

Nonionic diols for internal stabilization of polyurethane dispersion

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Abstract

In this paper a nonionic diol that can be built into a lateral position in a polyurethane backbone in order to achieve internal stabilization of polyurethane dispersions is presented. The benefits to be gained from using the nonionic diol, in terms of tolerance of the resulting dispersion against electrolytes, cold temperatures and shear forces, have been investigated and compared to nonionic adduct technology as well as pure anionic stabilization. In addition the tolerance of the resulting polyurethane coating against polar solvents has also been studied. The nonionic diol was observed to be an efficient dispersant functioning well together with anionic stabilization in the form of Bis-MPA (dimethylol propionic acid). The lateral placement of the nonionic segments was observed to greatly improve the dispersion stability and reduce the sensitivity of the corresponding polyurethane coating to solvents.

Introduction

Internal stabilization of polyurethane dispersions (PUD), compared to the use of external emulsifiers, has the advantage of a simplified dispersion process leading to a finer particle size distribution and subsequently improved dispersion stability [1, 2]. Internal stabilization is also an approach that solves the problem of migration of the emulsifiers in the coating, prepared from such PUDs, leading to improved resistance to water and other polar as well as nonpolar liquids [3].

Internal stabilization can be achieved by incorporating ionic or nonionic hydrophilic groups into the polyurethane (PU) backbone. Anionic stabilization, which is the dominant means of stabilization, offers efficient stabilization, fine particle size distribution and excellent film properties but has disadvantages in terms of sensitivity towards electrolytes, freezing and high shear forces. Furthermore carboxylate types require the use of a neutralizing agent, often in the form of a volatile tertiary amine, which cause odor problems and when applied to wood substrates can increase the migration of tannins to a substrate surface.

Nonionic stabilization can support the shortcomings of anionic stabilization as it is generally insensitive to electrolytes, freezing and high shear forces [1, 2]. In addition, the ability of the nonionic segments to stabilize the dispersion is not dependent on a neutralizing agent, which reduces odor and migration of tannins in wood. However, nonionic stabilization often has disadvantages in terms of sensitivity to higher temperatures, larger particle sizes and increased water sensitivity of the resulting PU, although the latter can be minimized by cross-linking [1, 2]. Given the advantages and disadvantages of both anionic as well as nonionic stabilization, it is often beneficial to employ a combination of the two.

Internal nonionic stabilization can be achieved by incorporating polyethylene oxide (PEO) segments in medial, terminal or lateral positions in the PU backbone [1,2, 4-6]. Medial placement is often inefficient and requires the replacement of a large portion of the hydrophobic macrodiol with PEO, resulting in high water sensitivity of the PU film. Terminal and lateral placement has been found more efficient, requiring a lower fraction of PEO to achieve a stable dispersion. The former involves addition of a mono-functional PEO with respect to the isocyanate addition reaction, and may require addition of trifunctional polyols to achieve the molecular weight necessary for desirable film properties. Lateral stabilization on the other hand relies on the use of difunctional oligomers having a pendant PEO chain which therefore can be built directly into the PU backbone in lateral positions.

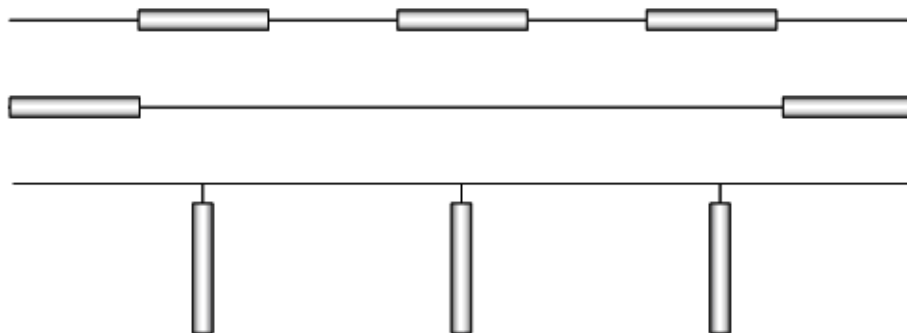


Figure 1. Top) polyether segments, represented as grey boxes, built into medial positions in the polyurethane, represented as black lines. Center) polyether segments in terminal positions Bottom) polyether segments built into lateral position in the polyurethane.

Lateral placement of nonionic PEO segments along the PU backbone is an efficient method of internal stabilization and can be achieved by the use of specifically modified diols or adduct technology. The use of modified diols is preferred when short cycle times are important. While modified diols can simply be introduced at the same time as the other PU components, i.e. macrodiols, isocyanates and carboxylates in adduct technology often require a multiple step synthesis. Furthermore, depending on the type of adduct technology employed and the length of the PEO segment, a significant portion of the nonionic group is devoted to imparting the necessary functionality, which reduces the formulation freedom.

In this paper we present a modified diol specifically designed for internal nonionic stabilization of polyurethane dispersions. The performance of PUDs, which are internally co-stabilized using this modified diol in combination with Bis-MPA (dimethylol propionic acid), and the resulting PU film are presented and compared to other types of internal nonionic as well as anionic stabilization.

Experimental

Materials

4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI) supplied by Bayer AG, Germany was used in the preparation of prepolymers together with polyhexanediol adipate supplied by Chemtura Corp., USA, having an hydroxylnumber of about 112 mg KOH/g. Dibutyltin dilaurate (DBTL) from Sigma-Aldrich, Sweden, was used as catalyst for the isocyanate addition reaction. The neutralizing agent, triethylamine (TEA) and chain extender, ethylenediamine (EDA), were obtained from Sigma-Aldrich, Germany and Fluka Chemie, Germany. Film forming and wetting agents, dipropylene glycol n-butylether (DnPb) and BYK 333, were supplied by Univar AB, Sweden, and BYK Chemie, Germany.

For medial nonionic stabilization polyethylene glycol (PEG), having a molecular weight of about 600 g/mol, Sigma-Aldrich, Sweden, was used. The anionic stabilizing segment was dimethylol propionic acid (Bis-MPA) from Perstorp Specialty Chemicals AB, Sweden. Lateral nonionic stabilization was achieved using a 1,3-polyethylene glycol diol from Perstorp Specialty Chemicals AB, Sweden, which is a waxy solid at room temperature and has a hydroxyl-number of about 120 mg KOH/g, from hereon referred to as the nonionic diol. The hydrophilic chain in the nonionic diol is approximately 18 ethylene oxide units. It has a melting range of about 20-40°C and the viscosity at 50°C is about 61 mPas. Lateral nonionic stabilization was also achieved using adduct technology, from hereon referred to as the nonionic adduct. The nonionic adduct, which is difunctional with respect to the isocyanate addition reaction, was prepared in-house and consisted of diethanolamine, isophorone diisocyanate (IPDI) supplied by Bayer AG, Germany and polyethylene glycol monomethylether (MPEG) having a molecular weight of about 750 g/mol, supplied by Clariant, Germany. Terminal stabilization was obtained using polyethylene glycol monomethylether (MPEG) having a molecular weight of about 1000 g/mol, supplied by Clariant, Germany. Trimethylol propane (TMP) supplied by Perstorp Specialty Chemicals AB, Sweden, was used to introduce a degree of branching in the terminal stabilized product.

Prepolymer synthesis

The dry polyesterdiol, Bis-MPA and the nonionic stabilizer, e.g. the nonionic diol, PEG, MPEG or the nonionic adduct, were charged, according to the recipe in Table 1, to the reactor with agitation. In the case of synthesis B, which excludes the nonionic part, it was also necessary to add co-solvent to dissolve the Bis-MPA. The co-solvent, n-methyl pyrrolidone (NMP), was not necessary when including a nonionic stabilizer, with the exception of synthesis E and E', where it was also added. In synthesis E and E', TMP was charged to introduce a degree of branching to preserve the molecular weight due to the chain stopping MPEG. Vacuum was applied to assure a dry reactor which was followed by introduction of dry nitrogen. The catalyst (DBTL) was charged and the temperature was increased to 50°C. Thereafter the isocyanate was slowly charged in drops, with agitation. After isocyanate addition was completed the reaction temperature was further increased to 75°C and the synthesis was continued until the desired isocyanate-conversion was reached. After completion the temperature was reduced to 40°C.

Table 1. Recipes and theoretical data for prepolymers.

	A	B	C	D	E	E'
4,4'-dicyclohexylmethane diisocyanate	37.8	39.4	39.3	37.1	37.9	25.0
polyhexanediol adipate	49.0	44.7	49.3	47.5	34.0	47.8
Nonionic diol	10.6					
Bis-MPA	2.6	5.1	2.6	2.6	1.3	1.5
PEG 600 g/mol			8.8			
MPEG 1000 g/mol					7.3	7.2
Trimethylol propane					3.0	1.0
Nonionic adduct				12.8		
dibutyltin dilaurate	0.04	0.04	0.04	0.04		0.04
N-methyl pyrrolidone		10.8			16.7	17.5
Theoretical data						
NCO/OH molar ratio	1.8	1.8	1.8	1.8	1.8	1.3
Ethylene oxide based on dry content (wt%)	8.8	0	8.8	8.8	7.2	7.1

Neutralization and dispersion

The neutralizing agent (TEA) was charged to the reactor at a temperature of 40°C according to the recipe in Table 2, and after about 10 minutes the agitation speed was increased. At a high agitation speed the water was added in drops. Once the prepolymer was dispersed, and most of the water was added, the remaining water was mixed 1:1 with the chain extender, ethylenediamine (EDA). The EDA mixture was charged slowly and after about 5 minutes the prepared polyurethane dispersion was cooled to room temperature.

From prepolymer E it was not possible to form a stable dispersion, thus the recipe had to be adjusted with a lower NCO/OH ratio and quantity of TMP, synthesis E'.

Table 2. Recipes for neutralization, dispersion and chain extension of prepolymers.

	A	B	C	D	E	E'
prepolymer ¹	33.7	35.8	33.5	33.8	40.8	41.2
triethylamine	0.6	1.3	0.6	0.6	0.4	0.4
water	64.7	61.7	64.8	64.6	57.6	58.0
diethyleneamine	1.0	1.2	1.1	1.0	1.3	0.4

Theoretical data

Degree of neutralization (%)	90	90	90	90	90	80
NH/NCO molar ratio	0.8	0.8	0.8	0.8	0.8	0.8

¹Composition described in Table 1.

Evaluation of PUD stability

The stability of the PUD's was tested against electrolytes, in the form of hydrogen chloride (HCl) and calcium chloride (CaCl₂), freeze/thaw cycles and shearing.

Electrolyte stability - testing procedure

1M Calcium Chloride (CaCl₂) and 2.7M Hydrogen Chloride (HCl) solutions were added in drops to 5 ml PUD, with a maximum addition corresponding to 0.2M, in plastic vials while gently shaking the vial. Thereafter the PUD was filtered and any coagulate was collected and dried in the oven for 24 hours at 50 °C and weighed.

Freeze/thaw - testing procedure

The PUD viscosity was determined using a Stresstech Rheometer with 20 mm plate and plate system at shear interval from 10-100 s⁻¹ at 23 °C. Thereafter a glass vial was filled with 15 ml PUD. The PUD was then subjected to repeated cycles of 16 hours at -26°C followed by defrosting and storage at 23°C for 8 hours. After each cycle the PUD was inspected for any visual changes in clarity and coagulation. The viscosity was re-measured after completion of the fifth cycle.

Shear stability - testing procedure

The PUD viscosity was determined using a Stresstech Rheometer with 20 mm plate and plate system at shear interval from 10-100 s⁻¹ at 23 °C. A glass vial was filled with 40 ml PUD and placed in a water bath at 23°C. The PUD was exposed to shearing using an IKA®-Ultra-Turrax® T25 operating at a speed of 10000 rpm for 20 minutes. The viscosity was re-measured after shearing.

Coating preparation

Film forming and wetting agents were added to the prepared PUDs A, C, D and E' according to Table 3. Dispersion B included co-solvent in the synthesis and no further additives were used. Despite the fact that PUD E' contained co-solvent the film forming and wetting agents were still required. After additions the PUD's were left for 24 hours before applying to substrates, i.e. glass and aluminum plates, or before preparing free thin films. The PUD was applied to aluminum and glass plates using a 150µm applicator tool and thin films were prepared by application on polyester films using a 200 µm tool followed by careful removal of the polyurethane film. Tensile test specimens 25 mm long and 4 mm wide were cut from the free polyurethane films. The thickness of each film was around 0.3 mm and was measured separately.

Table 3. Formulation including film forming and wetting agents.

	PUD (A, C, D or E')	Dowanol DnPb	BYK 333
Mass (g)	96.7	3.5	0.8

Evaluation of coating performance

All coating tests were performed after a drying period of 72 hours at 23°C and 50% RH. In the case of tensile tests the drying period was for practical reasons extended to 14 days. The hardness, expressed in König seconds of cured coatings applied to standard glass plates, was determined using

a Pendulum Hardness Tester, BYK Gardner. The effects of polar solvents were investigated by exposing the coating surface to water, ethanol (48%) and acetone using the spot test method. The result after recovery is reported. The contact angle of water drops on cured coating was measured using a FTÅ200. Tensile properties were determined on neat and water exposed polyurethane films using a Zwick Z010 Table-Top Machine (A2047), load cell 100 N and video-extensometer at a deformation rate of 500 mm/min. Water exposed films were immersed in water for 24 hours followed by two hours of drying at room temperature before measuring the tensile properties.

Results

Electrolyte stability

Figure 2 shows the effect of acid in the form of hydrogen chloride (HCl) on the stability of polyurethane dispersions. Dispersions A and D, both co-stabilized with lateral nonionic segments, together with terminal stabilized dispersion E', display none or minimal coagulation up to a HCl addition corresponding to 0.2 M. Dispersion B, which is solely anionically stabilized, does however display significant coagulation as a result of the protonation of the carboxylic group, leading to reduced interparticle repulsion. Dispersion C, which is co-stabilized with medial nonionic segments, has the lowest stability against HCl. At an addition corresponding to 0.2M HCl, close to 85% of the dispersed particles have formed coagulum. The sensitivity of dispersion C to HCl demonstrates the inefficiency of medial nonionic segments in terms of particle stabilization. As the ionic repulsion is reduced the entropic repulsion is not strong enough to maintain stability.

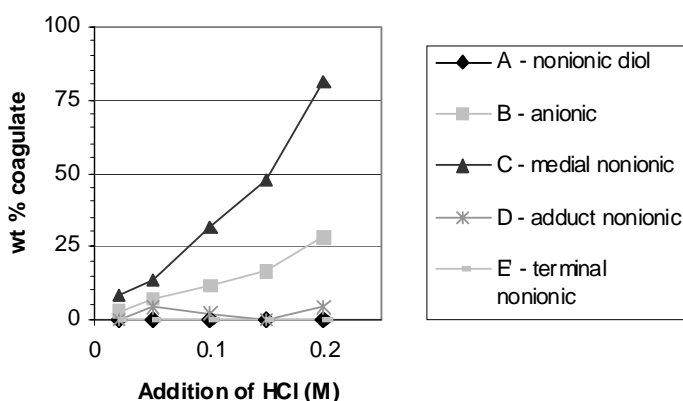


Figure 2. The % by wt of dry coagulum based on dry content in the polyurethane dispersion at varying addition of HCl.

Figure 3 shows the effect of inert electrolytes in the form of CaCl_2 on the stability of polyurethane dispersions. Dispersions A, C, D and E', all co-stabilized with nonionic segments, display none or minimal coagulation up to a CaCl_2 addition corresponding to 0.2 M. The anionically stabilized dispersion B is very sensitive to the divalent cations and at 0.2M CaCl_2 addition close to 100% of the dispersed particles have coagulated. The sensitivity of dispersion B towards CaCl_2 shows the reduced repulsion between electrical double layers as the electrolyte concentration increases.

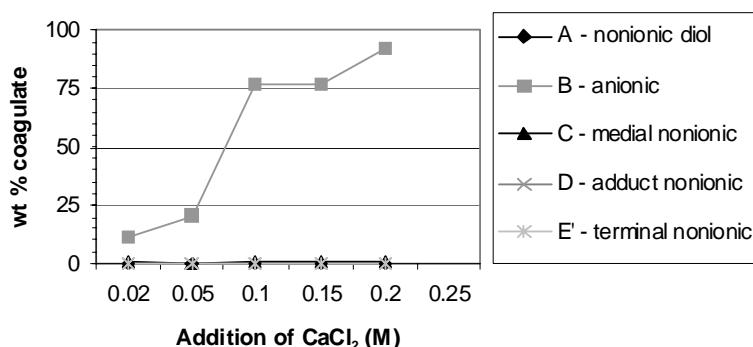


Figure 3. The % by wt of dry coagulum based on dry content in the polyurethane dispersion at varying addition of CaCl_2 .

Figure 4 shows the effect of freeze/thaw cycles on the dispersion viscosity. Dispersions A, B and D are virtually unaffected while dispersion C, which is co-stabilized with medial nonionics, is a wax-like solid after freeze/thaw treatment displaying an increased and shear rate dependent viscosity as a result of the treatment. The terminal co-stabilized dispersion E' displayed a slightly lower viscosity after the freeze/thaw cycles. As ice crystals are formed in aqueous dispersions the pressure on the dispersed particles is increased. If the stabilizing layer, in the form of anionic or nonionic units, is not strong enough and if the glass transition of the urethane polymer is below freezing point, i.e. if the polymer has sufficient mobility, the dispersion structure can be irreversibly damaged, which is observed in the case of dispersion C [7].

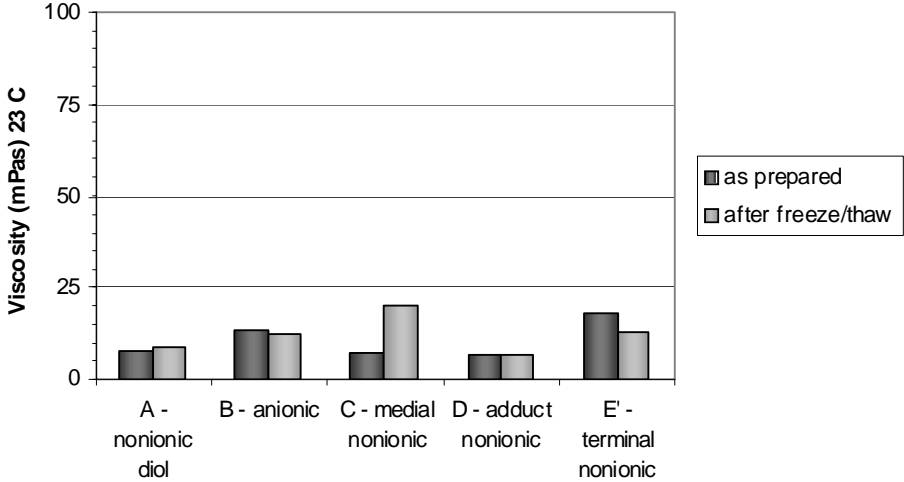


Figure 4. The PUD viscosity at 100 s⁻¹ and 23 °C measured before and after freeze/thaw treatment.

High speed mixing has a significant effect of the structure on dispersion C, see figure 5. After subjecting the dispersion to shearing the dispersion is a wax-like solid and has increased and shear rate dependant viscosity. Dispersion A, co-stabilized by lateral nonionic, although having a higher viscosity, maintains its Newtonian character. Dispersion B displays a slight reduction in viscosity while Dispersion D is virtually unaffected. Dispersion E' shows an increase in viscosity after shearing and displays a shear thinning behavior both before and after it was subjected to the high speed mixing. High shear rates can cause undesirable changes to the dispersion structure due to, for example, particle collision followed by aggregation [8]. An efficient stabilizing layer is an important factor when aiming at maintaining the undisturbed dispersion structure during coating processes such as pumping, mixing and spraying. Figure 5 shows that laterally placed nonionic segments have a higher efficiency than those in medial positions in this respect.

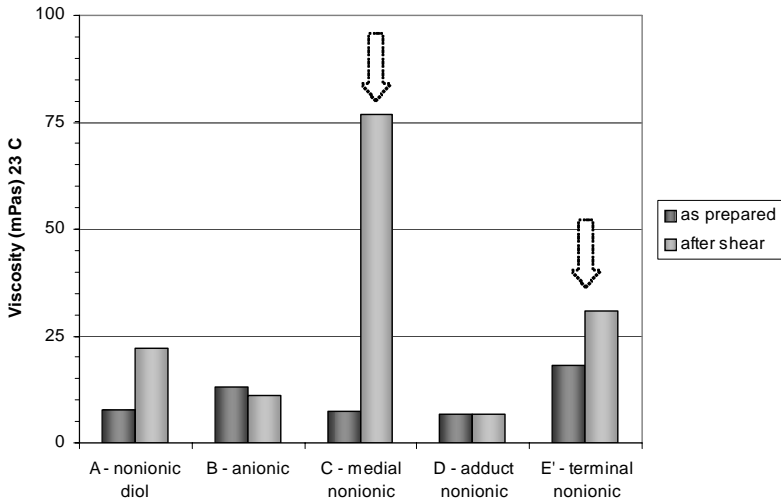


Figure 5. The PUD viscosity at 100 s⁻¹ and 23 °C measured before and after high-speed mixing. The arrow indicates a non Newtonian behavior.

Not surprisingly, the four tested formulations, three of which have a content of 8.8 % by wt of ethylene oxide and a NCO/OH value of 1.8, see Table 1, clearly build polyurethanes of different character. The hardness varies from 108 to 32 König seconds, see figure 6. Although the hardness can be partly correlated to the urethane/urea content and the type of stabilizing unit, the positioning of the stabilizing unit appears to have some effect on the coating hardness.

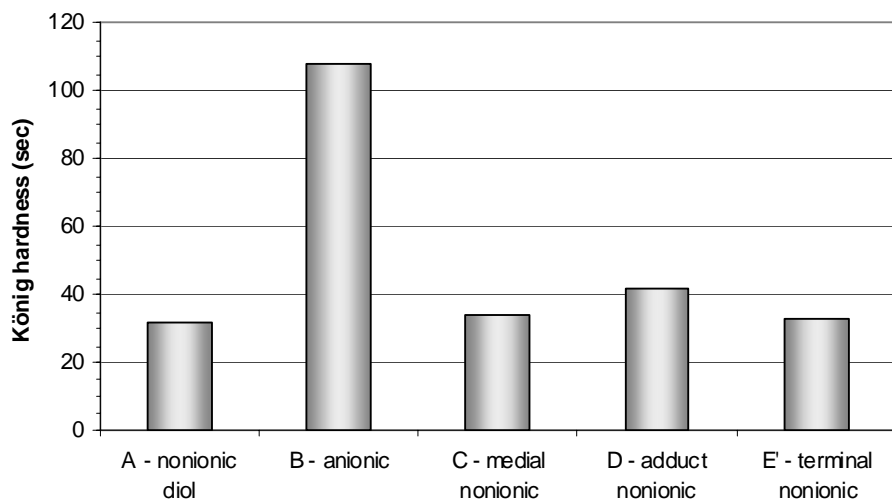


Figure 6. König hardness of polyurethanes on standard glass plates. The thickness of coatings was 40, 43, 28, 27 μ m and 45 respectively for A, B, C, D and E'.

The surface energy is greatly affected by the choice of stabilizing unit. Nonionically stabilized polyurethanes A, C, D and E' all have higher surface energies compared to the anionically stabilized polyurethane B, as determined using the water drop contact angle, which is shown in figure 7. The positioning of the nonionic segment appears to have less effect on the surface energy while the content of urethane/urea has a more profound effect, which can be seen when comparing the difference in surface energy between e.g. polyurethane A and D.

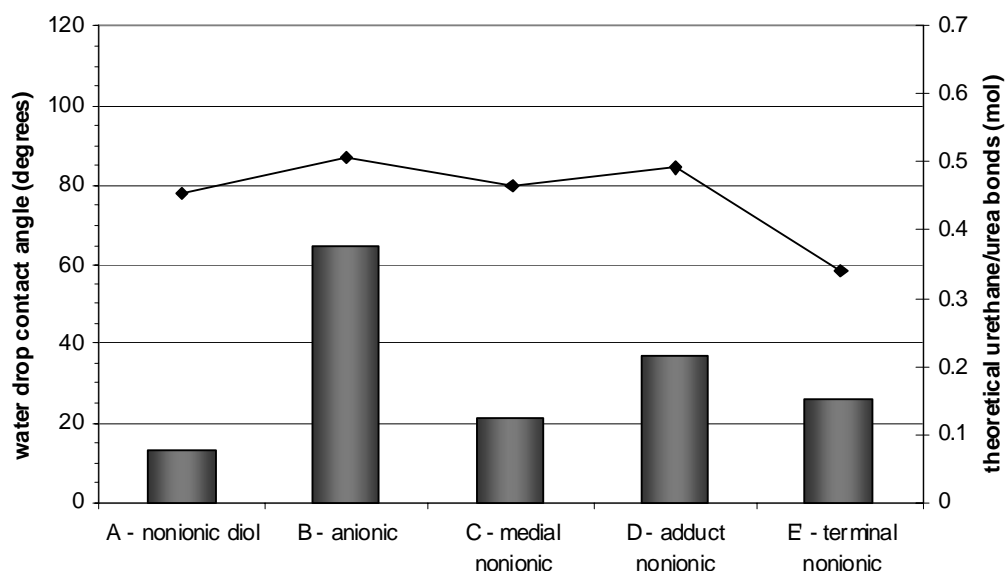


Figure 7. Water drop contact angle on polyurethane coatings.

Spot tests revealed a significant difference between the solvent resistances of the four polyurethanes. Polyurethane A displayed the best resistance towards the three tested liquids, while polyurethane E'

followed by polyurethane C had the lowest resistance overall, see figure 8. The very poor resistance of Polyurethane E' might be partly explained by possible low molecular weight polymers present as consequence of the chain stopping MPEG and by the lower quantity of urethane/urea bonds. Polyurethane A, having lateral nonionic segments using the nonionic diol, displays, see figure 5, a very good solvent resistance, despite its hydrophilicity. This behavior can be the result of its flexible internal structure, which reduces the build-up of internal stresses caused by solvent absorption, and permanent damage can thereby be avoided.

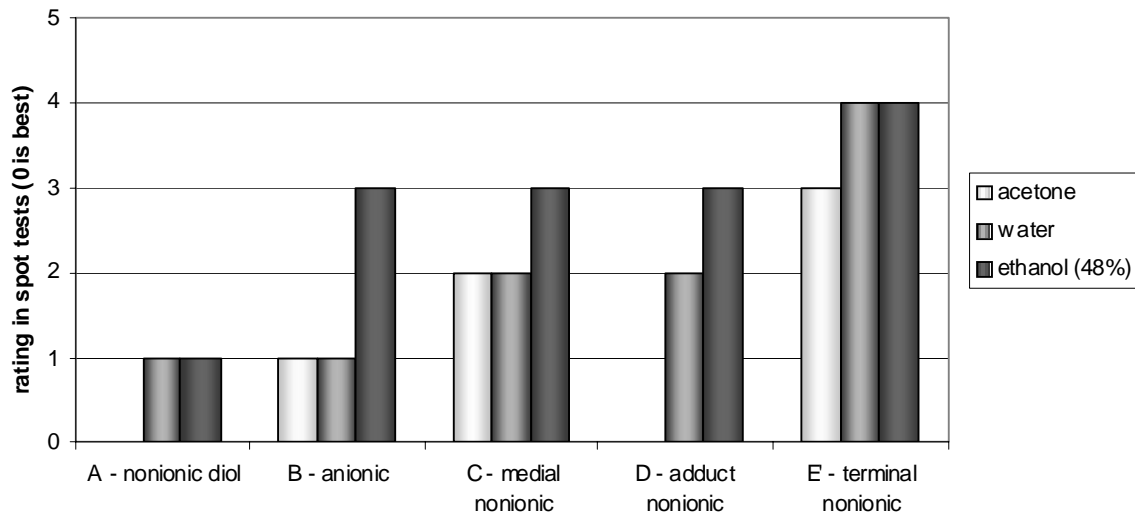


Figure 8. The result of spot tests using acetone, water and 48% ethanol as test liquids. 0 = no effect on the coating and 5 = sever damage. The coatings were exposed to the liquids for 2 minutes (acetone), 24 hours (water) and 6 hours (ethanol) and allowed to recover for 2 hours.

The tensile stress-strain curves in figure 9 shows that Polyurethane A, co-stabilized with lateral nonionic segments using the nonionic diol, forms a relatively soft and tough polymer. The behavior is similar to that of Polyurethane C, having medial nonionic segments. Polyurethane B, solely stabilized with anionics and therefore having a higher content of urethane and urea segments, behaves as a hard and tough material. Polyurethane D, which is co-stabilized using lateral nonionic adducts, is inferior in terms of toughness. The prepared coating of Polyurethane E' to be used in the tensile testing was very brittle and could not therefore be included in either the tensile measurements or the water immersion test.

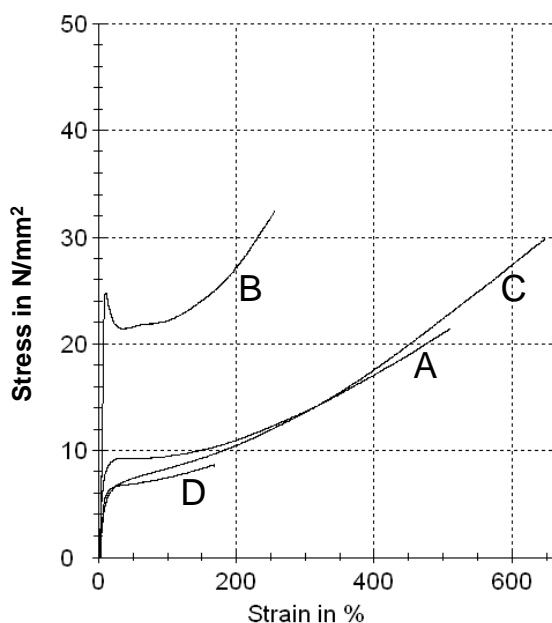


Figure 9. Tensile stress-strain curves of polyurethane films A-D. Deformation rate was 500 mm/min.

Table 4. The water up-take of polyurethane dispersions after immersion for 24 hours.

Polyurethane	A	B	C	D	E'
Water uptake (wt%)	17	9	16	9	N/A

In order to explore how well these polyurethanes retain their properties after exposure to large quantities of solvent the films were immersed in water for the purpose of performing tensile tests on the films after this procedure. Table 4 displays the water up-take of the four polyurethanes after immersion in water. Polyurethanes A and C, being softer and containing a higher fraction of hydrophilic segments, absorb roughly twice as much water as B. A twofold increase in water uptake can also be observed when comparing Polyurethanes A and C with D.

Before repeating tensile tests on the exposed films they were allowed to recover. Polyurethanes B and D did not tolerate the water treatment and were severely deformed after recovery i.e. warped and cracked. Polyurethanes A and C, on the other both showed good recovery with only minor changes in their visual appearance. Polyurethanes B and D, due to their severely damaged state, could not be measured, while Polyurethanes A and C were placed in the tensile testing machine. Figure 10 shows that both polyurethane A and C retain their mechanical properties. Polyurethane A, having lateral nonionic segments using the modified diol, displays a minor increase in toughness while maintaining its flexibility. Polyurethane C, modified using medial nonionic segments, shows some reduction in toughness.

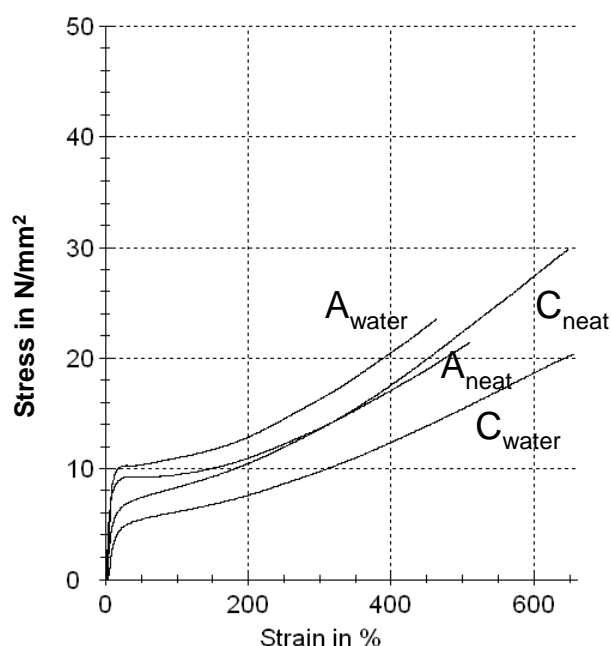


Figure 10. Tensile stress-strain curves of polyurethanes A and C before and after immersion in water followed by recovery. Polyurethanes B and D did not survive the water treatment and could not be measured.

Discussion

Nonionic internal stabilization can solve many of the shortcomings of ionic internal stabilization. Problems with sensitivity to electrolytes can easily be overcome through the use of a combination of Bis-MPA and nonionic segments in polyurethane backbone. The use of neutralizing amines, which are problematic not least with respect to odor, can be minimized. Furthermore, based on these experiments, it is a clear advantage to have nonionic segments in lateral positions along the polyurethane backbone, as opposed to medial placement. While this can be achieved using adduct-technology this is limiting both with respect to processing time and formulation freedom. A simple route towards a robust polyurethane dispersion may therefore be to use the modified diol, here referred to as the nonionic diol, which is specifically designed for internal stabilizing not requiring additional components and synthesis steps. Furthermore, an additional advantage is obtained when using Bis-MPA as the anionic co-stabilizer, as no or less co-solvent is necessary in the prepolymer synthesis for dissolving the Bis-MPA.

In terms of coating performance it was also observed that lateral placement, combined with the flexibility that can be achieved due to the formulation freedom using the nonionic diol, builds a coating which, although of a hydrophilic character, can recover faster and more completely compared, for example, to a strictly anionically stabilized polyurethane or one stabilized using the adduct technology. The reason for this improvement is likely to be a combination of placement itself but also the lower fraction of rigid segments.

Conclusion

The polymerizable nonionic diol, specifically modified to be incorporated into lateral positions in a polyurethane backbone for internal stabilization, is an efficient means of stabilization which works well together with anionic stabilization in the form of Bis-MPA. The non-ionic diol could be used directly without an additional adduct step, which costs extra processing time and might have a negative effect on quality consistency. A non-ionic approach also requires no, or less, co-solvent in the manufacture of the polyurethane dispersion pre-polymer. Polyurethane dispersions, stabilized with the above-mentioned nonionic diol and Bis-MPA, display excellent stability to electrolytes and freeze/thaw cycles, and are resistant to shear. In addition, the resulting flexible polyurethane coatings have improved resistance to polar solvents.

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