formulations containing  $\geq 5\%$  NMP will have to be labeled as toxic. In the US on March 14, 2003, the state of California *Office of Environmental Health Hazard Assessment* (OEHHA) issued a Notice of Proposed Rulemaking to adopt regulatory levels for NMP listed pursuant to the Act as known to the State to cause reproductive toxicity (Title 22, California Code of Regulations, Section 12000).

It is the desire of Bayer MaterialScience to make the safest products possible. Therefore, the search for a NMP free route to make these products is of highest importance.

Different approaches have been described towards NMP free PUDs already. Materials that have less than half of the polymer in the hard-block can often be made without co-solvent since these exhibit lower viscosity prepolymers. These polymers will often coalesce to make a continuous film without additional solvents. Products that have higher than one half of the polymer in the hard-block will require some co-solvent to process and to coalesce. One alternative for materials with large amount of hard-block is the synthesis of products with comparable VOC content using other solvents. The solvents have to be non-reactive towards isocyanates. Examples for suitable alternatives to NMP are e.g. N - Ethylpyrrolidone, N - Methylcaprolactam and N - Methylvalerolactam as well as Dipropylenglycol – dimethylether (PGME), triethyleneglycoldimethylether, butylacetate, methoxypropylacetate, etc. [2-5]. These approaches all have drawbacks such as poorer solubility of the polyurethane prepolymer, higher price, or limited availability.

Another possibility that avoids all sorts of low molecular weight compounds in the product is available by the acetone process. In contrast to the prepolymer mixing process the complete build up of the polymer chain in the acetone process takes place in the organic phase, leading to high molecular weight polyurethanes with predominantly linear character [7]. The acetone used during the synthesis is distilled off the finished dispersion.

Another approach has been the use of polymerizable acrylic monomers as reactive diluents in the polyurethane formation step [8]. These monomers are polymerized by emulsion polymerization in the aqueous phase following completion of the PUD. This leads to solvent free acrylic-polyurethane hybrid dispersions. These materials do not have the same properties as typical PUDs.

### **Potential solvents for Prepolymer Mixing Process**

Suitable solvents for the synthesis of PUD must be inert towards isocyanate groups. The most suitable candidates for the replacement of NMP in existing recipes seem to be, for different reasons, PGME and acetone. Taking into account the Hansen parameters the best solvent to replace NMP out of these two is acetone (Table 1). All three values, dispersion force component ( $\delta_d$ ), hydrogen bonding component ( $\delta_h$ ), and polar component ( $\delta_p$ ) are close to those of NMP. This indicates that both solvents, NMP and acetone dissolve the same range of polymer types, especially those that are very important for polyurethanes. The polarity and the hydrogen bonding capability of PGME are much different from what NMP and acetone provide. This should be a drawback for

solubilizing urethanes, containing polar groups and segments forming hydrogen bonds. Indeed our experiments with PGME showed in some cases drawbacks in polymer solubility.

Table 1: Hansen Parameters of selected solvents

	$\delta_d$ [ MPa <sup>1/2</sup> ]	$\delta_p$ [ MPa <sup>1/2</sup> ]	$\delta_h$ [ MPa <sup>1/2</sup> ]
NMP	18.0	12.3	7.2
Acetone	15.5	10.4	7.0
PGME	14.9	2.1	3.8

Besides the favorable solubility parameters, acetone provides the possibility to obtain solvent free dispersions. Acetone, as a low boiling compound, can be distilled off after the formation of

the dispersion. Acetone is already used in what is known as the acetone process (fig. 1), where an isocyanate terminated prepolymer is synthesized in a first step and then diluted in acetone. The rather diluted polymer solution is chain extended with a polyfunctional hydrophilic amine, and subsequently dispersed by the addition of water [1].

The prepolymer mixing process (PMP) in NMP differs slightly from the aforementioned acetone process. A hydrophilic isocyanate terminated prepolymer is synthesized in NMP in a first step. The isocyanate terminated prepolymer, if not hydrophilic itself, is usually neutralized just prior to the dispersing step. With the dispersion step an isocyanate terminated dispersion is obtained and subsequently chain extended resulting in the formation of urea bonds (Fig. 2).

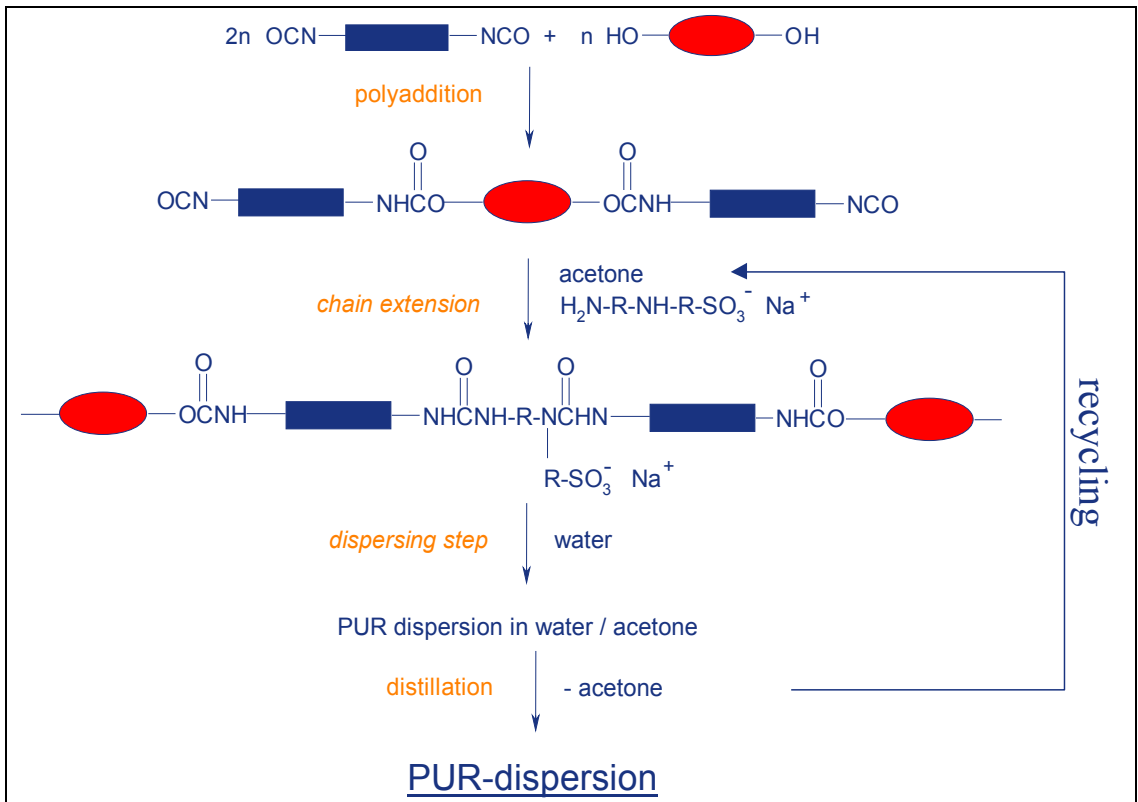


Figure 1: Schematic drawing of the acetone process

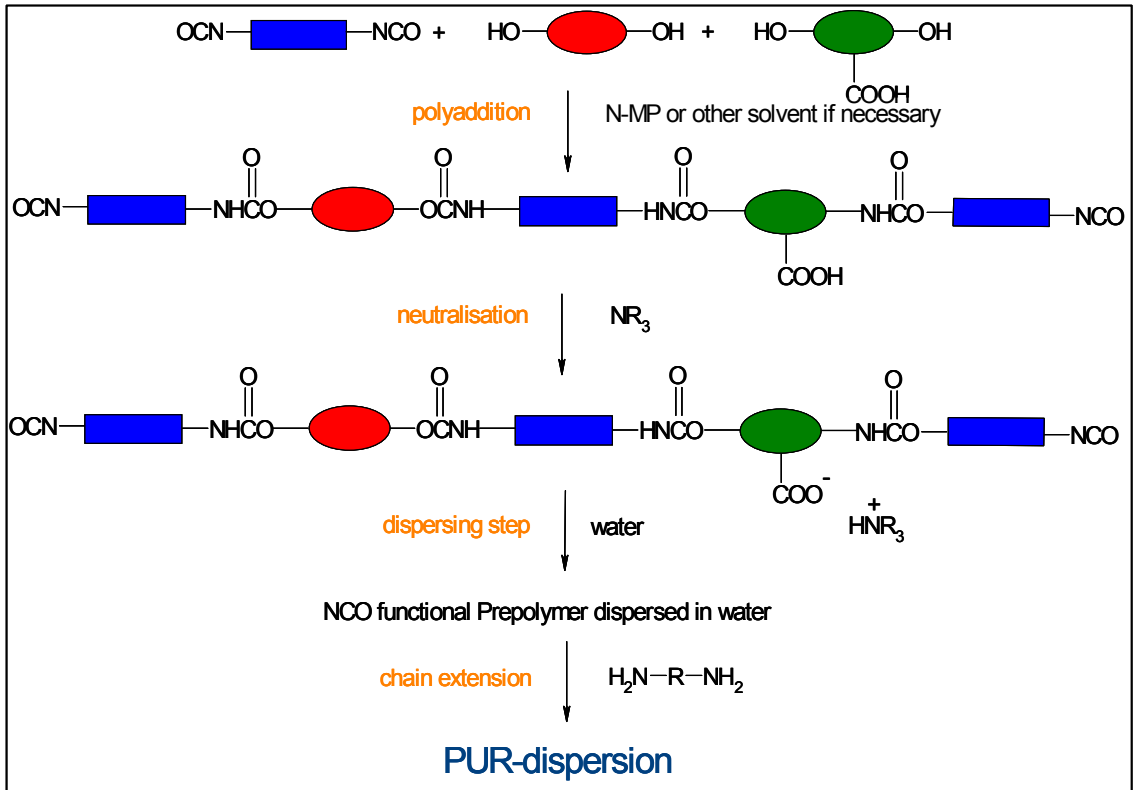


Figure 2: Schematic drawing of the prepolymer mixing process

Usually the carboxylic groups are incorporated into the polymer backbone via OH-functional carboxylic acids like dimethylolpropanoic acid (DMPA). By using NMP, an excellent solvent even for this high melting point compound, a smooth incorporation into the polymer backbone is guaranteed. However, the solubility of DMPA is weak in polyols and acetone. This leads to high particle size materials or very long reaction times.

We have worked on two approaches to solve this problem for products that require co-solvent:

1. Replace DMPA with DMBA (dimethylolbutanoic acid).
2. Preneutralize DMPA prior to reaction with isocyanates.

### **DMBA as the Ionic Source**

DMBA is more soluble in acetone and the polyols used in polyurethane dispersions than DMPA. Mitsubishi Chemicals showed the usefulness of this compound in the acetone process (2). Our work has shown that DMBA reacts into the polyurethane more completely than DMPA in the acetone process. Prepolymers made with polyether and DMPA are cloudy while the same prepolymer made with DMBA is clear. This homogeneous nature translates into better incorporation in the polymer, higher molecular weight, and improved physical properties of materials made from the resulting dispersion. This is shown through the following experiment.

Identical formulations were made with either DMBA or DMPA as the ionic group, polyether polyols, aliphatic diisocyanates and diamine chain extenders. This formulation is designed for sealant or coating uses. Figure 3 shows the tensile strength of the resulting polymers (labeled for the ionic source used). Figure 4 shows the elongation of these same polymers.

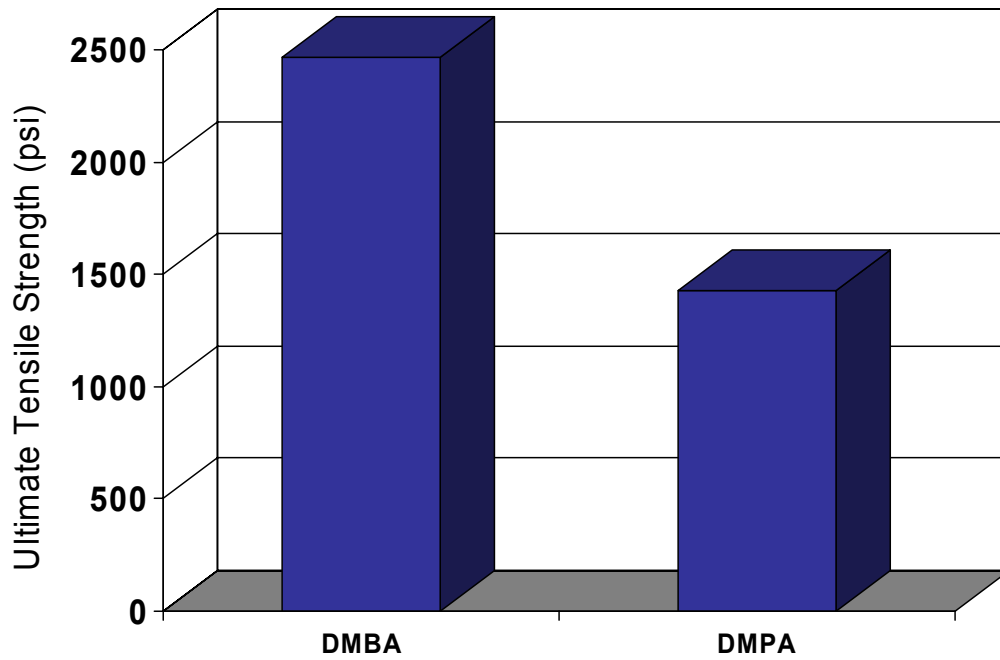


Figure 3 – PUD made from DMBA and DMPA

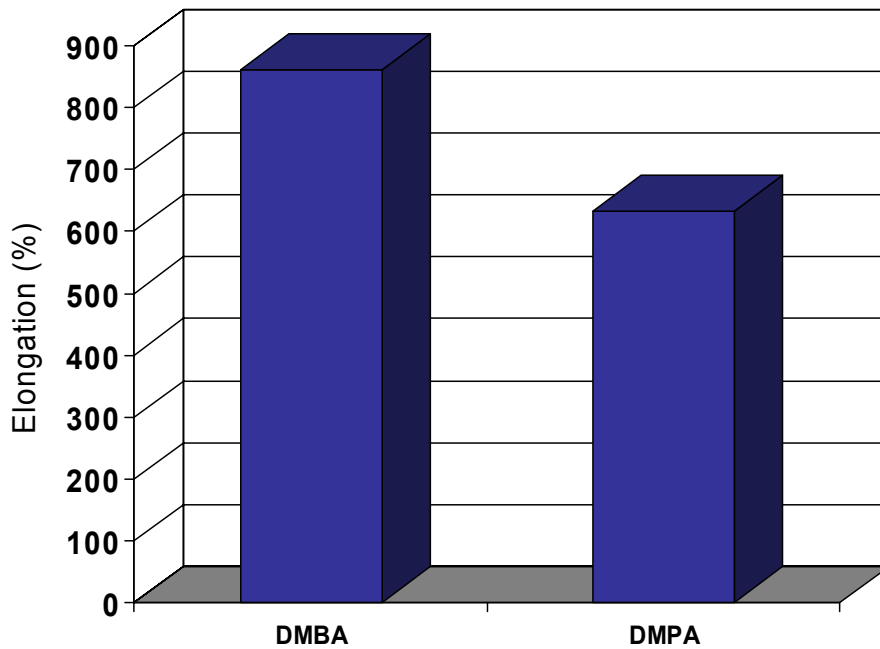


Figure 4 – Elongation of PUDs made from DMBA and BMBA

DMBA has two drawbacks. It is not listed on EINECS and its use under the new REACH legislation is unclear. The second drawback is that it is expensive. Therefore, finding a process that will allow the use of DMPA is desirable.

## **Preneutralizing DMPA**

The carboxylic acids can be neutralized by the addition of a tertiary amine before reacting with isocyanates [9]. The salt of DMPA is much more soluble in polyols than DMPA itself. This broadens the number of suitable solvents for the polyurethane prepolymer to include acetone. Using the salt allows one to use the acetone process described above and leads to products with no co-solvent. Materials with high hard segment content will require a coalescing solvent to make a continuous film; however, the range of acceptable coalescing solvents is much larger than acceptable PMP process solvents. It includes hydroxy functional materials like diethylene glycol monobutylether (BDG).

The tertiary amine is also a good catalyst for the urethane reaction so that the prepolymer reaction occurs much faster. This makes the manufacturing process more efficient.

## **Acetone versus NMP in PUD synthesis**

### **Dispersion characteristics**

Three different samples with the same overall composition (containing preneutralized DMPA) were produced via: the acetone process (sample A), the PMP process with NMP (sample B) and the PMP process with acetone (sample C).

The dispersion properties of the three different samples A to C are listed in Table 3. The two dispersions obtained via the PMP process show very much the same values for pH, particle size (mean) and viscosity. Sample A, obtained via the acetone process, shows different properties, the pH and the particle size of this sample are rather high compared to sample C. The particle size distribution of sample A determined by ultra centrifuge reveals a bimodal particle size distribution whereas both other samples are mono modal (Figure 5).

The observed bimodality is not characteristic for this formulation obtained via the acetone process; it is rather because the recipe used was optimized for the PMP process, as described earlier.

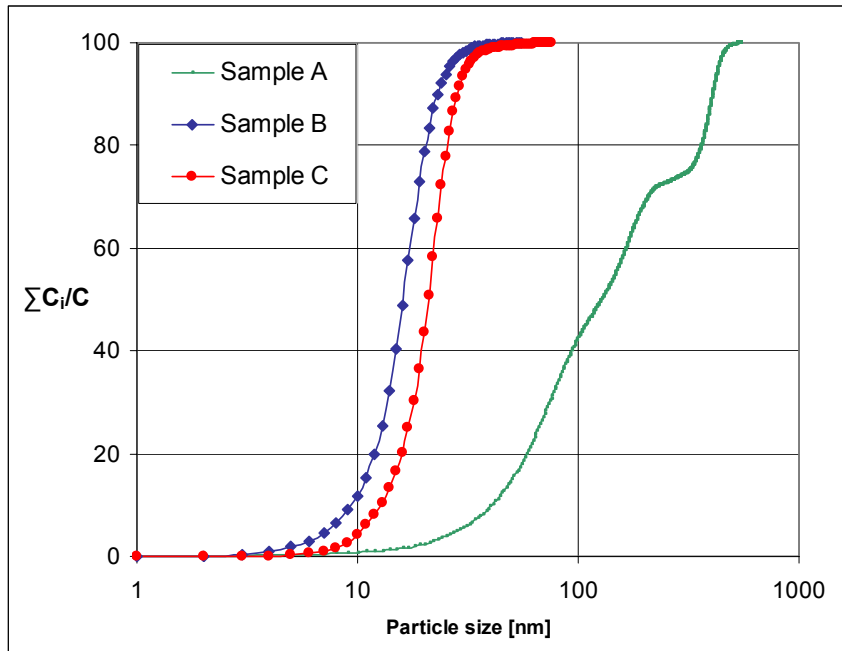


Figure 5: Particle size distribution (Integral)

Table 3: Physical properties of solvent free and NMP containing dispersions

<b>Process</b>	Sample	pH (10 % solid)	Solid content [%]	Particle size Z-average [nm]	Viscosity [mPa s]
<b>acetone</b>	A	8.3	37	173	17
<b>pmp in NMP</b>	B	7.7	38	71	34
<b>pmp in acetone</b>	C	7.7	39	61	42



## Polymer characteristics

When we compare DSC data obtained from the three samples no major difference is observed for neither  $T_g$  nor  $T_m$  values, as shown in Fig. 6, however the energy for these two transitions is somewhat lower in the case of sample B. This is especially true for the melting point. Residual NMP that was not completely evaporated could be one explanation for the decreased energy at the transition states, since the samples were measured in closed pans. The molecular weights of A and B are almost identical (see Figure 7)

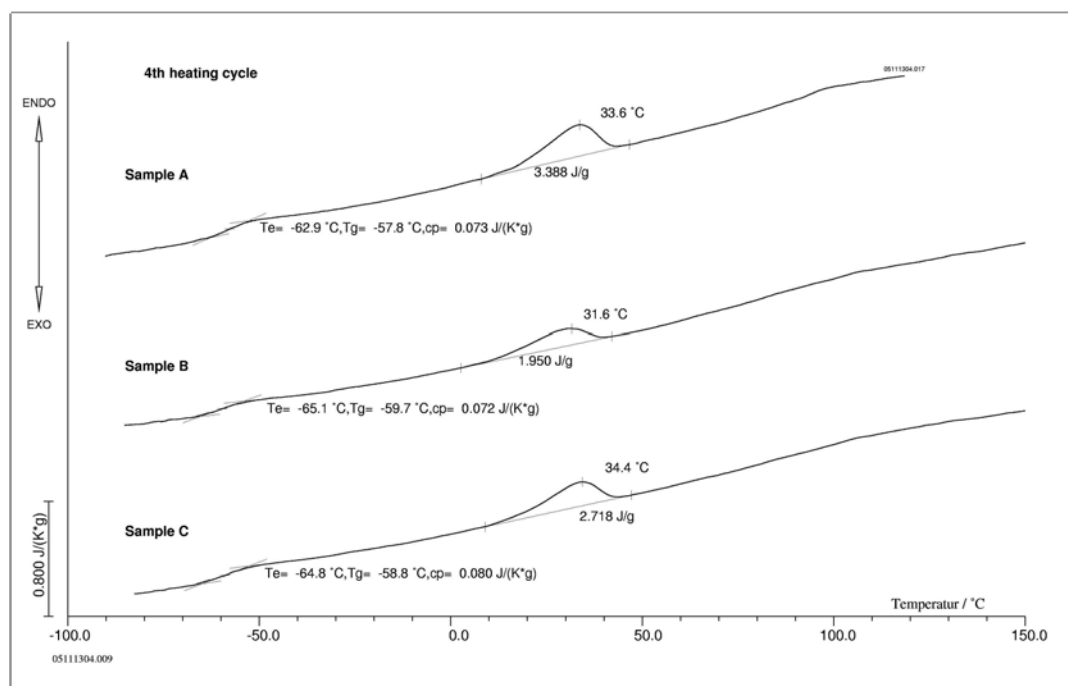


Figure 6: DSC plots from dried samples A, B and C, 4<sup>th</sup> heating cycle

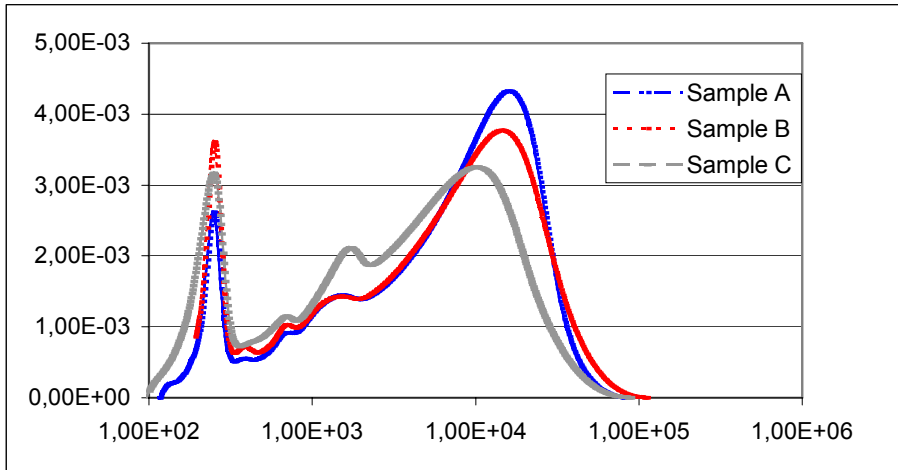


Figure 7: Molecular weight distribution of different samples A, B and C

Sample C shows a slightly lower molecular weight; however, this small difference does not have an impact on the mechanical properties, as shown in figure 8.

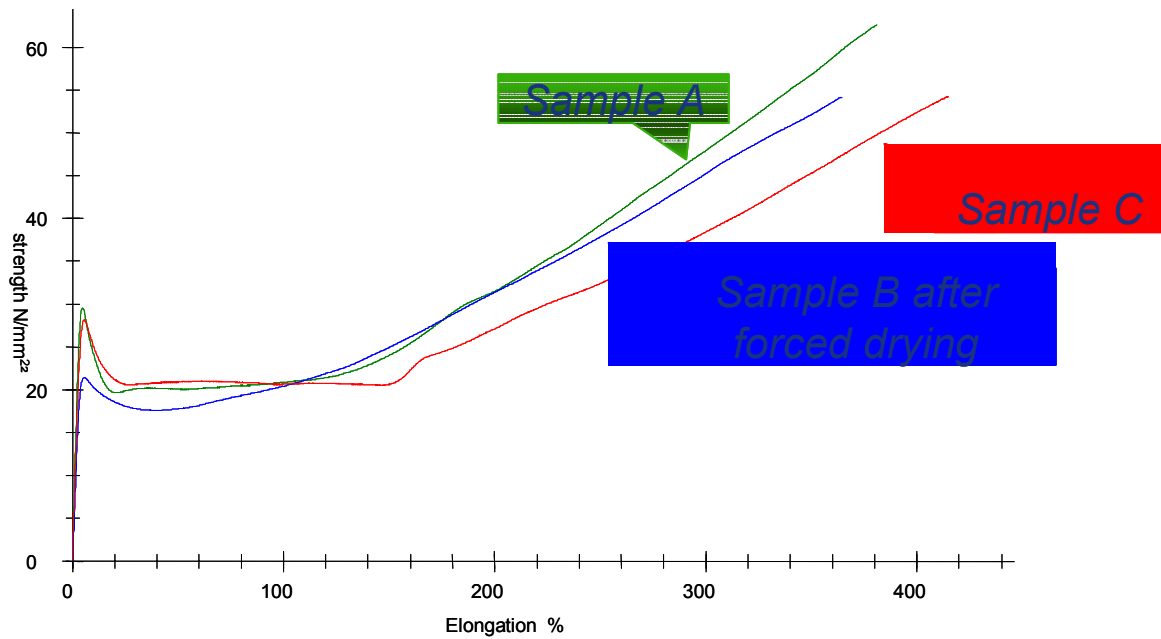


Figure 8: Elongation at break and tear strength of sample A and C.

## Film formation and films

Comparing film formation properties of the samples made by the PMP process with each other, it becomes obvious that the new products require less of the cosolvent diethylene glycol *n*-butylether (BDG) for smooth film formation than their NMP containing equivalents. Figure 9 shows three different compositions made with the PMP process and using either NMP (C', D' and E') or acetone (C, D, and E). Slight changes with respect to the recipes and/or the process had to be done when the solvent was switched from NMP to acetone. As mentioned earlier, the low solubility of DMPA in acetone is one reason for the necessary adjustments.

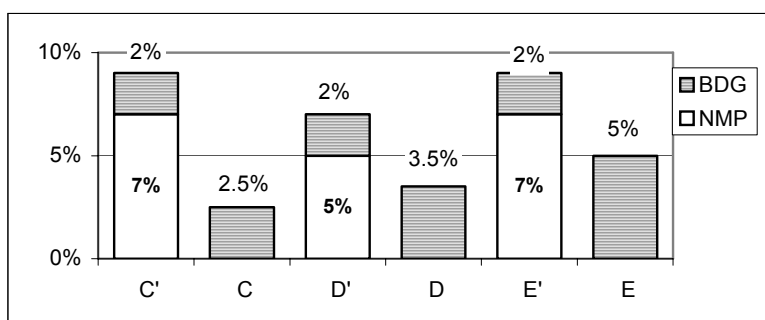


Figure 9: Co-solvent demand for film formation @ 4 °C on oak in a one component formulation

It is noteworthy mentioning that in all three examples the cosolvent BDG demand for forming excellent coatings could be brought under the 5% threshold needed in Europe. Of particular note is that sample C has properties similar to sample C' even though it uses 70% less solvent. This is beneficial ecologically and economically. One reason for the reduced cosolvent demand might be the higher degree of swelling of the particles obtained by the PMP process in acetone, compared to their NMP counterparts. A more intense and even quicker interparticular entanglement of polymer chains is achieved. However, further tests on the solvent free products formulated with NMP as a coalescing solvent showed a somewhat higher solvent demand for smooth film formation compared with the same products formulated with diethyleneglycol-*n*-butylether (BDG).

The properties of coatings obtained from the solvent free dispersions in 1K formulations are shown in Table 4. The properties match those obtained with the NMP containing products, but with less VOC.

Table 4: Selected properties of one component coatings from solvent free PUDs

Bayhydrol	Sample A	Sample D	Sample E
Tack free	1.5 h	1.5 h	1.5 h
Pendulum hardness (s) 1d / 3d/ 7d	60 / 110 / 125	60 / 80 / 95	70 / 105 / 120
<b>Cosolvent demand</b>	2.5%	3.5%	5%
<b>Resistance / 30min alcohol</b> after recovering	2-3 3	2-3 3	2-3 3
Resistance / 24h water after recovering	5 5	5 5	5 5
BHMR	1	4	4
Abrasion (Taber/CS10/1kg/1000rev)	10 mg	12 mg	35 mg

5 =no damage to the film; 0 = film completely destroyed

Smooth coatings can be obtained even at temperatures as low as 4°C by using at most 5% cosolvent in the case of the samples A, D and E. Sample A requires only 3,5% BDG. For further improved chemical resistance of the coatings two component formulations are used. They can also be formulated with less than 5% cosolvent successfully, as shown in table 5.

Table 5: Cosolvent demand for one and two component formulations on different substrates at 4°C

		One component		Two component	
		Sample A	Sample E	Sample A + Hydrophilic Polyisocyanate*	Sample E + Hydrophilic Polyisocyanate *
T	Substrate	3.5% BDG	3.5% BDG	3.2% PGME 1.0% BDG	3.2% PGME 1.0% BDG
4°C	Glass	4	5	5	4
	Uncoated wood	3-4	5	5	3-4
	Precoated wood	4	5	5	4
		4.9% BDG	4.9% BDG	3.2% PGME 1.7% BDG	3.2% PGME 1.7% BDG
4°C	Glass	5	5	5	5
	Uncoated wood	5	5	5	5
	Precoated wood	5	5	5	5

\*Available from Bayer MaterialScience AG

5 = good film formation; 0 = no film formation, strong cracking

## Conclusion

It has been shown that the acetone process is possible for a wider variety of polyurethane compositions if the DMPA is either neutralized prior to reaction or is replaced by DMBA. It has also been shown that the prepolymer mixing process can be used with acetone instead of NMP, despite the somewhat lower solvating power of acetone, if one adapts the process and/or recipe. The resulting dispersions allow the formulation of coatings with the same or even better properties than dispersions made by the prepolymer mixing process using NMP. Additionally, the minimum film formation temperature is significantly reduced for the new products and the dispersions need much less organic solvent for good coalescence and film formation.

## Literature

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- [4] Offenlegungsschrift DE 10 2004 015095
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- [8] EP-B 189945
- [9] WO 200102509