Tailoring crosslinking performance

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Polycaprolactones – resin modifiers that enhance physical properties

Pär Jörgensen

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Polyurethane technologies have for several years been known to offer many technical advantages over competing coating systems. Two component polyurethane (2K PUR) coatings in particular are widely used in application areas including the automotive sector, windmills, aircraft, transport etc.

Even though it is such a well-established technology there is a constant pressure to improve and fine-tune technical properties such as abrasion resistance, scratch resistance and outdoor durability. Regulations also force formulators to further reduce VOCs in high solid (HS) formulations to meet further demands or as another option look at waterborne (WB) solutions.

Very low viscosity polycaprolactones can influence both VOC and technical properties to give lower emissions and prolong the life-cycles of coating systems, important criteria for improved sustainability.

Properties and benefits of polycaprolactones

Perstorp has produced polycaprolactones for 40 years and offers a range suitable for modifying and fine-

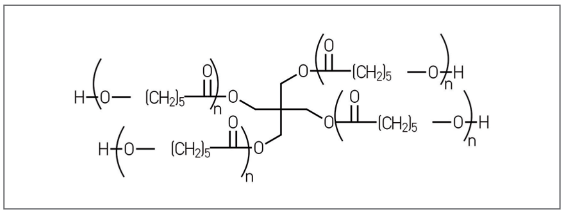

Figure 1: General structure of a tetrafunctional polycaprolactone

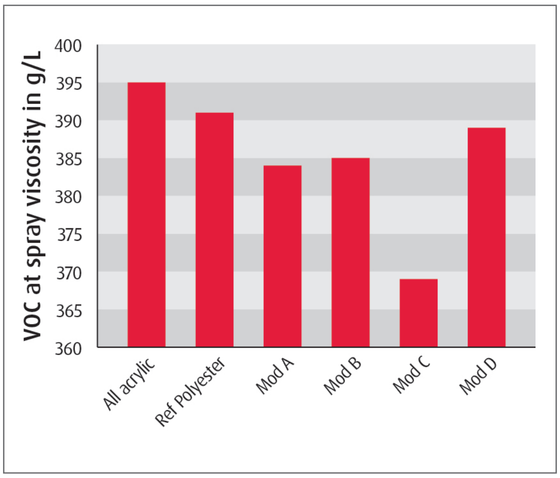

Figure 2: VOC at spray viscosity

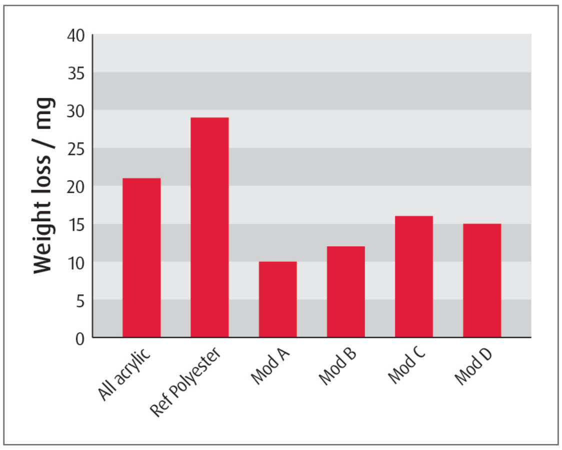

Figure 3: Abrasion tests on steel panels with a Taber Abraser ("Model 5135") using CS10 wheels, 500 g load and 1000 cycles (film thickness 40-60 µm)

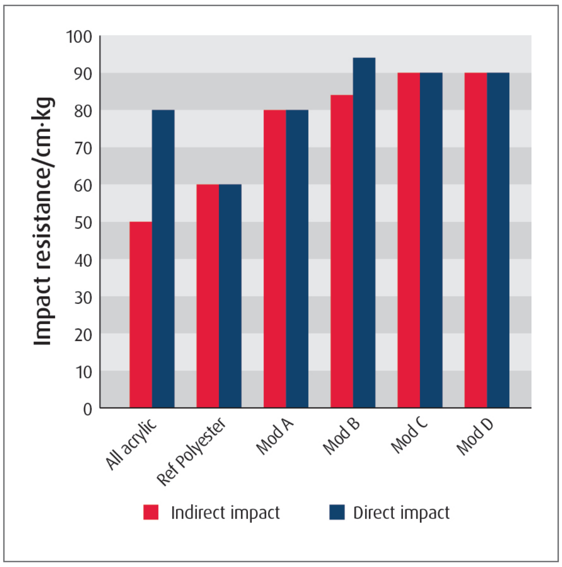

Figure 4: Impact resistance at −25 °C, by Afnor impact resistance equipment (film thickness 40-60 µm)

tuning crosslinked coating formulations such as 2K and 1K PUR systems. Caprolactone chemistry can target specific requirements in different coating systems by utilising a controlled ring-opening polymerisation onto hydroxyl groups, resulting in a very low acid number (< 0.25 mg KOH/g). Semi-crystalline polyols with a precise functionality and narrow molecular weight distribution can be prepared in a reproducible way.

By choosing between different hydroxy-functional initiators, a versatile range of aliphatic, low T_g (around -60 °C), solvent-free, low viscosity polyols can be chosen from when formulating a high performance crosslinked coating for various application areas including automotive, aviation, protective, windmills and flooring (see *Figure 1*).

With a range of "Capa" polyols varying in functionality from 2 to 4, OH-content between 4.1-17 % and molecular weight between 300-2000 g/mol it is possible to technically fine-tune coating formulations. Normally replacing between 5 and 20 wt-% of standard polyols – acrylics or polyesters – will give significant improvements from caprolactones.

They can be added as resin modifiers in solventborne (SB) systems based on acrylics, polyesters or polyaspartics and various crosslinkers since they have a wide compatibility range. This makes the number of combinations almost unlimited.

The fact that they are solvent-free and liquid at room temperature makes them suitable as reactive diluents for solvent-free systems. Grades with very low viscosities are also suitable for use in waterborne dispersion formulations, where the low viscosity and relatively high water acceptance caused by high hydroxyl numbers allow the polyols to migrate into the emulsion droplets.

This study shows the influence of adding different levels of a tri-functional and a tetra-functional polycaprolactone

Results at a glance

››› Polycaprolactones are aliphatic, liquid, solvent-free polyols suitable as reactive diluents in many types of crosslinked coatings. They are prepared by a ring-opening polymerisation which results in low acid numbers and exactly defined functionality.

››› They can easily be incorporated into solventborne formulations by simple mixing. Test results are provided to demonstrate that appropriate formulation can enhance flexibility, impact resistance and abrasion resistance without compromising hardness or chemical resistance.

››› Because caprolactones are hydrophobic with a low acid number, they cannot be dissolved in water. However, low molecular weight types with high hydroxyl values can migrate into emulsion droplets, where they also act as reactive coalescing agents, thus reducing the VOC content required and often promoting better levelling.

to a HS 2K PUR system. It also describes the principle of using them in waterborne emulsion based systems.

Impact of polycaprolactones on solventborne formulations

Polycaprolactones are easily incorporated in solventborne formulations at any stage of paint preparation. Due to their excellent pigment wetting properties they should preferably be added in the grinding part when used in pigmented formulations. In general, normal formulation principles are used when working with them and conventional tools – additives, solvent and crosslinkers - are utilised during development work. Their well-defined molecular weight and functionality guarantee robust contributions to the final properties of the coatings.
Even though polycaprolactones by nature have a low T_g derived from aliphatic structures – and consequently less contribution to the final hardness from physical drying – formulations can easily be made where hardness and mechanical properties are maintained or even increased. This is explained by the increased crosslink density – a consequence of a high hydroxyl number - resulting in higher mechanical strength due to strong hydrogen bonding between the many urethane bonds formed.
Gloss and haze are also maintained or in many cases improved due to perfect compatibility and improved flow is derived from their low viscosity. Generally, polycaprolactones have a high reactivity towards isocyanates due to their pendent primary hydroxyl groups at the end of flexible aliphatic chains. A desired balance between cure speed and pot-life can be adjusted by the amount of catalysts.

Test formulations summarised

All solventborne formulations were based on a high solids acrylic. Details are provided in *Tables 1* and *2*. In the test formulations Mod. A-C a conventional polyester polyol was replaced by a trifunctional polycaprolactone applying different principles. In Mod. A it was replaced on a weight basis, in Mod. B on the basis of hydroxyl content and in Mod. C the amount was doubled in order to further stretch the influence on properties. In Mod. D it was replaced by a tetrafunctional polycaprolactone, on the basis of hydroxyl content. The NCO/OH-ratio was kept constant at 1.05.
The low viscosity of polycaprolactones effectively reduces VOC in a formulation which can already be considered to be high solids. It is appropriate to refer to them as reactive diluents. The additional reduction in Mod. C further emphasises the effect but also highlights the importance of using a low viscosity HDI-trimer to reach low VOC values (see *Figure 2*).

Physical properties and UV resistance are improved

The aliphatic, semi-crystalline structure of the cured films results in a low T_g, but the film has high mechanical strength. A high crosslink density combined with a low T_g result in a rubbery, elastomeric character of the film which is beneficial for good abrasion resistance (see

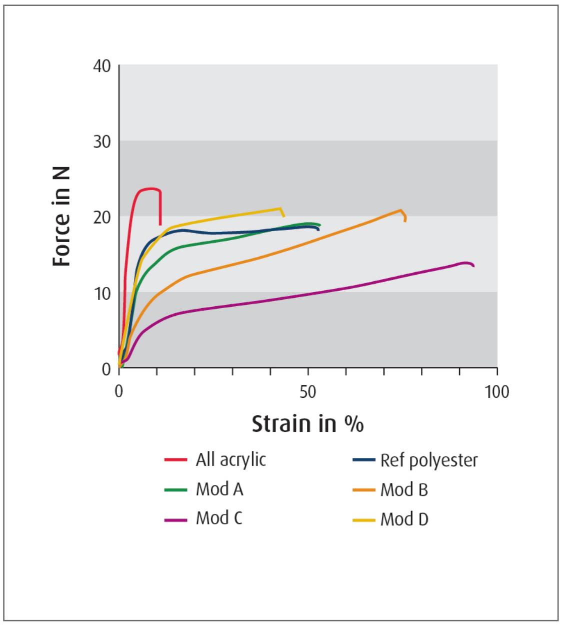

Figure 5: Tensile tests on free films

Table 1: Properties of hydroxyl-functional components in test formulations

	Solids content wt-%	Viscosity m•Pas @23 °C	OH-content in %	Mw g/mol	Functionality
Acrylic polyol	75	5 400	4.5 (s)	n.a.	n.a.
Polyester polyol	78	6 000	5.4 (s)	n.a.	n.a.
3-func. polycaprolactone	100	1 200	9.4	540	3.0
4-func. polycaprolactone	100	1 900	6.6	1000	4.0
Acrylic emulsion	40	600	3.5 (s)	n.a.	n.a.

Table 2: Summary of solventborne test formulations

	Control A	Control B	Mod. A	Mod. B	Mod. C	Mod. D
PART A	All acrylic	Ref Polyester	3-func.	3-func.	3-func.	4-func.
Acrylic polyol	79.11	71.43	71.43	71.43	61.50	71.43
Polyester polyol		7.68				
3-func polycaprolactone			7.68	3.44	7	
4-func polycaprolactone						4.9
Solvent mixture	17.96	17.96	17.96	22.2	28.57	20.74
Additive package	0.93	0.93	0.93	0.93	0.93	0.93
DBTDL (1 % in BuAc)	2.0	2.0	2.0	2.0	2.0	2.0
Total:	**100**	**100**	**100**	**100**	**100**	**100**
PART B						
Low viscosity HDI-trimer	30.11	30.84	35.7	30.84	30.8	30.84
Solvent mixture*	16.4	16.6	20.7	10.4	0	13.5

*Used to set final viscosity @ 22 sec in DIN Cup 4

Table 3: Scratch resistance on glass panels by Taber "Model 550" (rotation speed 0.5 rpm)

	Control A	Control B	Mod. A	Mod. B	Mod. C	Mod. D
Plastic / plastic transition	10 g	10 g	10 g	10 g	10 g	10 g
Plastic / fracture transition	140 g	140 g	180 g	220 g	230 g	200 g

Figure 3). This property enhancement is found in many applications of polycaprolactones.
The aliphatic structure of caprolactones significantly improves impact resistance. To demonstrate this, further tests were performed on metal panels which were heated at 80 °C for 24 hours in order to ensure full cure, and then cooled down to -25 °C for 3 hours in order to check mechanical properties in cold climates, as shown in *Figure 4*.
Results show that the low T_g of polycaprolactones also decreases the T_g of cured coatings, a property which for example can improve stone chip resistance in automotive coatings and rain erosion resistance for windmill blades in harsh climate conditions.
Scratch resistance was evaluated by applying an indenter with a progressively increased load to the coating. As long as no scratch was observed, only elastic deformation of the surface was formed, which was quickly regenerated by reflow. When the load is further increased into the plastic deformation region, scratches are eventually be generated as long as temperature is above T_g. Eventually the load increases to the point where an irreversible scratch is formed, and the coating is fractured. Results in *Table 3* show the effect on T_g, reducing the brittleness and risk of creating permanent scratches. Semicrystallinity introduced by caprolactones also reduces internal stress and increases viscoelastic properties, which also improves reflow properties.
Elongation and flexibility are improved, especially compared to a pure acrylic system. The effect is emphasised by the increase of strain when the amount of polycaprolactones is further increased. By varying the amount and functionality of the polycaprolactones it is however possible to avoid making any compromise on strength and toughness. Tensile tests were performed on free films, and the results are summarised graphically in *Figure 5*.
Clearcoats were formulated without additional UV absorbers or hindered amine light stabilisers (HALS), applied onto a white base coat and exposed to QUV-B for 2000 hours using a standard cycle. The aliphatic structure and the very low acid number (< 0.25 mg KOH/g) provide both good UV resistance and very good hydrolytic stability. *Figure 6* shows that the resistance is better than the pure acrylic system, and the effect is even more pronounced in the formulation with double amount of polycaprolactones (Mod. C).

Some types can be used in waterborne formulations

Polycaprolactones can conveniently be used in both solventborne and solvent-free formulations by straightforward addition into formulations. They are however essentially hydrophobic, making them impossible to dilute and dissolve directly into water, and since they have an extremely low acid number it is not possible to make them water dilutable by neutralisation of carboxylic groups.
They can however be used as resin modifiers in waterborne systems based on acrylic emulsions when they are allowed to migrate into the emulsion droplets, without adding additional emulsifiers. Since both hydrophobicity and viscosity of caprolactones are governed by molecular weight, it is preferable to use low molecular weight polycaprolactones with high hydroxyl content.
Both properties make it easier for them to migrate into the emulsion droplets during a dispersion process. They form a complex equilibrium in this kind of system, where molecular weight and viscosity of the acrylic but more importantly the type and amount of emulsifiers have a crucial impact on success.
The amounts of different caprolactones that can be added to a specific acrylic emulsion vary and might not always be successful. In one commercial emulsion tested, up to 16 wt-% of the trifunctional caprolactone can be incorporated, with the particle size distribution remaining intact. However with 32 wt% addition, the peak is moved towards higher emulsion droplet sizes, and with 40 wt% addition a distinct bimodal particle size distribution is formed, which indicates fast phase separation (see *Figure 7*).

Both physical properties and coalescence are improved

The general benefits of polycaprolactones are similar in waterborne systems and solventborne ones. Even VOC can be reduced since the need for fast-evaporating cosolvents is less. Influence on scratch resistance and impact resistance can be even more pronounced in these cases, since the molecular weights of waterborne acrylics usually exceed that of a conventional solventborne acrylate. The influence of an addition of low T_g and semi crystalline caprolactones can in these cases be even more significant.
A well-known drawback with WB 2K PUR systems is that it is more difficult to achieve high gloss and low haze due to the topography of a cured surface with patterns formed by the remains of the emulsion droplets. This effect can be reduced by adding an organic cosolvent which reduces T_g and minimum film formation temperature (MFFT), promoting coalescence and levelling during physical drying. Due to their low viscosity and perfect compatibility with acrylic resins, polycaprolactones can fulfil the same function.
Since polycaprolactones, in contrast to fast evaporating organic solvent, remain in the film, physical drying and levelling can be prolonged allowing even better levelling. This can be seen by an increase in gloss but is especially pronounced when haze is reduced.

In solventborne and solventfree systems, polycaprolactones can naturally be referred to as reactive diluents, but in waterborne emulsion based systems they can more correctly be regarded as reactive coalescing agents.

Benefits of polycaprolactones summarised

Polycaprolactones are aliphatic, liquid, solvent free polyols suitable as reactive diluents. They are prepared by ring-opening polymerisation which results in low acid numbers and exactly defined functionality which make them versatile tools when formulating various crosslinked coatings.

When partly replacing conventional hydroxyl functional resins, they should be regarded as normal raw materials, but formulations should be balanced in order to take advantage of their unique properties. Even though they are aliphatic, semi-crystalline polyols with low T_g, a balance can easily be found where flexibility, impact resistance and abrasion resistance can be significantly improved without compromising hardness or chemical resistance.

This makes them suitable for demanding applications where good mechanical properties are needed in order to provide properties such as stone chip resistance, abrasion resistance and rain erosion resistance.

Caprolactone polyols should preferably be used as resin modifiers in formulations that need to be taken to the next level, where they can improve sustainability by prolonging life-cycles and reducing emissions.

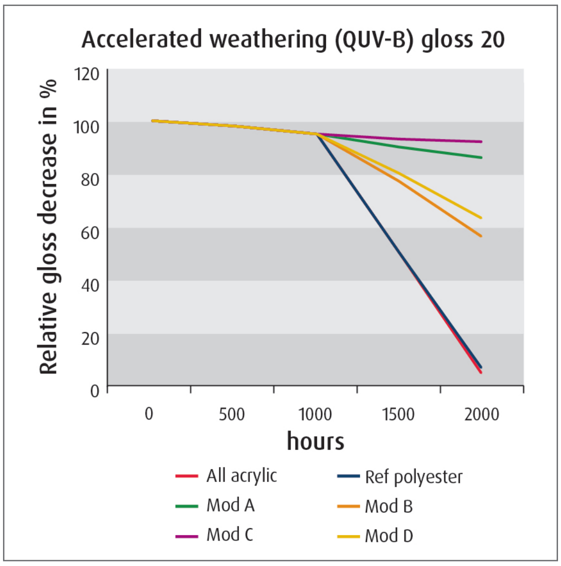

Figure 6: Accelerated weathering test results

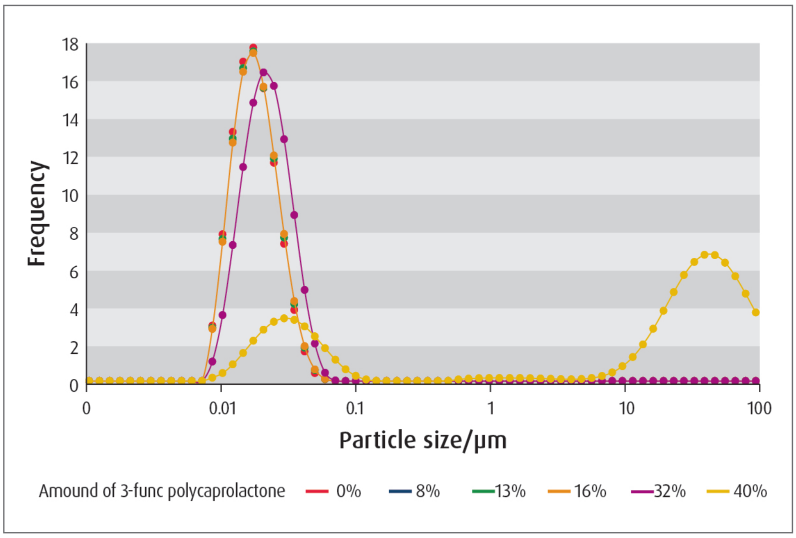

Figure 7: Effect of additions of 3-functional polycaprolactone (wt-%) on particle size distribution of an uncured acrylic emulsion

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