

New technology for improved compatibility

Poor compatibility is a well known problem when formulating polyurethane systems. When a hydrophilic liquid is mixed with a hydrophobic liquid the incompatibility often results in phase separation. Other reasons for incompatibility are for example differences in molecular weight or in microstructure. To get around this problem, end users are forced to mix the incompatible liquids at the point of use in order to achieve homogeneous end products. An example where incompatibility is often found is when a commonly used chain extender, 1,4-butanediol, is blended with a standard polyester or polyether polyol. 1,4-butanediol is often selected as a chain extender in both CASE and footwear applications because it gives a good balance between low temperature flexibility and hardness. New technology has been developed that helps to overcome this problem and allows the formulator to blend incompatible chain extenders with the polyol for an extended period of time without the disadvantage of phase separation occurring. This technology leads to a new class of polymeric additives featuring well defined structures with high interfacial activity. In this paper we propose a working mechanism of the new specialty additives. It will also include some practical examples of the additives working in real formulations.

1. Introduction

Formulators in every field of the polyurethane industry are facing the demand for new and/or better products. The requirement may come from the “green” trend to use more renewable resources or it may be driven by the request to reduce emissions especially from household and automotive products. Furthermore, improvements in user friendliness, reduction in cost and better physical properties are on the wish list of the downstream users. In order to achieve these targets the application of processing additives becomes inevitable.

Many formulators are dealing with raw materials that cause solubility challenges. This means they are dealing with emulsions rather than with solutions. Emulsions, however, are having an inherent drawback: they are not permanently phase stable, they have a tendency to separate. As a consequence, additives giving emulsion stability are gaining more and more attention. Using them, new improved products can be produced.

For a more detailed description of emulsions in general and also for the specific issues in flexible and rigid foaming the reader is referred to our previous papers [1].

With this paper, we want to introduce new additives for the stabilization of what we call chain extender emulsions. They are consisting of polymeric glycols and relatively small chain extender molecules. Many elastomers and also some specialty foams require the use of e. g. butanediol, propyleneglycol or other short chain hydrophilic glycols. The chain extenders are used to adjust and control the physical properties of the final products.

The application level of chain extenders varies in a broad sense from just a few percent

up to 25 % or even higher, depending on the polyolblend. Of course combinations of chain extenders are used as well. Besides the bi-functional chain extenders, tri- or poly-functional glycols are formulated to adjust the physical properties of the final articles. Typically, chain extenders with functionality higher than two are called crosslinkers. They contribute to a three-dimensional network rather than just extending chains in two dimensions. In this paper however, we focus on the emulsion formation with such molecules and not on their function in the polymer network formation. Whether we are blending base polyols with two-functional (chain extenders) or poly-functional glycols (crosslinkers) does not make any difference as to the stability of emulsions. Therefore, whenever we use the term “chain extender” in this paper this shall include both the true bi-functional chain extenders and the crosslinkers.

2. The systems

This paper shows the results of our work with four systems. Two test systems that we used for our development were of the generic type. We have used common base polyols and blended them with chain extenders (**tab. 1**). The base polyols were PTMEG of a molecular weight of 2,000 Daltons and we used a tri-functional polyetherpolyol for the manufacturing of high resilience foams. Chain extenders were butanediol and PEG 200.

Tab. 1: Chain extenders in polyurethane formulations (examples)

Alcohol-based chain extenders	
Aliphatic diols:	
Ethylene glycol (EG)	1,3-propanediol (PG)
1,4-butanediol	2,3-butanediol
1,5-pentanediol	1,6-hexanediol
PEG 200	Dipropyleneglycol (DPG)
Aliphatic polyols:	
Glycerol	Trimethylolpropane
Alkoxylates thereof	
Aromatic diols:	
1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene	
Hydroquinone diether (HQEE)	
Amine-based chain extenders:	
Primary and secondary di- and polyamines	

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The more challenging systems for the development of the new additives came from the market. In the area of elastomers we have been working with a customer system based on polyester resin. The other customer system came from the automotive sector; it is used to produce thermoformable open cell rigid foam. The elastomer system is used in combination with butanediol, the thermoformable rigid foam is used with propyleneglycols and further low molecular weight diols and triols.

Both customer systems (#3 and #4) separate completely within less than a few hours. The same happens with system #2. Less than half an hour is enough to clearly see separate layers. This is a major disadvantage in the application of such systems at fabricators and manufacturers. The use of phase instable systems requires special attention and equipment (e. g. stirred day tanks, more careful planning of the production). Less flexibility in the production process and high risk for out of spec products is the result of these instable systems.

2.1 Effect of silicone surfactants and water on phase stability

Fully formulated systems do contain many components. Besides the base raw materials the systems will often contain chemicals such as catalysts, silicone surfactants, pigments, surface modifiers and other chemicals. In the end, the applicator is not too interested in the compatibility of parts of the system – the applicator wants a fully formulated phase stable system.

Formulation developers may find it interesting to see that the screening of a portion of a future system may not be meaningful. For the purpose of simplification it seems logical to test the major incompatible components only. However, in terms of phase stabilization two formulation components need special attention.

The first component that influences the emulsion stability more than the application level reveals is silicone surfactants. The intended property of silicones is their high surface activity. The differentiation between the liquid-gas interface and the liquid-liquid interfacial layer is not perfect. As a result of this, high cloud point silicones are to some extent competing with the compatibilizers positioning themselves on the droplet. This causes more fluctuation at the interface and thus less stable emulsions are formed. Under these circumstances re-considering the selection of the silicone surfactant can help to end up with a better stabilization of the emulsion.

The second important formulation component that needs to be mentioned is water. Water is of course playing a role when foams are to be made. Solutions made of polyols and chain extenders may become emulsions when water is added, even though water might be perfectly soluble in all polyol blend components separately.

2.2 The additive

Long term emulsion stability of weeks, maybe months could not be achieved with estab-

lished “on the market” emulsifiers. Additives of the Byk range including the recently published [2] double comb type emulsifiers were not efficient enough in the new systems. While the double comb compatibilizers were giving good stability to bio-polyols blended with conventional polyols and also EO rich cell opening polyols with conventional polyols, these double comb compatibilizers are giving only marginal improvements when chain extenders are to be stabilized.

In the course of recent years, Byk has accomplished the implementation of a new polymerization technology. The so called “controlled polymerization technology” (CPT) [3, 4] allows the synthesis of very well-defined polymer structures by means of controlled radical or ionic polymerization processes. Typical structures which can be prepared by these methods are dual-block and multi-block copolymers of the A-B, A-B-A or A-B-C type. In block copolymer emulsifiers with an A-B structure, the gradient part of the polymer chain (i. e., the change of different monomer unit concentrations along the molecular chain) connecting the A-part with the B-part of the molecule is critical. Conventional radical polymerization results in the formation of poorly controlled products without a well defined architecture like block structure and block gradients. CPT however, is capable of giving these critical parameters of the emulsifier’s molecular structure the design that is needed.

As a result of our access to CPT, we can create amphiphilic block copolymers, e. g.,

Fig. 1: Pair of amphiphilic polymers in BYK-P 9909

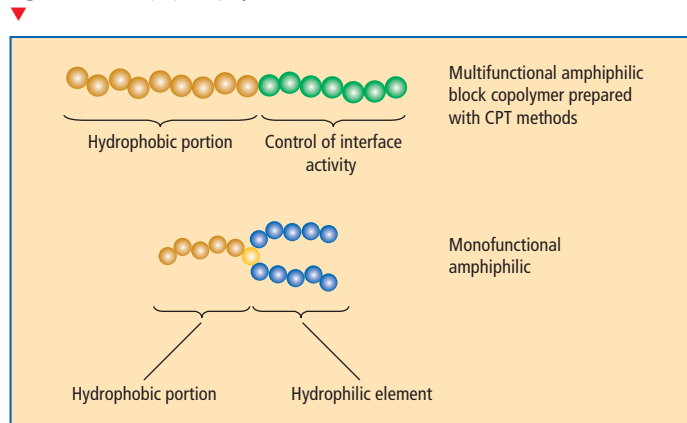
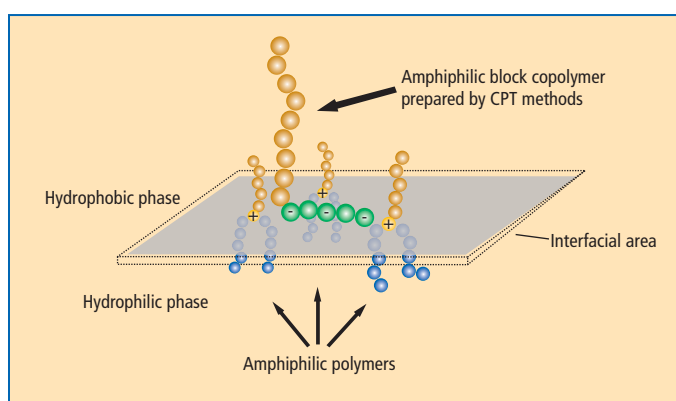


Fig. 2: Arrangement of the pair of amphiphilic polymers at the Interface of BYK-P 9909

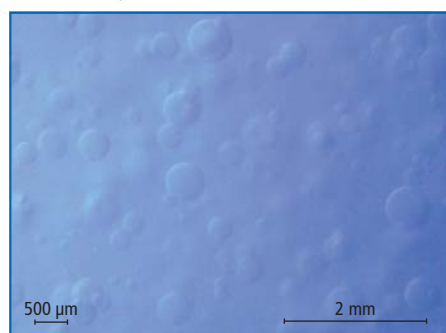


of the A-B type with A and B portions of several thousand Daltons and a well defined gradient. In many cases it turned out that such A-B amphiphilic copolymers made by CPT were not able to stabilize the demanding phase separation problems on their own. However, the fact that such molecules can be made with either basic or acidic functionalities opens the door for a synergistic concept.

Figure 1 illustrates a pair of amphiphilic polymers combined in the BYK-P 9909. De-protonation of the acidic functionality of the multifunctional copolymer by means of a basic molecule leads to an anionic structure (negative charge). As the de-protonation occurs several times in each polymeric A-B chain, the result is a polyelectrolyte bearing many negative charges in one polymer chain. In our additive concept the de-protonating agent is an emulsifier itself. In its protonated form, positively charged, each molecule – as a monoelectrolyte – compensates negative charges of the A-B polyelectrolyte. The result is a polymeric salt structure.

With BYK-P 9908 the situation is analogous. The A-B polymer obtained from the CPT reaction carries several basic groups (green balls in **fig. 1**), the monofunctional amphiphilic copolymer holds the acidic functionality.

Fig. 3: Droplets of 1,4-butanediol in the continuous phase of PTMEG in the absence of a compatibilizer



Tab. 2: Test systems

System	Type	Resin	Chain extender	Compatibilizer
1	Generic	PTMEG 2000	1,4-butanediol	BYK-P 9908
2	Generic	Polyether polyol (OH 35; F=3; 15 % EO)	PEG 200	BYK-P 9909
3	Elastomer	Polyester-based resin	1,4-butanediol	BYK-P 9908
4	Thermoformable foam	Mix of PO and EO-based DPG and polyether polyols	Trifunctional ethoxylates	BYK-P 9909

Each of the two components in BYK-P 9908 or BYK-P 9909 is not sufficient in terms of stabilization power, but both components together are. Here we clearly have a situation where each pair of amphiphilic polymers gives more performance than the components alone – at the same application level. We believe that the arrangement of the components at the interface plays an important role. **Figure 2** shows a possible arrangement of the molecules at the interface.

In a series of synthetic work we have screened all the variables in the composition of the new additives. We found the best ratio of A to B in the amphiphilic block copolymer, we have optimized the gradient from the A-portion to the B-side of the block copolymer and, furthermore, we have optimized the monofunctional amphiphilic polymers used for salt formation in terms of substructure and molecular weight. This work has shown us that the block ratio, the gradient and the molecular weight of the A and B portion play the most important role in terms of efficiency of the new additives.

3. Experimental results

Experimental work was done in two ways. First, we have evaluated the phase stabilizing performance of the new additives. Second, we have tested how the use of the additives affected the properties of the final polyurethane article.

Testing for phase stability of an emulsion is a rather simple task. The systems as given in **table 2** are mixed with typical lab mixers until a homogeneous emulsion is obtained. The compatibilizers were added at levels from one to five percent based on the weight of the polyol blend. The emulsions were filled

into 100 ml glass vials and kept at ambient conditions for regular visual inspection.

Typically, emulsions are turbid liquids in which the small droplets lead to a light scattering depending on the difference in the refractive index of the continuous versus the discontinuous phase. This is a very well known phenomenon we all have seen in milk, for example. During the stages of phase separation, the droplets of the discontinuous phase coalesce leading to fewer and bigger droplets. The increase in droplet size reduces the turbidity. Differences in the density of incompatible liquids will finally lead to a phase separation to a bottom and a top layer.

In the following we describe our results in the stabilization of the four above mentioned systems (**tab. 2**): two relatively simple blends of polyols plus chain extender and two customer systems which are basically fully formulated systems. The only minor change from real life formulations is that we have left out the pigments for better visibility of the phase separation.

The first example is a blend of PTMEG and 1,4-butanediol. The liquids actually appear miscible at the level of 8 % 1,4-butanediol in the polyol blend (system #1) and an obvious phase separation into two separated layers does not occur over the observation period of 14 days. The naked eye does not see any change in such a blend which is kept at 40 °C. Under a microscope, droplet formation becomes obvious as can be seen in **figure 3**. In contrast to the untreated blend where droplets as big as 500 μm have developed through coalescence processes, the BYK-P 9908 treated blend still appears homogeneous with droplets not bigger than 5 μm, not visible in the magnification selected below.

The performance of BYK-P 9908 in the elastomer system #3 is shown in **figure 4**. The picture in **figure 4** shows the situation after 14 days at 40 °C. Similar to many elastomer systems, this blend has a quite high viscosity at room temperature, so it has to be heated to about 40 °C to assure good

processing in production. We used similar conditions for the stability test. The system without chain extender is stable and no phase separation can be observed. The situation is completely different after the addition of 20 parts of chain extender to 80 parts of the system (a high but still typical ratio of chain extender vs. polyol). After only one day, the incompatibility of the components makes it impossible to process the blend. In the upper part of the vial an almost clear separated layer becomes obvious (Control II in **fig. 4**). BYK-P 9908, added at concentrations of 1, 3 and 5 %, changes the situation. The tendency towards phase separation is so slow that the processing in a production process is possible without stirring – after 14 days and even longer.

Figure 5 shows what has happened with a blend of PEG 200 and a trifunctional 4800 molecular weight HR polyol (system #2) within eight hours after mixing. The glass tube on the left contains the almost completely phase separated components. The turbid ring between the upper and the lower phase is the not yet separated portion. The vial on the right of **figure 5** (which contains BYK-P 9909) contains the still homogenous mix with no sign of larger droplet formation yet.

Figure 6 gives an impression on the quick propagation of the separation in the control sample. Already after 30 min the unstirred day tank stored blend could not be used for production purposes any longer. In contrast to the very quick separation without additive, the sample with BYK-P 9909 is still stable after two weeks. Phase stabilization is the most important feature the new additives pro-

vide. At the same time they should not interfere with the kinetics of the chemistry involved nor negatively influence the physics of the final product. In both customer systems the application of the additives could easily be transferred from first positive lab results to the real production.

4. Summary and outlook

BYK-P 9908 and BYK-P 9909 are new compatibilizers that have shown their outstanding performance in the stabilization of chain extender and crosslinker emulsions with base polyols. While the BYK-P 9908 is the first choice for 1,4-butanediol blends, the BYK-P 9909 works best in the emulsion stabilization of low molecular weight hydrophilic glycols. The present work based on real systems revealed that only the new concept of CPT made polyelectrolyte paired with amphiphilic monoelectrolytes gives sufficient stability to the interfacial layer.

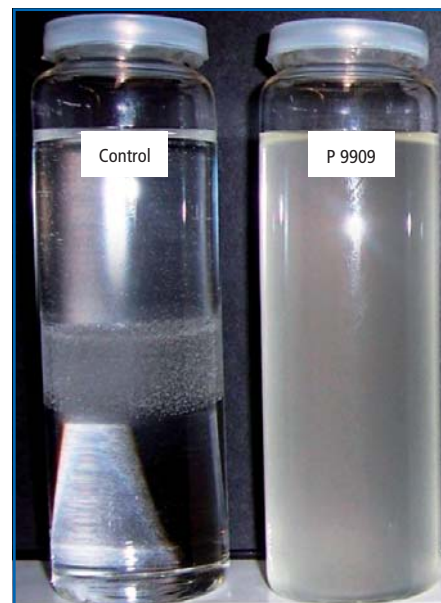
The additives offer new options for formulators and for the marketing of systems. Blends of incompatible components, so far impossible to be marketed due to quick phase separation, can now be considered for commercialization. Systems, so far sold as a three component mix, might be turned into easier to handle more customer friendly two component products. The application of the additives gives downstream producers of polyurethane products more flexibility and safety in the production. Therefore the BYK-P

9908 and BYK-P 9909 can help to minimize out of spec production and reduce cost.

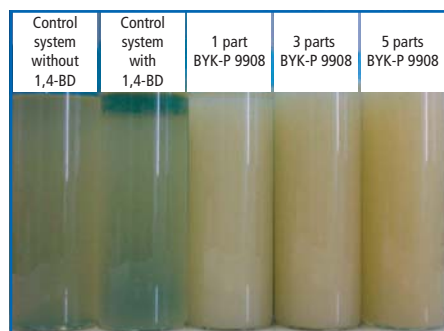
5. References

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▼ **Fig. 5:** System #2 after 8 h



▼ **Fig. 4:** System #5 after 14 days with 1,4-butanediol at 40 °C



▶ **Fig. 6:** Emulsion stability test with BYK-P 9909 (system #4)

