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Novel polyurethane based systems for pre-insulated pipes applying the continuous spray technique

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Abstract

Large diameter polyurethane pre-insulated pipes are widely used for the transport of oil and chemicals and for district heating and cooling systems. Application of the continuous spray technique offers advantages compared to conventional discontinuous operations. Apart from the ability to produce pipes in any desired length, the reduction of foam density and reduction of the casing pipe thickness can also lead to cost savings for the pipe manufacturers.

Huntsman Polyurethanes have developed a new generation of pipe insulation systems for spray application that ensure an optimal balance between high reactivity, good mechanical composite properties and foam thermal resistance. New tailor-made base polyols providing a high intrinsic reactivity were designed and evaluated in comparative accelerated thermal ageing studies. A large difference was found between polyols based on conventional amine initiators and more complex initiator combinations. An outstanding performance was found for aromatic/amine co-initiated polyols. This is in line with previous findings showing that polymer aromaticity and cross-link density have a major impact on the thermal resistance.

Systems based on the best candidate base polyols were optimized in terms of processing performance using in-house pilot equipment to mimic the process of spraying onto a rotating pipe. In this way a substantial insight into processing aspects was gained. Based on this development, a fully water blown system and a dual blown system were tested on industrial scale equipment. Both processing performance and foam end properties fulfilled all the set requirements. For both systems a superior thermal resistance was achieved.

Introduction

A number of different production methods can be used for the production of pre-insulated pipes. In general, one can distinguish between two types of techniques, the discontinuous and the continuous production technique [1].

In discontinuous production techniques a pipe pre-assembly is made by positioning the steel inner pipe centrally in a slightly shorter casing pipe.

To keep the steel pipe in the centre of the casing pipe, distance holders are arranged around the steel pipe. At both ends the gap between the steel and the casing pipe is sealed off by end-caps that fit tightly around the steel and the HDPE casing pipe. The end-caps are equipped with holes for foam injection and air venting. In principle, pipes of any length up to approximately 16m can be used, but standard steel pipe lengths are 6, 12 and 16m.

Continuous pipe production techniques consist of two stages. In the first stage, the foam is applied on the inner pipe. In the second stage, the casing pipe is extruded or wound around the pre-shaped foam. Continuous techniques allow fast and consistent production of a large number of pipes of the same dimension, at comparatively low variable costs. Although the initial investment into these techniques may be higher, cost savings are achieved due to reduction of foam filling density and a reduced thickness of the high density polyethylene casing pipes. Compared to discontinuous pipe filling, the continuous pipe filling process requires a change of foam reactivity, viscosity build-up and cure characteristics which is achieved via different polyol systems technology [2].

continuous production techniques

allow cost savings due to

reduction of foam filling density

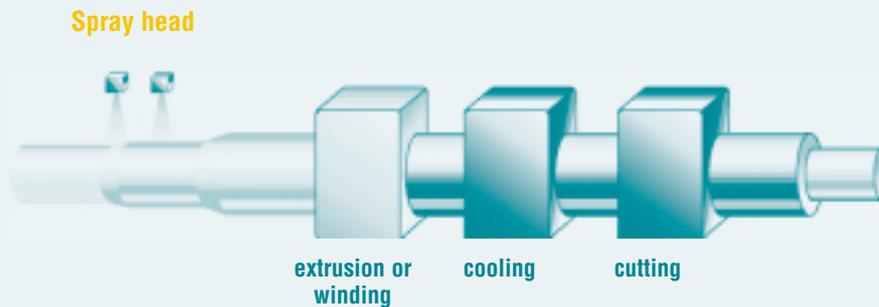
and reduced thickness of the HDPE casing

Spray onto continuously rotating pipe

For continuous pipe manufacturing, the continuous spray technique is particularly useful for medium and large diameter pipes. In the continuous spray technique the reacting foam mixture is sprayed on the outside of the rotating medium pipe, see Figure 1. Obviously the foam has to react very quickly, so that the foam adheres well to the pipe surface and does not spin off. Various layers of foam may be applied to obtain the required insulation thickness. Very uniform foam is created over an extremely short flow path. Virtually any insulation thickness can be produced by spray application. Large and long pipes can be insulated using small foaming machines.

Principle of a continuous spray line

Figure 1



Afterwards, the HDPE casing pipe is extruded or wound around the insulation. Alternatively, a polyurea coating can also be applied as casing using the spray technique. In comparison to discontinuous pipe insulation, applied foam densities can be lower because of smaller differences between overall and core densities. The HDPE casing pipe can be thinner since it does not have to withstand the high foam pressure that occurs during conventional pipe filling and hence, material savings are possible. In practise, the spray technique is particularly suited for large diameter pipes. Application of this technique to small diameter pipes may generate too much waste and hence may not be economical.

Applying the continuous spray technique requires specially formulated polyurethane foam systems. For processing reasons, high foam reactivity is demanded. This increased reactivity is often obtained through high catalyst dosing or through the use of amine initiated polyols that have a high intrinsic reactivity. However, it is well known that the presence of amine groups in the foam network can lead to a reduced thermal stability [3]. In particular the continuous long-term thermal stability might be considerably reduced. It is therefore a challenging target to develop polyurethane systems for this technique that both provide high thermal resistance of the foam and ease of processing.

Foam requirements

The combination of good mechanical composite properties and high foam thermal resistance is a particular requirement often encountered in pipe insulation. Obviously, required foam performance properties might vary depending on the end application of the pre-insulated pipes. In district heating applications, a continuous high temperature resistance is demanded for a service period of 30 years. Nowadays, also for oil pipelines that are insulated with polyurethane foam, there is a trend to demand an increased thermal resistance for polyurethane foam.

Table 1: Typical foam properties for pipe insulation foam

Property	Unit	Test method [4]	Requirement according to EN 253 [4]
Average cell size	mm	5.3.2.1	<0.5
Closed cell content	%	5.3.2.2	>88
Foam density	kg/cm ³	5.3.3	>60
Compressive strength	MPa	5.3.4	>0.3
Water absorption	% vol	5.3.5	<10
Shear strength before ageing			
axial at 23°C	MPa	5.4.2.1	>0.12
axial at 140°C	MPa	5.4.2.2	>0.08
tangential at 23°C	MPa	5.4.3	>0.20
Thermal conductivity at 50°C	W/m.K	5.4.5	<0.033
Calculated continuous operating temperature, 30 years	°C	5.4.4	>120

In Table 1, typical foam performance requirements are listed as specified by the European norm EN 253 which was developed for pre-insulated bonded pipe systems for underground hot water networks [4]. This norm is often taken as reference for applications outside district heating, e.g. for oil pipelines.

spray applied foam systems that can provide

continuous long term heat stability

require specific foam systems

Base polyols selection

The selection of base polyols to meet the requirements as outlined previously is one of the most critical steps in the formulation design. At a first glance high intrinsic reactivity to support optimal processing performance seems to be antagonistic towards the required long-term thermal integrity of the pre-insulated pipe composite.

On the other hand, the Huntsman Polyurethanes polyols grade range encompasses a wide variety of base polyols, which combined with a powerful set of mathematical and physical models linking foam end properties and polymer network parameters should enable us to achieve the target [5, 6].

It is well known that thermal properties such as softening temperature and mechanical strength at elevated temperature are related to cross-link density and polymer aromaticity, see Figures 2 and 3. With regard to long term thermal performance of pipe composites a working group of CEN/TC107 has established a method to determine expected lifetime.

Based on tangential shear strength measurements on pipe assemblies that are aged for at least 1000 hours at three elevated temperatures, as a minimum, and assuming an Arrhenius-type relationship, the Calculated Continuous Operating Temperature (CCOT) is determined [4].

Our investigations have shown a relationship between the CCOT and the polymer network parameters of foams based on aliphatic, non-amine containing polyols. This enables us to predict the long-term thermal performance of new systems for pipe composites. A comparison of predicted and measured CCOT values is shown in Figure 4.

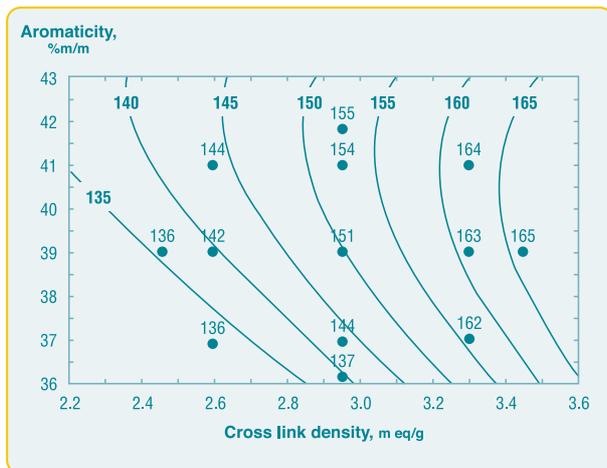


Figure 2: Contour plot representing the influence of the network parameters on the softening temperature (°C) of a c-pentane blown system for pipe insulation

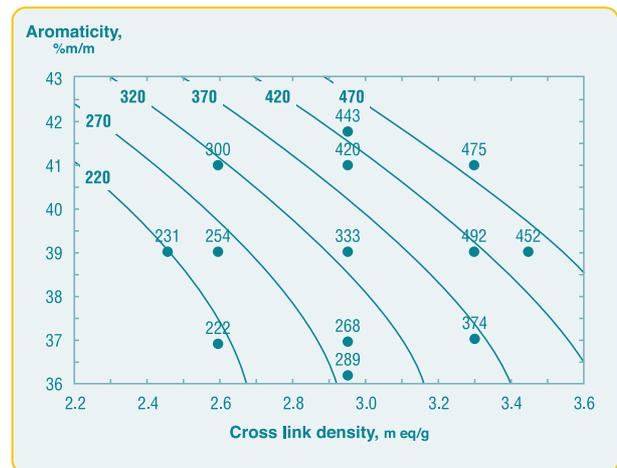


Figure 3: Contour plot representing the influence of the network parameters on the compressive strength (kPa), measured at 130°C for a c-pentane blown system for pipe insulation

For spray applied pipe applications, however, amine co-initiated polyols are used. As expected, in most cases this reduces the foam thermal resistance. Our studies have shown that adding around 20-40% of aliphatic amine co-initiated polyols to a standard pipe insulation polyol reduces the CCOT from around 130°C to 80-90°C, which clearly is unacceptable for most pipe insulation applications.

Yet, by increasing cross-link density and polymer aromaticity by combining specific aromatic/amine co-initiated polyols with high functionality aliphatic polyols, it is possible to retain a high thermal resistance. For a range of combinations, CCOT values exceeding the target of more than 120°C continuous resistance for a period of 30 years were achieved.

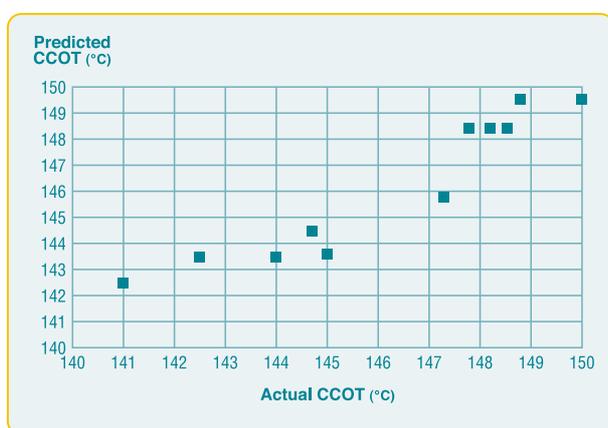


Figure 4: Actual and predicted Calculated Continuous Operating Temperature (CCOT)

Experimental

Materials

Based on the selection of polyether base polyols as described in the previous paragraph, a series of experimental polyether polyol blends were prepared and reacted with Suprasec 5005, Huntsman Polyurethanes' polymeric MDI. The usual ancillary chemicals were used.

Spray equipment

The foam systems were sprayed using a high pressure Gusmer H-2000-E machine with a GX-7 spray gun. The equipment allows a variable mixing ratio of polyol to isocyanate. Polyol and isocyanate were pre-heated and the temperature was maintained via temperature controlled hoses. To simulate industrial conditions, the foam was sprayed on in-house made rotating pipe equipment with outside diameters of 25 and 50 cm.

Property measurements

Foam samples were left for at least 24 hours to cure before cutting and carrying out mechanical tests. The test methods applied are described in the European Standard EN 253, drawn up by the Technical Committee CEN/TC 107 [4]. Other specific test standards are indicated in the tables. The foam softening temperatures were measured on a Perkin Elmer TMA7 Thermal Analysis System in penetration mode using a heating rate of 10°C per minute.

Huntsman Polyurethanes' polyols grade range
encompasses a wide variety
of base polyols

Results and systems properties

Development of HCFC-141b blown systems for spray onto a rotating pipe

CCOT calculations have shown that a polyol/MDI volume ratio of 100/100 will not allow a permanent thermal foam resistance to temperatures higher than 120°C, although the short term temperature resistance, e.g. expressed as softening temperature, can easily be above 120°C. We have therefore decided to use MDI/polyol volume ratios higher than 100/100.

Systems covering a density range from 40 up to 63 kg/m³ were developed. Based on our prediction model, we calculated for these systems a CCOT of 130°C to 140°C for 30 years. The foam systems were optimised in our laboratory using our spray facilities in combination with in-house made rotating pipe equipment. Processing parameters such as line and rotational speed and distance of the spray gun to the pipe appeared to be of importance for the processing of the foam system. Processing parameters such as pattern control disk selection (PCD), mixing module or components pressure are essential for the good mixing of the components and consequently for the fine cell structure as well as for the surface appearance of the foam. These parameters should be optimised and fine-tuned to each piece of spray equipment.

All systems proved to have a smooth processing performance resulting in foam that had a fine and regular cell structure in combination with a smooth surface, both in evaluations at our laboratory and on customer's equipment. Preheating of the pipes is advantageous as it improves adhesion between foam and steel and leads to faster build-up of mechanical foam strength. A typical line speed is 2-3m per minute, a typical foam layer thickness is approximately 5cm. A good interlayer adhesion was found when more foam layers were applied.

System Daltofoam TE24206/Suprasec 5005 gives foam with a core density of 40 kg/m³. System Daltofoam TE24207/Suprasec 5005 gives foam with a core density of 63 kg/m³. Both systems provide a CCOT of 130°C according to our model.

System Daltofoam TE24205/Suprasec 5005 was developed to withstand a further increased heat resistance. Therefore, a volume ratio polyol to MDI of 100/150 was selected. The increased level of isocyanate results in an increase of the calculated continuous operating temperature up to ca. 140°C for 30 years. Also the initial softening temperature increased significantly to ca. 170°C. A typical foam core density for this system is 61 kg/m³.

The system Daltofoam TE24205/Suprasec 5005 can also be applied at a lower volume mixing ratio polyol to MDI, e.g. 100/120. The foam core density will then reduce to ca. 52 kg/m³ and as a result of this, mechanical foam properties, e.g. compressive strength, will be slightly lower.

Foam properties that were measured on sprayed foam sample systems are listed in Table 2. Daltofoam TE24207 was also processed with Rubinate M, the American polymeric MDI equivalent to Suprasec 5005. Comparable processing behaviour and foam properties were obtained.

Table 2: Typical properties obtained with Daltofoam TE24205, TE24206 and TE24207 in combination with Suprasec 5005

Properties	Unit	Daltofoam TE24205	Daltofoam TE24206	Daltofoam TE24207
Volume ratio polyol/MDI	Vol/vol	100/150	100/125	100/125
Core density	kg/cm ³	61	40	63
Compressive strength	kPa	577	309	573
Closed cell content	%	95	94	94
Water absorption after boiling test	%	3.1	9.3	3.3
Initial softening temperature	°C	173	141	142
Thermal conductivity 10°C	mW/m.k	19.7	18.9	19.2
Calculated continuous operating temperature	°C/30y	140*	130*	130*

*estimated according to Huntsman Polyurethanes model based on selected polymer network properties

Development of water blown system for spray onto a rotating pipe

Because of the phase out of HCFC-141b, we have also developed a spray system that is fully water blown, Daltofoam TE44208 / Suprasec 5005. Again, the system was based on a careful selection of polyols that provide a high temperature resistance of the foam, but also offer a high intrinsic reactivity to support optimal processing performance. Together with a balanced catalyst package, the polyols contribute to a fast but smooth reactivity profile of the system required for the use of the continuous spray technique.

Processing parameters were optimised as discussed for the HCFC-141b blown systems. Similar line speed and layer thickness can be applied for the water blown system. The right selection of PCD, mixing module or components pressure should be fine-tuned on the individual spray equipment. The foam properties of the samples produced were assessed according to the EN 253 norm. Typical properties are summarised in Table 3.

At a core density of 61 kg/m³, a compressive strength of 509 kPa was recorded. High closed cell content and a low water absorption after a boiling test of ca. 3% was found. The high initial softening temperature of 160°C is already an indication of the high thermal stability of the system.

In order to determine the calculated continuous operating temperature, pre-insulated pipes were produced using the continuous moulding technique [2]. The continuous moulding technique allows the production of small diameter pre-insulated pipes, DN50 type pipes, that are required to carry out the accelerated ageing in order to calculate a continuous operating temperature, using high reactivity foam systems. A CCOT of 129°C for 30 years and 133°C for 20 years was found for the system Daltofoam TE44208/Suprasec 5005.

This foam system was evaluated at selected customer sites. The encouraging results obtained in our laboratory in terms of processing and mechanical foam properties could be repeated under industrial conditions.

Table 3: Typical properties obtained with Daltofoam TE44208 in combination with Suprasec 5005

Properties	Unit	Daltofoam TE44208
Volume ratio polyol/MDI	Vol/vol	100/150
Core density	kg/cm ³	61
Compressive strength	kPa	509
Closed cell content	%	94
Water absorption after boiling test	%	3.1
Initial softening temperature	°C	160
Axial shear strength at 23°C*	MPa	0.24
Axial shear strength at 140°C*	MPa	0.21
Tangential shear strength at 23°C*	MPa	0.36
Tangential shear strength at 140°C*	MPa	0.20
Calculated continuous operating temperature*	°C/30y	129

*measured on DN50 pre-insulated pipe composite

Conclusion

A new generation of pipe insulation systems was developed that can be spray applied onto a rotating pipe. These systems are based on careful selection of polyether polyols, which allow the formulation of foam systems that provide a long-term thermal integrity of the polyurethane pre-insulated pipe composite at continuous service temperatures of ca. 130°C and higher for a period of 30 years. For short-term exposure, the developed foam systems can even resist peak temperatures considerably higher than 130°C. The developed foam systems comply with the EN 253 norm.

The use of mathematical and physical models that link polymer network properties to foam end properties proved again a very powerful tool during the development process. It allows considerably reduced development time for new, tailor-made, polyurethane foam systems.

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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 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.

Thomas Bronnum

Thomas Bronnum completed his Chemical engineering studies at Danmarks Ingeniorakademi in Copenhagen, Denmark. After having held various positions within the urethanes industry he joined Shell Chemicals in 1989. In 1990 he was transferred to the Chemical Research Centre of Shell in Louvain-la-Neuve, Belgium, where he until 1993 was responsible for development and technical service activities in the field of polyurethane foams for pipe insulation. In 1993 he took up a position as department manager for the group dealing with application research, product development and technical service for rigid polyurethane foams. In December 1999 he joined Huntsman Polyurethanes, Belgium, as a technical liaison officer for rigid foams.

Tony AbiSaleh

Tony AbiSaleh received a BS degree from Ryerson Polytechnic University, Canada. He has been with ICI/CIL for 26 years and joined Huntsman Polyurethanes in 1999. He is currently the Technical/Production Manager at the Huntsman Polyurethanes site in Mississauga, Ontario, Canada.

The information, technical data and recommendations in this paper are, to the best of our knowledge, reliable. Tests performed and referred to in the paper do not necessarily represent all possible uses or actual performance as this is very much dependent on the particular circumstances the product or foam is used in. Suggestions made concerning the products and their uses, applications, storage and handling are only the opinion of the Huntsman Polyurethanes group and users should make their own tests to determine the suitability of these products for their own particular purpose. Huntsman Polyurethanes makes no guarantee or warranty of any kind, whether express or implied, other than that the product conforms to its applicable Standard Specifications. Statements made herein, therefore, should not be construed as representations or warranties.

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