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ASSESSMENT OF MINIMUM DESIGN TEMPERATURES OF 3-LAYER POLYOLEFIN COATINGS

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Abstract

The external coating process of pipes for gas and oil transportation is required to avoid corrosion during long term service. In the case of three layer polyolefin coatings the pipe is covered with a fusion-bonded epoxy (FBE) layer, an adhesive and a polyethylene (PE) or polypropylene (PP) “top coat” layer.

These polyolefins used as "top coat" layer in 3-layer coatings exhibit their mechanical properties only in a limited temperature range. Below a critical temperature the coating gets brittle and external mechanical load can lead to cracking and mechanical spalling of the coating. The lower temperature limit below which coating embrittlement might occur is of general interest in order to choose the appropriate coating for the intended temperature range.

This paper describes a basic impact test method suitable to assess the minimum design temperatures of 3-layer coatings.

Impact tests were performed by use of a 10 kg drop weight with a planar surface. Drop height was fixed to 1 m. The temperature of the specimens was varied until cracking or mechanical spalling of the coating was observed.

Utilization of pipe sections for testing gives reliable results including the effect of internal stresses of the coating and the influence of the extrusion process. Minimum recommended temperatures were determined for 3-layer coatings with PP, linear low density polyethylene (LLDPE), low density polyethylene (LDPE) and high density polyethylene (HDPE) top coats.

1. INTRODUCTION

Polyolefins are an important raw material for the pipe industry since a long period of time. They are mainly used as top layer of 3-layer coatings for steel pipes and as base material for plastic pipes. Due to their usage over already several decades much knowledge and experience about their mechanical properties and their limitations are available. The strength behaviour of polyolefins can be described well theoretically and also in practice while the fracture behaviour is very difficult to assess. This is caused by different mechanisms for the fracture behaviour at low and at higher temperatures. Additionally the susceptibility to fracture depends on many factors like: Dimensions, magnitude and speed of the load and the condition of the polyolefin material. Aged polyolefins e.g. show an enlarged susceptibility to fracture and brittle behaviour.

This paper covers brittle behaviour of polyolefins at low temperature. The background for the investigations were two causes of damage, where PP top coats of 3-layer PP coated steel pipes showed intensive cracking at low temperature.

Case 1:

3-layer PP coated pipes were installed trenchless below the river Danube. The outer diameter was 450 mm and the average thickness of the PP top coat was 10 mm. Cathodic protection measurements showed irregularities and an excavation was carried out to find the cause. During the excavation deep cracks in the PP top coat were found in an area reaching from 10 to 2 o'clock position like pictured in Figure 1. The pipes were installed in February 2008 and the case of damage was found in autumn 2008.

Figure 1: Cracks in area from 10 to 2 o'clock position for case 1

Case 2:

Another case of damage was observed in winter 2008/2009 also for 3-layer PP coated pipes. The pipes had an outer diameter of 500 mm and the average thickness of the PP top coat was 10 mm. Similar damage like before was observed at the free end of a trenchless installed part of the pipeline. Like it can be seen in Figure 2 cracking as well as spalling occurred. During installation the surface of the PP top coat was slightly damaged with deep scratches. This predamage was not the real cause for the observed cracking and spalling, because on a pipe stack there where found some not yet installed pipes where cracking occurred either (Figure 2).

Figure 2: Cracking at pipe at the end of a trenchless installation (left) and at a pipe on the pipe stack (right)

In both cases of damage the pipes were handled and installed during the cold season. Concerning the coating there were no problems observed during production and the coating material passed all required quality control tests. Analysis of damaged top coat excluded degradation of the top coat as cause for the damage, what could have led to a similar failure mode [1].

The observed embrittlement of the PP top coat was not totally unexpected, because in the literature [2, 3, 4, 5] embrittlement of the PP homopolymer is well know since a long period of time. The cause of the embrittlement of PP homopolymer at low temperatures is a glass transition temperature of about 0 °C [6]. Modifications of the polymer like copolymerization, blending or inclusion of additives improve the mechanical properties of PP at low temperatures [5, 7]. Generally PP is not used for very low design temperatures (down to –40 °C), but within the temperature range of Western Europe no further concerns regarding low temperature embrittlement of modified PP top coats have been reported. Furthermore in the common standards design temperatures much below 0 °C (Table 1) and in the product data sheets of the manufacturers no remark about embrittlement at lower temperatures can be found. Unfortunately the source for the minimum design temperatures and how they were determined is usually not provided. This necessitates verification of those values.

Table 1: Minimum design temperatures

Standard	LDPE	MDPE	HDPE	PP
ISO/FDIS 21809-1 [8]	–20 °C	–40 °C	–40 °C	–20 °C
Specification A	–20 °C	–40 °C	–20 °C	-

Within this paper a test method was developed to assess the minimum design temperatures of pipeline coatings. The work was performed with the focus on verifying common data and avoiding cases of damage in future by providing the customer appropriate coatings.

2. GENERAL APPROACH

2.1 Establishment of a suitable test method

According to literature [7] information on embrittlement of plastics can be obtained by performing tensile tests or impact tests at low temperature. In the case of tensile tests e.g. elongation at break gives information about embrittlement.

The only specified test where a coating system can be tested under an external load is impact testing. In Table 2 the general test conditions for impact testing on 3-layer PP coatings are summarized. All standards make use of a hemispherical head for the tests.

German standard DIN 30678 [9] mentions that polypropylene shows embrittlement during impact tests at low temperature. This is the explanation why 0 °C was chosen as test temperature.

Table 2: Overview of test conditions for impact testing

Standard	Test temperature / °C	Minimum impact strength
DIN 30678 [9]	0 ± 2	5 J/mm
ISO/FDIS 21809-1 [8]	23 ± 3	10 J/mm
NF A49 - 711 [10]	20 ± 5	10 J/mm
Specification B	0 ± 2 and 23 ± 2	12.5 J respectively 25 J

Figure 1: Impact testing according to DIN 30678 [9] with a 10 kg drop weight.

For first trials to determine the temperature, where 3-layer polypropylene coatings start to become brittle, specimens with an outer diameter of 168 mm, a wall thickness of 4.5 mm and a 3.3 mm thick top layer of longitudinally extruded PP were used like pictured in Figure 1. Despite the thickness the PP top coat was analogue to the cases of damage.

When performing impact testing according to DIN 30678 [9] with an impact energy of 9.81 J cracks were observed at a temperature of –30 °C, but at –20 °C no cracking took place. Increasing the impact energy to 98.1 J was leading to occurrence of cracking at –20 °C, while at –10 °C no cracking was observed (Figure 1). The results of the performed impact tests with a hemispherical head did not correlate with the situation observed in the field.

According to literature [11] charpy impact testing is a suitable method to investigate embrittlement of plastics. In ISO/FDIS 21809-1 [8] a notched impact test according to ISO 179 [12] at –20 °C is required for the PP top coat as well as for the PP adhesive. For the PP top coat and for the PP adhesive notched impact strengths of at least 3 kJ/m^2 are demanded.

As test for assessment of a minimum design temperature for 3-layer coatings notched charpy impact test appear unsuitable. In the field the mechanical load on the coating is different than in charpy impact tests and the 3-layer system may behave different than a notched specimen of the top coat. Furthermore there is no evidence that the coating has sufficient mechanical resistance at low temperature, when the notched impact strength at –20 °C is 3 kJ/m^2 or above as required in ISO/FDIS 21809-1 [8]. This makes the results of notched charpy impact tests concerning the embrittlement of 3-layer coatings difficult to interpret.

The motivation of the following work was to develop an easily applicable test method providing a good estimation of the threshold temperature, below which embrittlement of a 3-layer coating is likely to occur.

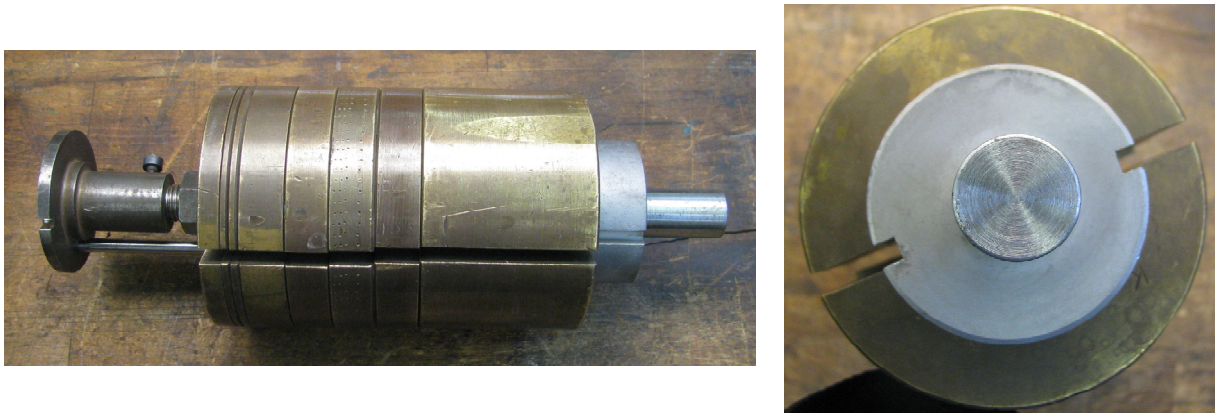

Figure 2: Modified drop weight

For further investigations on the missing correlation between the results in the field and the performed impact tests with a hemispherical head, different tools were used to damage the PP top coat at low temperature in laboratory. It was observed that cracking and spalling occurred most easily when the plain surface of a hammer was used to create the damage. According to this observation the drop weight was modified. The usually used hemispherical head was replaced by a head with a planar surface, where the edges were also rounded off (Figure 2). The diameter of the head is 21 mm. When using this modified head for impact testing, cracking and spalling were observed in a similar temperature range like in the field (Figure 3).

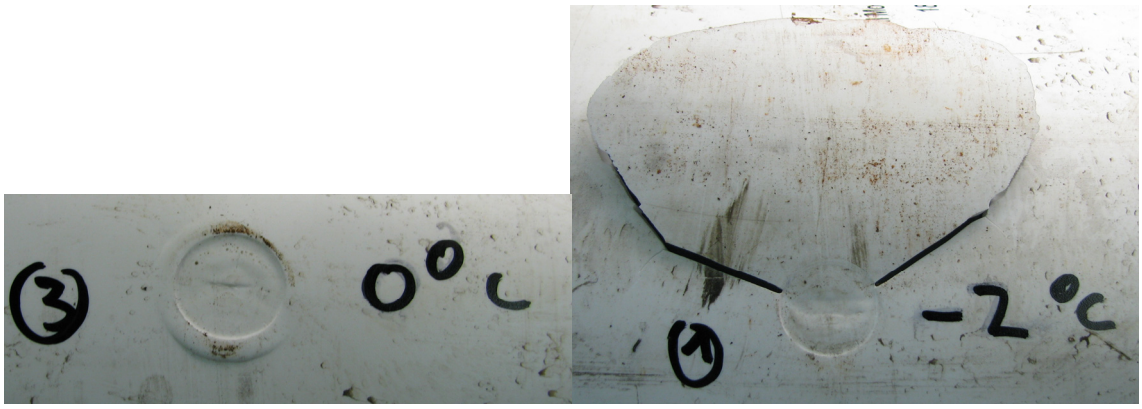

Figure 3: Impact testing of 3-layer PP coating with the modified drop weight at different temperatures. Test passed at 0 °C (left) and failed at –2 °C (right), because of cracking and spalling.

To assess embrittlement of 3-layer pipeline coatings the following test procedure was established: Pipe segments were tested at different temperatures with the above mentioned modified drop weight. For each temperature 3 impacts were performed at a drop height of 1 m and a drop weight of 10 kg. The temperature was varied until the lower temperature limit was found, where no cracking and spalling took place. This temperature is regarded as minimum recommended temperature for the coating system. When interpreting the results of the impact tests one has to be aware that the temperature where embrittlement is observed strongly depends on the weight of the drop weight used for testing. Generally, when the weight is increased cracking and spalling already take place at higher temperature.

As specimens pipe segments with 3-layer coating were used in order to be as close to the situation in the field as possible. Especially internal stresses in the coating like present in the field were kept in the specimens.

2.2 Results of modified impact tests

Impact testing with the modified drop weight was performed on 3-layer coated specimens with longitudinally extruded LLDPE, LDPE, HDPE and PP top coats. For polypropylene 3 different commercially available products offered for pipe coating were tested. PP1, PP2 and PP3 are polypropylene copolymers from different manufacturers. Furthermore sheets of the extruded top coat were tested. Additional 1-layer coated specimens, where the top coat was extruded directly on the blasted pipe surface, were tested for polypropylene.

Pipe segments of 219 mm in outer diameter coated with 1-layer respectively 3-layer PP coating were used for testing. The minimum temperatures, where no cracking and no spalling occurred for 3 impacts, were determined and are listed in Table 3.

For 3-layer PP coatings cracking and spalling were observed already at relatively high temperatures for all tested coating materials (PP1, PP2 and PP3). Surprisingly cracking takes places at much lower temperature for 1-layer PP coatings and PP sheets except for PP3. Generally 1-layer PP coatings and PP sheets give comparable results. In the product data sheets and in ISO/FDIS 21809-1 [8] a value of –20 °C is provided for the minimum design temperature. For the tested 3-layer PP coatings embrittlement is already observed much above this temperature.

The results lead to the conclusion that the composite in the 3-layer coating has a wide influence on the embrittlement. So far there are two different theories explaining this fact. The increased brittleness observed for 3-layer PP coatings can be caused by bonding the more or less flexible PP with an adhesive on the rigid FBE. Another explanation is that the adhesive is the cause for the brittleness at lower temperature. The adhesive is generally a functionalized PP and it is expected that functionalization causes dipolar interactions in the polymer chain. These additional dipolar interactions

are assumed to increase crystallinity and hereby make the adhesive more brittle than the unfunctionalized polypropylene.

Table 3: Minimum temperatures without cracking and spalling for PP.

Top coat	Specimen	Minimum temperature / °C	Average thickness of coating / mm
PP1	3-layer coating	+6 °C	3.0
PP1	1-layer coating	–12 °C	2.5
PP1	sheet	–10 °C	2.5
PP2	3-layer coating	+4 °C	2.8
PP2	1-layer coating	–20 °C	2.4
PP2	sheet	–15 °C	2.5
PP3	3-layer coating	0 °C	2.9
PP3	1-layer coating	0 °C	2.5
PP3	sheet	–5 °C	2.6

For PE top coats the minimum temperatures, where no cracking and no spalling occurred for 3 impacts, are listed in Table 4. As specimens pipe segments with an outer diameter of 168 mm were used. Like for PP the sheets show brittleness at lower temperatures than 3-layer coatings. The determined minimum temperatures for 3-layer coatings with different polyethylene top coats are in good agreement to the minimum design temperatures given in ISO/FDIS 21809-1 [8]. This confirms the reliability of the developed test method.

Table 4: Minimum temperatures without cracking and spalling for PE

Top coat	Specimen	Minimum temperature / °C	Average thickness of coating / mm
HDPE	3-layer coating	–40 °C	2.6
HDPE	sheet	< –50 °C	4.4
LDPE	3-layer coating	–27 °C	2.5
LDPE	sheet	–33 °C	2.5
LLDPE	3-layer coating	–35 °C	3.2
LLDPE	sheet	< –50 °C	2.9

2.3 Tensile tests

Tensile tests at different temperatures give further information about the mechanical properties of polyolefins. With the data obtained from tensile tests of polyolefins it should be possible to assess their tendency to embrittle at low temperature. This would be a further confirmation of the results of the modified impact tests.

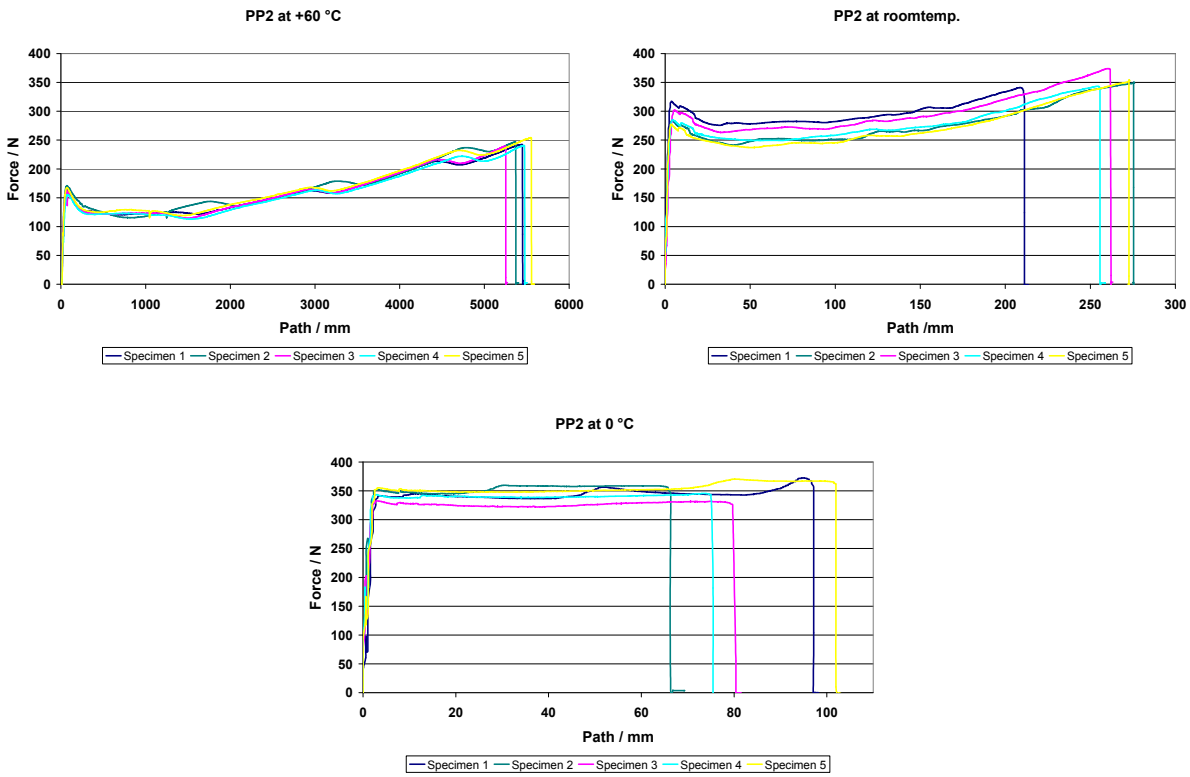

Figure 4: Force path diagrams for PP2 at different temperatures

For the polypropylene specimens PP1, PP2 and PP3 tensile tests were performed at +60 °C, room temperature and 0 °C according to ISO 527-2 [13] (speed of testing: 25 mm/min, specimen type: A5). As example the force path diagrams of PP2 are illustrated in Figure 4.

The temperature dependence of the yield strength (σ_y) and tensile strength at break (σ_B) for the different PP top coats are illustrated in Figure 5. For all polypropylenes the yield strength seems to increase nearly linearly with decreasing temperature between +60 °C and 0 °C (regression coefficient $R^2 \geq 0.98$). For the tensile strength at break this linearity is not present any more in every case.

The temperature where σ_B and σ_Y are equal is supposed to be critical, because this indicates that the polymer starts to become brittle. The fibres of the polymer are already stretched when the yield strain (ε_Y) is reached. When σ_B and σ_Y are equal the necessary force for stretching the fibres further is not increased any more. For the case when σ_Y is smaller than σ_B, further stretching of the fibres of the polymer requires an increased force.

From Figure 5 the temperature, where σ_B and σ_Y are equal can only determined for PP1. With the available data from the tensile tests no statement concerning the brittle behaviour of the PP top coats at low temperature can be made. We suppose that the evolved heat during stretching of the specimens was influencing the results of the measurements.

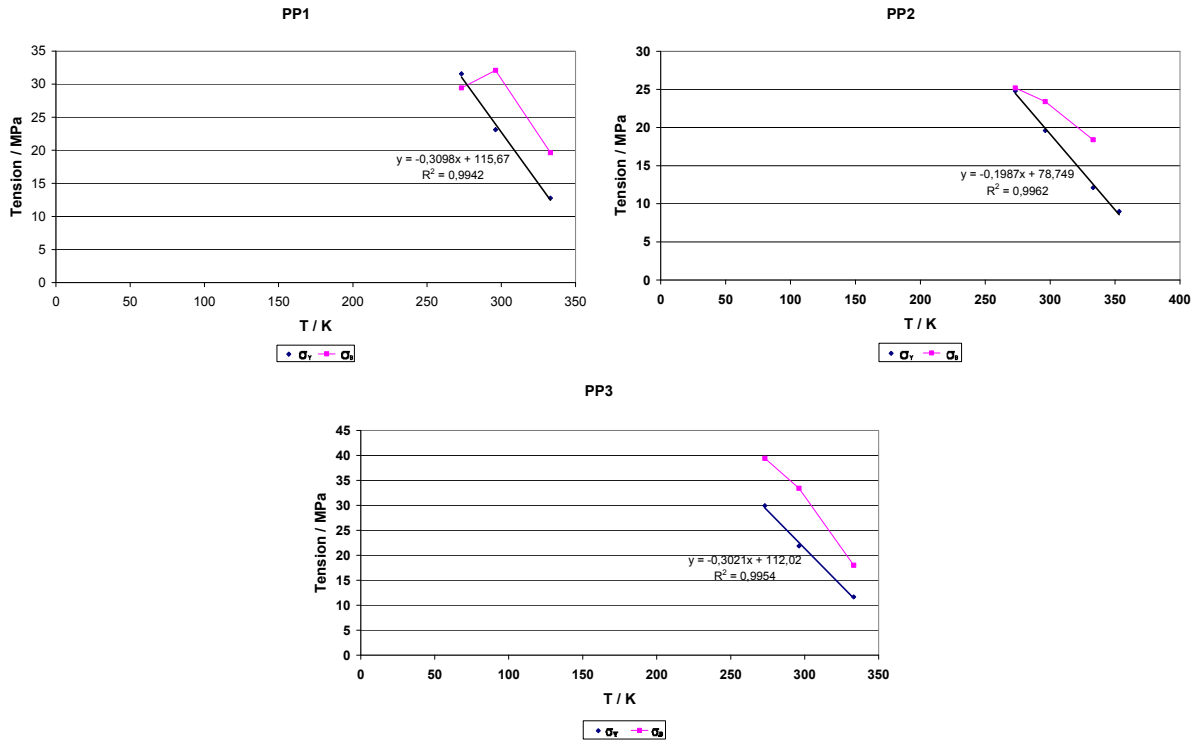

Figure 5: Temperature dependence of yield strength (σ_y) and tensile strength at break (σ_B) for PP1, PP1 and PP3

2.4 2-notch creep tests (2NCT tests)

2NCT testing provides information about cracking at elevated temperatures in presence of a wetting agent. This test is a modification of the full notched creep test (FNCT), which is commonly used to test the fracture mechanical properties of polyolefin pipes [14, 15, 16].

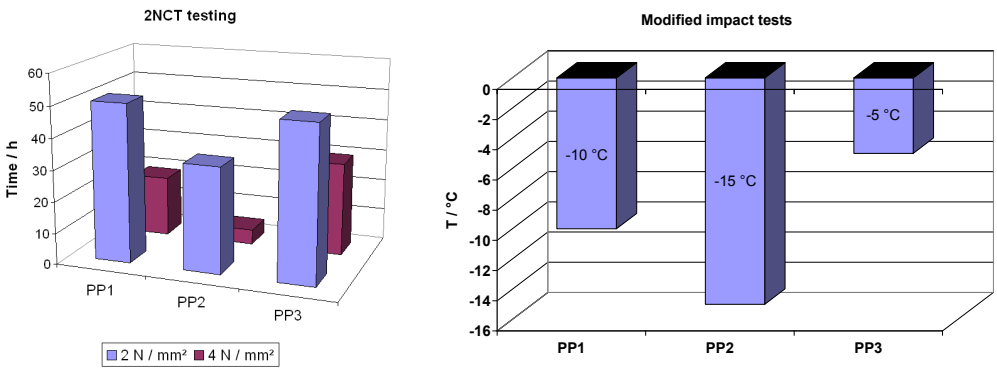

Figure 6: Missing correlation of 2NCT tests and modified impact tests. 2NCT tests: Time to failure (left). Impact tests: Minimum temperatures without cracking of extruded sheets (right)

The specimens for 2NCT tests were cut in radial direction. Testing was performed according to DIN EN 12814-3 [17] at 90 °C in an aqueous solution containing 2 wt.-% of the wetting agent NM5. The results of 2NCT testing of the 3 different polypropylenes at a stress of 2 N/mm^2 and 4 N/mm^2 are illustrated in Figure 7. PP1 and PP3 show similar susceptibility to slow crack growth while PP2 is more susceptible.

When comparing the results of the 2NCT tests and the modified impact tests (Figure 6) it becomes obvious that the results do not correlate. This can be explained by different mechanisms for the formation of the cracks.

3. SUMMARY AND OUTLOOK

A test method for assessment of minimum design temperatures of 3-layer polyolefin coatings has been developed and 3-layer coated specimens with common top coats have been tested. Additionally extruded sheets of these top coats have been tested. The test method consists of an impact test with a modified drop weight, where the usually applied hemispherical head is replaced by a head with planar surface (diameter approx. 21 mm). A drop weight of 10 kg and a drop height of 1.0 m gave representative results.

The test method has been approved for application in practice and the test yields repeatable results. The test results for the 3-layer polypropylene coatings are in good agreement to the situation observed in the field. For the 3-layer PP coatings brittle behaviour was found in both cases at about 0 °C. Furthermore the results for the different PE top coats are in good agreement to the values given in ISO/FDIS 21809-1 [8] for the minimum design temperatures.

The results of the modified impact tests demonstrate that the composite of the 3-layer coating can have a big influence on low temperature embrittlement. The embrittlement strongly depends on the weakest part of the composite. The different test performance of the polypropylene materials PP1, PP2 and PP3 when tested as extruded sheets was not expected. According to the manufacturers all of them are designed for usage down to –20 °C.

Tensile testing in the temperature range +60 °C down to 0 °C was not suitable to assess the lower temperature limit, where the coating material started to embrittle. This is still a topic of further investigations.

The results of 2NCT testing of the polypropylene materials did not correlate with the results of the modified impact tests.

Product information of the coating material itself might not be sufficient for choosing the appropriate top coat and adhesive. Performing additional impact tests with modified drop weight on 3-layer coated specimens is recommended in order to ensure sufficient mechanical resistance at low temperature.

4. LITERATURE

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