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Development of new generation polyols for semi-flexible foam systems for the production of flexible polyurethane pre-insulated pipes

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Abstract

Flexible pre-insulated pipes offer both ease of handling during installation and a cost saving potential as compared with rigid pipes. Obstacles can more easily be bypassed and excavation costs for the pipe laying in the ground can be reduced.

Huntsman Polyurethanes have developed new generations of semi-flexible foam systems that provide a combination of high flexibility and increased thermal resistance, usually two antagonistic properties. This was achieved through a careful balance of short and long chain polyether polyols.

The thermodynamical incompatibility of short and long chain polyol, which can lead to phase separation during polyol storage, could be overcome and storage stable polyol systems are now available.

These polyol systems can be used for both the continuous and the discontinuous manufacture of pre-insulated pipes. Further, foam systems could be developed which significantly retard the fast λ -ageing often encountered with semi-flexible foam systems. It was found that the nature of the long chain polyol is of paramount importance to slow down the λ -ageing of the foam but retain the combination of high flexibility and high thermal resistance.

Introduction

Flexible pipes are being used more and more frequently because of the ease of handling. Installation is very simple, e.g. house connections can be made without a lot of preliminary planning since obstacles can be bypassed simply by bending the pipe. Flexible pipes can be laid continuously in lengths up to several hundred metres and hence fewer joints are required which avoids the time consuming welding of the service pipes and the subsequent joint filling. This can result in a higher laying speed and hence contribute to cost reduction. The trench profile for flexible pipes is usually narrower and therefore excavation costs are lower, in particular for smaller pipe diameters.

Design of a flexible pipe composite

Flexible pipes are pipe in pipe systems with service pipes produced from materials such as:

- thin-walled steel
- soft annealed copper
- cross-linked polyethylene (PEX)
- polybutylene
- aluminium and PEX

For the majority of flexible pipes, PEX service pipes are used. The insulation material is normally a polyurethane foam. Forward and return flow service pipes can be fitted into a shared casing pipe. The casing pipe can be steel, high or low density polyethylene. Low density polyethylene is preferred as it imparts a higher flexibility. Corrugated service and casing pipes are sometimes employed. This enhances the flexibility and helps to retain the adhesion between foam and pipe during and after the bending of the pipe.

Flexible pipes are mostly manufactured in a continuous mode with lengths up to several hundred meters. They are coiled up directly after production and delivered in coils or on reels.

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Requirements for the polyurethane foam

In order to prevent loss of integrity during coiling-up of the pipes after production and during the installation, a high degree of foam flexibility is necessary. However, the foam should also provide good mechanical properties and a high thermal resistance. For temperatures below 95°C where PEX pipes are normally used, a permanent heat resistance of the foam of 95°C is sufficient. For service temperatures up to approximately 130°C, where metal inner pipes of materials such as copper or steel are used, the foam system must also provide an increased heat resistance. An ideal semi-flexible foam system should be used for all types of service pipes.

High flexibility and high thermal resistance are antagonistic properties: a high flexibility usually requires a low cross-link density whereas a high thermal resistance asks for an increased cross-link density.

In the past we have developed and introduced water and cyclo-pentane blown systems which combine a high degree of flexibility with a high thermal resistance. These systems were based on a careful balance of long and short chain polyols. A dual network consisting of hard domains which are interconnected with flexible chains provides this combination of high flexibility and heat resistance [1].

Due to a thermodynamical incompatibility of the short and long chain polyol, separation occurred during storage. This required machine modification to ensure thorough mixing of the components prior to use to restore the correct blend composition. However, the improvements in foam end properties clearly outweighed this drawback.

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New generation of polyols for semi-flexible foams

We have now developed a new generation of semi-flexible foam systems which overcomes the separation tendency and allows storage stable systems. The combination of high flexibility and high thermal resistance is retained in these polyurethane foam systems. The key to overcoming the separation tendency was again a careful balance of short and long chain polyols. In particular the selection of the short chain polyol is of paramount importance.

We found that certain polyols which contain amine groups, can overcome the separation tendency. We believe that the presence of nitrogen changes the polarity of the short chain polyol which improves the compatibility between short chain and long chain polyol and therefore provides a better storage stability of the polyol system. These polyol systems can be used for both the continuous and the discontinuous manufacture of pre-insulated pipes. Patent protection is sought for this new development [2].

Typical properties of the two new systems, Daltofoam TE44200 and Daltofoam TE44203, and their respective foam properties are outlined in Table 1.

Table 1: Typical foam properties of Daltofoam TE44200 and Daltofoam TE44203 with Suprasec 5005

	Unit	Test method	Daltofoam TE44200 continuous technique	Daltofoam TE44203 continuous technique
Reactivity at 20°C	s	SMS 2318		
cream time		(bag-foam)	10	11
fibre time			30	35
Free rise density	kg/cm ³	ISO 845	57	56
Core density	kg/cm ³	EN253	65	64
Flexibility	mm	DIN 53423	16	14
Flexural strength	kPa	DIN 53423	850	970
Compressive strength	kPa	DIN 53421	210	260
Water absorption	%	EN253	<5	<5
Closed cell content	%	ASTM D2856	>90	>90
Softening temperature	°C	TMA	143	141

Note: The foam properties are typical properties which can depend on pipe diameter, pipe type and foam density applied

Both systems are fully formulated polyol blends and contain polyether polyols, water, catalysts and a silicone surfactant giving fully water blown foam systems. They are suitable for the continuous manufacture of flexible polyurethane pre-insulated pipes. Daltofoam TE44203 provides an increased compressive strength and is particularly suitable for the production of bigger diameter pipes, whereas Daltofoam TE44200 is adapted for the production of smaller diameter pipes.

The formulation of a dual blown system, which e.g. contains pentane as a physical blowing agent, is also possible. The storage stability is not affected and no separation occurs in systems containing pentane. Formulations applied with manufacturing techniques different from the continuous one, e.g. the pull-through technique or a discontinuous pipe filling technique requiring a reduced reactivity, are also possible with this new generation system.

Table 2 lists a water/pentane dual blown formulation for the continuous manufacture of flexible pipes, Daltofoam TE34209, and a water blown formulation for the pull-through technique, Daltofoam TE44207, and their respective foam properties. Also here, the combination of high flexibility and high thermal resistance is provided.

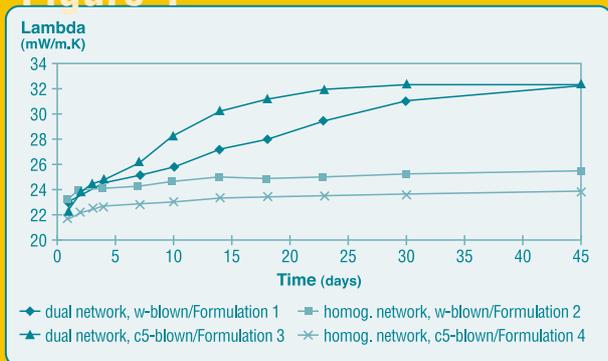
Table 2: Typical foam properties of Daltofoam TE44207 and Daltofoam TE34209 with Suprasec 5005

	Unit	Test method	Daltofoam TE44207 pull/through technique	Daltofoam TE34209 continuous technique
Reactivity at 20°C cream time	s	SMS 2318 (bag-foam)	50	14
fibres time			210	43
Free rise density	kg/cm ³	ISO 845	34	55
Core density	kg/cm ³	EN 253	90	59
Flexibility	mm	DIN 53423	>14	14
Flexural strength	kPa	DIN 53423	>1000	n.m.
Compressive strength	kPa	DIN 53421	380	200
Water absorption	%	EN 253	<5	<5
Closed cell content	%	ASTM D2856	>90	>90
Softening temperature	°C	TMA	130	142

Note: The foam properties are typical properties which can depend on pipe diameter, pipe type and foam density applied

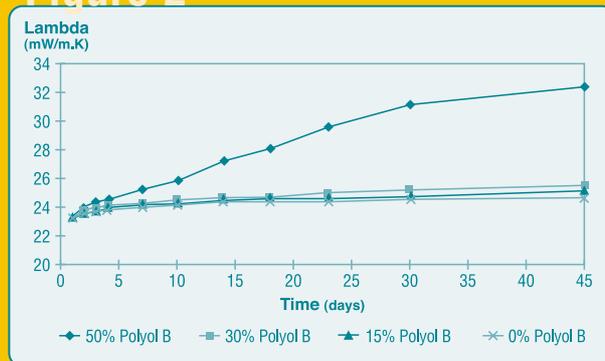
λ -ageing of semi-flexible foams with equal calculated network parameters but also dual and homogeneous network

Figure 1



λ -ageing as a function of the level of the long chain polyol, water-blown formulation

Figure 2



Lambda ageing of semi-flexible foam systems

It is well known that thermal conductivity of rigid polyurethane foam changes as a function of time [3]. This deterioration of the insulation capacity is referred to as thermal conductivity ageing or λ -ageing. Our experience with semi-flexible foam systems is that the thermal conductivity ageing can be much faster compared to rigid foam systems. Recent industry research also confirms the accelerated λ -ageing of water and cyclo-pentane semi-flexible blown foams [4]. In order to better understand the cause of this fast λ -ageing, we have evaluated the thermal conductivity ageing of a range of semi-flexible foams as a function of the long chain polyols used in the system. Water and c-pentane blown systems were evaluated. The thermal conductivity was measured at a mean temperature of 10°C in time intervals on unprotected foam plate moulds having a density of ca. 62kg/cm³. The foam samples were aged at an ambient temperature for up to 45 days.

7 different long chain polyols, polyol A to G, were evaluated. From A to F, the molecular weight decreases. Polyol G is a polyol with a molecular weight similar to the one of polyol B, but with a different distribution of PO- and EO- groups in the polyol backbone. During this part of the evaluation, polyol 1 was used as a short chain polyol. For comparison, polyol 2 was used. Polyol 2 is a short chain polyol based on a mixture of conventional short chain polyols. It was used to make

comparisons to foams known to provide a homogeneous network, but having the same calculated network parameters as the foams based on polyol 1 and the long chain polyol B, providing a dual foam network.

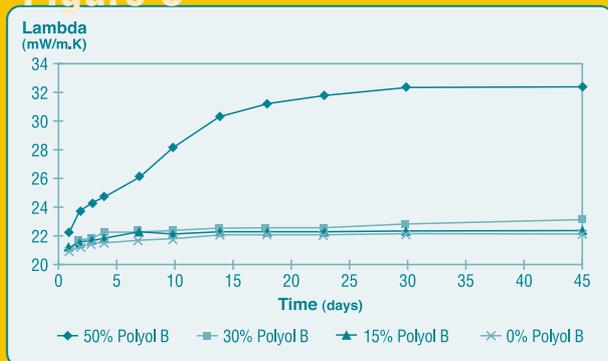
In a first series, a comparison was made between semi-flexible formulations based on a long chain polyol B, in combination with the short chain polyol 1 and a formulation based on polyol 2. A significant difference in λ -values was found, see Figure 1.

The systems based on the mixture of polyol 1 and the long chain polyol give an increase of 10 mW/m.K after 45 days of ageing, for the water as well as for the pentane blown system. The systems based on polyol 2, gave an increase of only 2 mW/m.K over the same ageing period.

The compared systems have the same calculated network parameters such as cross-link density, aromaticity and urea content. Formulation 1 and 3 are based on polyol 1 and polyol B, formulation 2 and 4 are based on polyol 2. Although the calculated parameters are identical, there is a strong presumption that the network build up of the comparative systems is completely different. An indication of this is the high softening temperature of 148°C for formulation 1, compared to 98°C for formulation 2, (both water blown). Whilst 140°C for formulation 3 compared to 92°C for formulation 4, (both pentane blown).

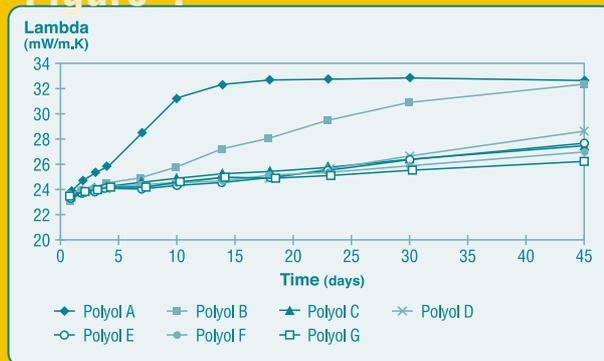
λ -ageing as a function of the level of the long chain polyol, pentane blown formulation

Figure 3



λ -ageing as a function of the nature of the long chain polyols

Figure 4



The high softening temperature is the result of a dual network as explained earlier. The mixture of conventional rigid polyols gives a homogeneous foam network resulting in much lower softening temperatures. It is likely too, that the dual network structure leads to an accelerated diffusion of pentane and carbon dioxide through the flexible chains which connect the rigid domains, resulting in a significant increase of the λ -value over a short period of time.

A second series of formulations permitted us to study the λ -ageing process of water blown and cyclo-pentane blown foams as a function of the amount of long chain polyol present in the matrix. The amount of the long chain polyol B, is gradually decreased from 50 pbw to 0 pbw and replaced by the short chain polyol 1. Obviously, the cross-link density and aromaticity of the foam increases as the amount of long chain polyol is decreased. The thermal conductivity ageing was considerably slowed down with a decreasing level of the long chain polyol, see Figures 2 and 3. From a polyol B content of 30 pbw onwards, almost no difference of the λ -value after ageing can be found.

The last series of water blown systems compares the effect on the λ -ageing when different types of long chain polyols are used, see Figure 4.

Polyol A which has the highest molecular weight, gives the fastest increase of the thermal conductivity. The ultimate λ -value of 32 mW/m.K is reached after approximately 25 days.

A reduction of the molecular weight of the long chain polyol leads to a reduced λ -increase as a function of foam ageing time, see polyol B to F. The choice of the long chain polyol can influence to some extent the properties of the semi-flexible foam, e.g. a significant increase of the molecular weight can result in slight reduction of the softening temperatures. However, a range of OH-value and molecular weight for the long chain polyol can be identified where the combination of high flexibility and high thermal resistance is retained but the λ -ageing is considerably retarded. Patent protection is sought for this development [5].

The λ -results obtained with polyol G are also noteworthy. Despite its high molecular weight similar to polyol B, a very slow λ -ageing of only 2.6 mW/m.K after 45 days of ageing was measured. The particularity of polyol G compared to polyol B is its significantly different distribution of PO- and EO- groups in the molecule. The λ -value increase obtained with this system is very close to the one obtained with the conventional rigid polyols. This could be explained by the fact that the use of polyol G does not give a foam with a dual network structure but rather a homogeneous network. The low softening temperature of this foam would also point in this direction.

a new generation of **semi-flexible foam systems**

was developed where the
thermal conductivity ageing
is considerably reduced

From this evaluation it seems clear that semi-flexible foams can have the drawback of an accelerated λ -ageing. However, the following approaches can be considered to reduce or overcome this problem:

- **The polymer structure of the system can be modified, going from a dual network to a homogeneous network, with the result of a considerably reduced gas diffusion rate. However, this will be at the expense of the thermal resistance.**
- **Reducing the amount of the long chain polyol leads to a significant improvement of the thermal conductivity. However, this might be at the expense of the foam flexibility which is a major requirement for the application.**
- **The nature of the long chain polyol and the molecular weight appears to be crucial. The screening done with a large number of long chain polyols allows identification of a range of polyols where the combination of high flexibility and high thermal resistance is retained and the thermal conductivity ageing is considerably reduced.**

Finally, the effect of the casing pipe as a diffusion barrier still needs to be considered. From previous studies it is known that the HDPE casing pipe acts as an efficient diffusion barrier for carbon dioxide [3], which in particular for water blown semi-flexible foams might result in a pronounced deceleration of the λ -ageing of a pre-insulated pipe. Nonetheless, applying a semi-flexible foam system which provides a considerably slowed down λ -ageing will result, in the longer term, in a reduced thermal conductivity increase of flexible pre-insulated pipes. This helps to keep the energy loss of pre-insulated pipes respectively of a pipe network low during the service time of the pre-insulated pipes.

Conclusion

Huntsman Polyurethanes have introduced new generations of semi-flexible polyol systems which allow formulation of foam systems, providing a combination of increased thermal resistance and high flexibility through a unique combination of short chain and long chain polyols. The polyol systems are storage stable and do not separate during storage. Patent protection is sought for this development.

Further, approaches were identified to retard the thermal conductivity ageing of semi-flexible foam systems. Again, a carefully balanced combination of short and long chain polyols is the key to retard gas diffusion processes leading to an increase of the foam thermal conductivity. In particular the nature of the long chain polyol is of paramount importance. Also for this development, patent protection is sought.

These foam systems are commercially available for market introduction for continuous and discontinuous manufacturing techniques. A range of fully water blown and pentane/water or HCFC-141b/water dual blown foam systems are available.

References

1. J. Kellner, P. Morton, P. Zarka, Polyurethane World Congress, Dallas, September 17-20 (1998), 61- 68
2. International patent application No. WO 99/20672
3. J. Kellner, V. Dirckx, "Change of thermal conductivity of polyurethane in pre-insulated pipes", Euroheat&Power Fernwärme international, 6/1999, 44-49
4. E. Geiss, M. Kraaz, "Diffusionsproblematik bei Kunststoffmediumrohren", Euroheat&Power Fernwärme international, 7/1998, 24-29
5. EPC patent application No. 99202916.5

Authors' biographies

Jürgen Kellner

Jürgen Kellner received an MS degree in Chemistry from the University of Regensburg, Germany and a PhD in Organometallic Chemistry from the Technical University of Munich, Germany. He joined Shell Chemicals in 1989 and held various positions in research, marketing and market development in the field of epoxy resin. In 1996 he took up a position in the Chemical Research Centre of Shell in Louvain-la-Neuve, Belgium as a Senior Research Chemist in Rigid Polyurethane responsible for applicational research, development activities and technical service for rigid polyurethane foam insulated pipes. In 1999 he joined Huntsman Polyurethanes, Belgium, and is now responsible for the global pipe insulation business.

Philippe Zarka

Philippe Zarka did his studies as a chemist at the High Technical Institute – Brugge in Belgium. He joined the Chemical Research Centre of Shell in Louvain-la-Neuve in 1990. He worked in the domestic appliances area and pipe insulation. In 1999 he joined Huntsman Polyurethanes, Belgium, and currently exercises a function as technical specialist being responsible for applicational research and technical service for rigid polyurethane foam insulated pipes.

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