WELDING OF PEROXIDE, SILANE AND ELECTRON BEAM CROSSLINKED PE PIPES

Scholten F.L. and Wolters M., GASTEC N.V., Apeldoorn, The Netherlands

ABSTRACT

An investigation has been carried out into butt welding and electrofusion welding of PEX pipes, which had been crosslinked using the peroxide, silane and electron beam processes (PEXa, PEXb and PEXc respectively). A new hypothesis was set-up to explain the good weld quality of PEXa pipes electrowelded with regular commercial couplers produced from MDPE and PE100 materials.

This "mixed crystal hypothesis" combined with the existing "adhesion" and "flow process" theories provides a theoretical basis to explain the welding behaviour of PEXa with MDPE and PE100 materials, both in the form of pipe and thin foils. It is based on modern views about the importance of tie molecules needed for good long-term properties.

The mixed crystal hypothesis postulates, that the strength of a weld between MDPE or PE100 and PEXa depends on formation of "mixed crystals" which contain chain parts from both the uncrosslinked and the crosslinked material. In these mixed crystals, thought to be formed on the welding plane during crystallisation of the weld at around 115 °C, tie chains from both materials are incorporated. This provides the strong physical bond between the two types of material needed to explain the good weld quality.

To test the model, measurements on welded thin foils of MDPE and PEXa were carried out. Peel tests showed that for degrees of crosslinking of PEXa between 70 and 90%, this parameter does not affect the good weld qualities obtained. Moreover, the presence of residual uncrosslinked molecular chains in PEXa is not a necessary requirement to obtain a good weld strength.

The good weld quality of PEXa pipes electrowelded using MDPE and PE100 couplers is illustrated by Scanning Electron Microscopy. However, the quality of electrofusion welds with PEXb and PEXc pipes was unsatisfactory.

Butt welding of PEXa pipes to MDPE pipes is still very difficult, due to frozen-in extrusion stresses in the PEXa pipes, which lead to poor weld quality.

INTRODUCTION

In the past 3 decades, thanks to many optimisations, PE materials for gas distribution systems have shown an ever increasing quality with respect to slow crack growth and rapid crack propagation[1,2,3]. During this whole period, electrofusion and butt welding of PE pipes were found to be safe and reliable methods to make joints in gas distribution systems. That is why gas distribution companies are considering weldability of possible new polymer materials for gas pipes one of the most important criteria for using such materials.

In recent years, parallel to the development of improved PEs, there has been an increasing interest in crosslinked PE (in this publication denoted as PEX) pipes, mainly because of their superior resistance against notches. For many years, however, the use of PEX for gas distribution has been hampered by the generally accepted belief, that this material cannot be welded, because it cannot flow under the action of the welding pressure. Although mechanical couplers for PEX pipes already exist for a long time and are presently under test in the laboratory of the authors, welding is the preferred technique for gas distribution systems.

In spite of the reservations with respect to welding, as early as the early nineties, Fleig[4] performed electrofusion welding experiments on PEX pipes, with remarkable positive results. Also Bowman[5,6] and Harget et al[7] have reported good results for welding of PEX pipes. Between 1994 and 1996, a theory for explaining these results was set-up and tested by Scholten and Oesterholt[8] concurrently with additional testing by a working group under auspices of DVGW (Bonn, Germany)[9].

This paper discusses weldability of 3 types of commercially available PEX types (Table I).

Table I. Codes, crosslinking methods and required minimum degrees of crosslinking for PEX pipes

PEX type	Crosslinking method	Minimum degree of crosslinking
PEXa	Peroxides	75 %
PEXb	Silane	65 %
PEXc	Electron beams	60 %

Existing welding theories

For measuring and understanding the weldability of PEX, a critical evaluation of existing welding theories for uncrosslinked PEs is essential. In 1982, Brinken[10] presented and discussed 4 welding theories for PE:

1. Adhesion theory[11]
2. Diffusion theory[12]
3. Viscoelastic contact theory[13,14]
4. Flow process theory[15,16,17].

The adhesion theory emphasises the importance of (nearly) zero contact surface energy between two polymer materials. This condition is best met with two polymers with the same composition, like when welding PE to PE. It may be expected, that PEX or at least some types of PEX differ so little in this respect from PE, that this condition may also be met when welding PEX to PE. On the other hand, additives and impurities may degrade the weld quality, depending on their types and concentrations. This will be discussed further below.

Brinken already concluded, that diffusion in high molecular weight polymers is far too slow to explain the good welding properties of PE. However, he did stress the importance of the fourth theory, the flow process theory, which is based on work of Potente[15-17] in Germany. It describes the beads being formed during butt welding and shows, that the strength of butt welds increases with increasing welding pressure, until a plateau in the weld strength is reached and there is almost no influence anymore of the welding pressure. This was also noted by Kimura and Uematu[18].
The viscoelastic contact theory[13,14] applies mainly to adhesion or "welding" of rubbers and is not suited for explaining the welding behaviour of the materials investigated here.

Based on a critical evaluation of these theories[8], combined with the Lustiger model[19] on the structure of PE, a new theory for the welding of PE and PEX has been developed, the so-called Mixed Crystal Hypothesis.

THE MIXED CRYSTAL HYPOTHESIS

A model for the description of the welding of PEX must be based on modern views regarding the structure of PE and PEX. Moreover, for the purpose of gas distribution, the quality of the welds must not only be shown in terms of short-term properties, but also in terms of long-term (e.g. 50 years) properties. To be able to do so, it must be understood, which molecular factors govern the long-term properties of PE and PEX and from this, the conditions which need to be fulfilled for obtaining good long-term properties of welds can be derived.
To be able to show which parameters are important with regards to long-term strength of PE pipes, the model of Lustiger[19] is used. This shows, that the long-term strength of a PE material depends on the concentration of tie molecules in the material. Tie molecules are long molecules which interconnect the different crystals in the material and bind these firmly together.

No matter how good the quality of PE or PEX pipes is, the welds are possible weak spots in a distribution network, unless they are of similar quality as the pipes. Therefore, in Germany, the butt welding factor for PE gas and water distribution systems must be at least 80%[20] in long-term constant-load testing. Moreover, experience has shown that welding factors of about 100% are attainable if the beads are removed before constant-load tests. This indicates that similar qualities of weld and pipe are possible in principle and it means that the molecular structure responsible for good long-term pipe properties, i.e. the tie molecules, must - at least in part - also be present in the actual weld plane. For welding PE to PEX, this means that the weld plane must be bridged by tie molecules, connecting PE and PEX crystals firmly. More specifically, the Mixed Crystal Hypothesis postulates that the actual weld plane consists of a layer of mixed crystals, which contain chain parts from both the PE side and the PEX side and that these mixed crystals form the strong physical bonds needed to obtain a good long-term weld quality (Figure 1).
To explain the welding behaviour of PEX with MDPE and PE100, the model based on the existing adhesion and flow process theories for uncrosslinked PE is completed by the new mixed crystal hypothesis. The possible role of the residue of uncrosslinked molecules in PEX and the degree of crosslinking has also been investigated.

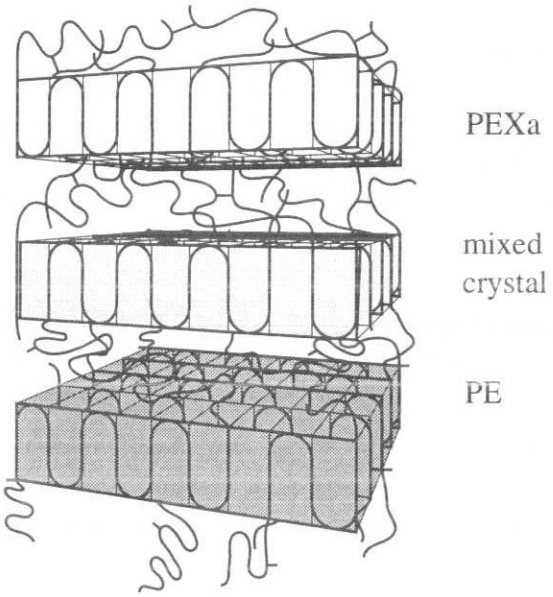

Figure 1. Formation of a layer of "mixed crystals" in the welding plane between PEX and PE, according to the mixed crystal hypothesis, derived from the Lustiger model[19]. PEX contains crosslinks and PE branches in the amorphous phase

EXPERIMENTAL METHODS

The investigated materials were PEXa pipes produced by Wirsbo A.G. in Heusenstamm (Germany) and Rehau A.G. in Erlangen (Germany), PEXb pipes produced by Watts Ocean n.v., Eerbeek (The Netherlands) and PEXc pipes produced by Hewing GmbH, Ochtrup (Germany). Electrofusion couplers produced by Georg Fischer AG in Schaffhausen (Switzerland), Friatec AG in Mannheim (Germany) and Plasson in Menashe (Israel) were used to weld the PEX pipes and MDPE and PE100 reference pipes.
Welding experiments on PEX were started on thin foils placed flat on top of each other and which were microtomed from 110 mm diameter pipes. The foils were 200 microns thick. Foils with 200 or 400 microns thickness were also cut from a 110 mm diameter yellow MDPE reference pipe, with MFI_5 of 0.85 gram/10 minutes at 190 °C.
For welding of foils, a thin aluminium foil was placed between the PE and PEX foils on one end. In this way, the end part could be used for clamping the sample for later peel testing. The foils were peel tested at a testing speed of 50 mm/minute using a 1196 Instron Tensile testing machine.

Electrofusion welds were made using couplers made of MDPE or PE100 and 4 types of 32 mm PEX pipes. All pipes were SDR11, except the PEXb and PEXc pipes, which had a wall thickness of 4.4 mm. From each weld, 4 strips were cut in axial direction. Each strip contained 2 welds, from the left-hand and the right-hand pipe. Thus, in each welded coupler, 8 samples could be evaluated. For comparison with PE, 32 mm SDR11 MDPE and PE100 pipes were welded and peel tested under the same conditions. For each test sample, the type of failure (adhesive or cohesive) was determined according to ISO 13954.

The welded samples were investigated using a Scanning Electron Microscope JEOL JSM840A. Etching of these samples, necessary for obtaining enough contrast, was carried out using the permanganate technique of Olley and Bassett[21]. Field Emission Scanning Electron Microscopy was carried out as well, on a chromium coated sample.

RESULTS

Welding experiments on foils

To obtain a first impression of possible differences in weldability, welding experiments were carried out on thin foils. PEXa foils with 70, 80 and 90% degree of crosslinking were welded to MDPE foils. The results of peel tests on these welds are presented in Table II. The weld was always stronger than the MDPE or the PEXa.

Table II: Peel tests on 200 micrometer thick PEXa foils welded to equally thick MDPE foils.

Gel content (%) of PEXa	Upper Yield Stress (MPa) Average (standard dev.)	Failures in PEXa	Failures in MDPE
70	17.0 (sd5=1.7)	0	5
80	19.5 (sd5=4.5)	0	5
90	17.8 (sd7=2.1)	2	5

Because most of the time, failure occurred in the MDPE foil, the experiments were repeated with the thickness of the MDPE foils doubled, but only on PEXa with 90% gel content. In

this set-up, the MDPE did not fail, but the PEXa, because this was thinnest. The results are shown in Table III. Here too, the weld was stronger than the weakest material.

Table III: Peel tests on 200 micrometers thick (xylene extracted) PEXa90 foils welded to 400 micrometers thick MDPE foils

PEX type	Upper Yield Stress (MPa) average (standard dev.)	Elongation[1] at break (%) average (standard dev.)
PEXa90	27.3 (sd3=8.1)	602 (sd3=557)
extracted PEXa90	19.1 (sd4=1.5)	136 (sd4=83)

Table III also shows, that PEXa foils, which were xylene extracted according to DIN EN579, to remove all uncrosslinked molecules and dried, can be welded.
Welds were then made on 200 micrometer thick foils of another type of PEXa and of PEXb and PEXc. In this case as well, the MDPE foils were 400 micrometer thick. The results are presented in Table IV.

Table IV: Failure type in the peel tests on foils of PEXa, PEXb and PEXc welded to MDPE foils. Welding pressure 0.06 MPa

Material	MDPE	PEXa	PEXb	PEXc
MDPE	C	C	C	C
PEXa	C	C		
PEXb	C		A*	
PEXc	C			C

C : cohesive failure mechanism (in the MDPE, if present)
A : adhesive failure mechanism (failure of the weld plane)
** : Even with a three times higher welding pressure of 0.18 MPa there is an adhesive failure mechanism in welds between PEXb and PEXb.*

Electrofusion welding with MDPE and PE100 couplers
Electrofusion welds were also made with PEXa, PEXb and PEXc 32 mm pipes and for reference with MDPE and PE100 32 mm pipes as well (Table V).

Table V. Electrofusion welds with PE100 couplers peel tested according to ISO 13954

Pipe type	% Cohesive fractures	Pipe type	% Cohesive fractures
PEXa manuf. A	75	MDPE	100
PEXa manuf. B	100	PE100	100
PEXb	13		
PEXc	25		

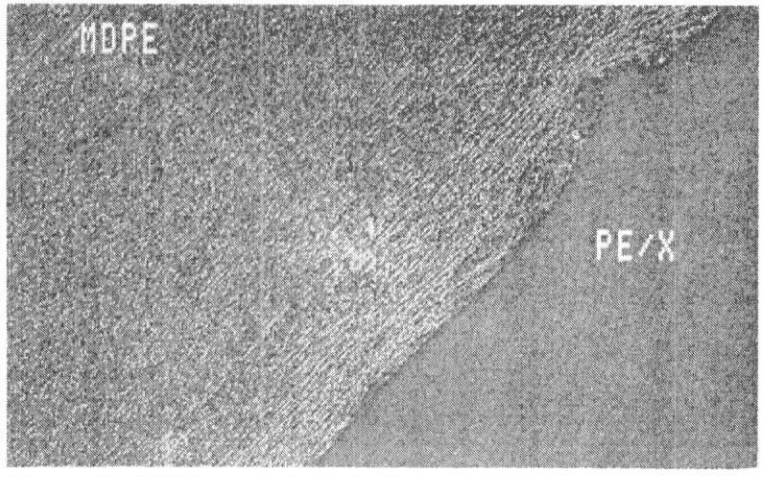

Figure 2. PEXa pipe (right) electrowelded using a MDPE coupler. SEM image, 230x.

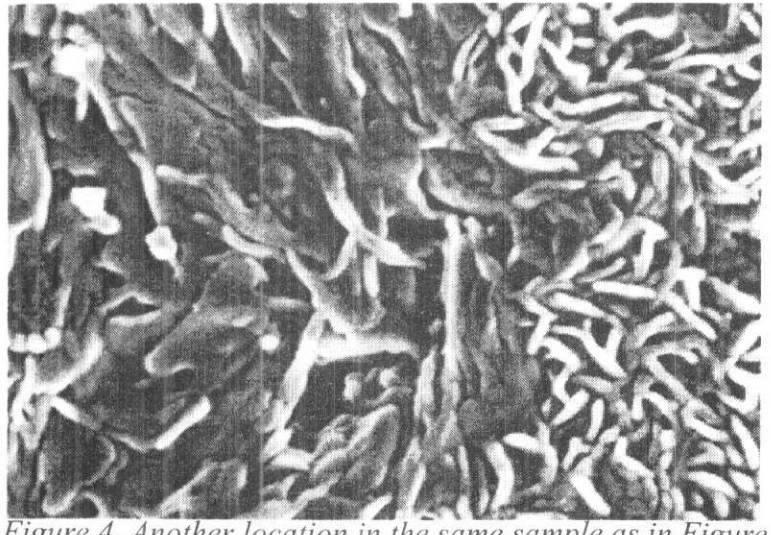

Figure 4. Another location in the same sample as in Figure 2. Field Emission SEM image, 50,000x

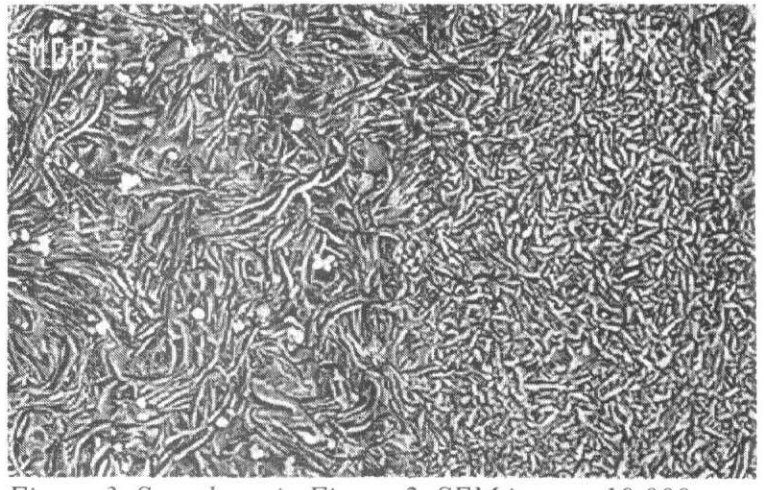

Figure 3. Sample as in Figure 2. SEM image, 10,000x.

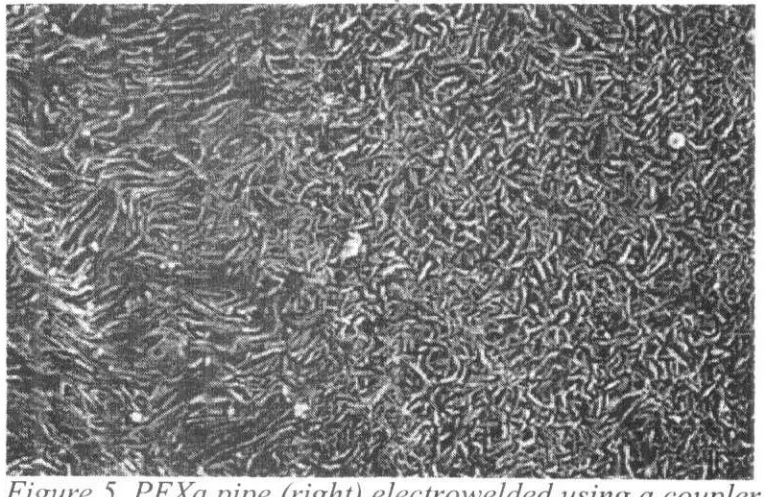

Figure 5. PEXa pipe (right) electrowelded using a coupler produced of PE100 material. SEM image, 10,000x.

Scanning Electron Microscopy (SEM)

Figure 2 shows an etched sample taken from a PEXa pipe electrowelded using a MDPE coupler. The coupler material in the vicinity of the welding surface shows flow lines, but the crosslinked pipe does not.

At higher magnifications (Figure 3), lamellar crystals[22] are observed in the coupler material, which is normal for MDPE materials. The lamellae are often curved and sometimes twisted, as described by Gedde et al[22,23]. Spherulitic superstructures are not observed. In the PEXa pipe, lamellar structures are present as well, although the length of the crystals is about three times as low. The white particles in the coupler material are carbon black pigment. The PEXa pipe was unpigmented. Recently, Bonten[24] has published similar SEM images for welds with PEXa.

Although there is a difference in structure between MDPE and PEX, the materials look very compatible, even at high magnifications. This is shown most clearly by using a Field Emission Scanning Electron Microscope, which is capable of reaching a much higher resolution than a traditional SEM. Figure 4 shows that again, there is no gap at the weld interface.

Other types of high resolution microscopy were used as well, like Transmission Electron Microscopy and Atomic Force Microscopy, but provided no additional information[8].

PEXa pipes electrowelded using couplers produced of PE100 material show a similar structure and compatibility between PE and PEXa (Figure 5).

Figures 6 and 7 show SEM micrographs of PEXb and PEXc pipes (right) respectively, electrowelded using a PE100 coupler. After etching, both PEX types show many small holes in the structure, as is obvious at low magnifications (not shown), due to components which have been dissolved in the etching solution. The lamellar crystalline structure is less clear in these cases, especially for PEXb. The PE100 material as well, as "internal reference" does not show such a well-resolved microstructure as in the case of welding with PEXa pipes. Obviously, the etching procedure for welds with PEXb and PEXc needs further optimisation.

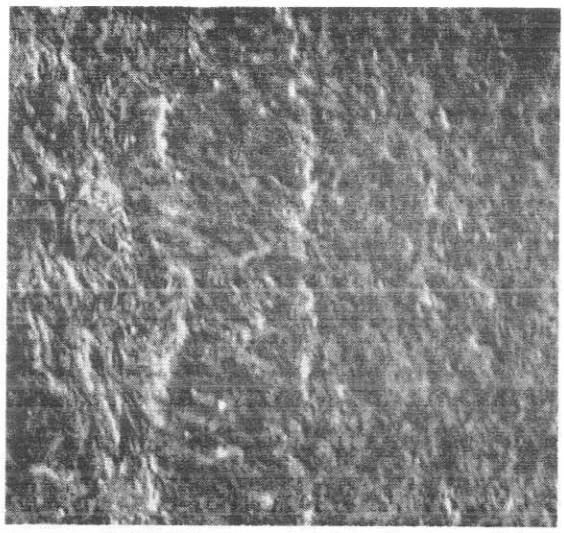

Figure 6. PEXb pipe (right) electrowelded using a coupler made of PE100 material. SEM image, 5,000x

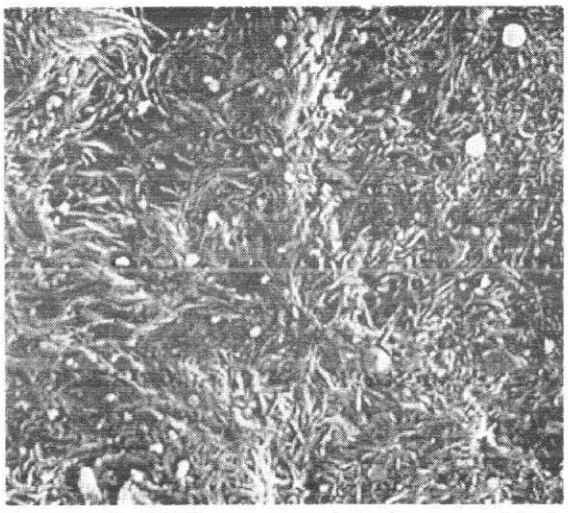

Figure 7. PEXc pipe (right) electrowelded using a coupler made of PE100 material. SEM image, 10,000x.

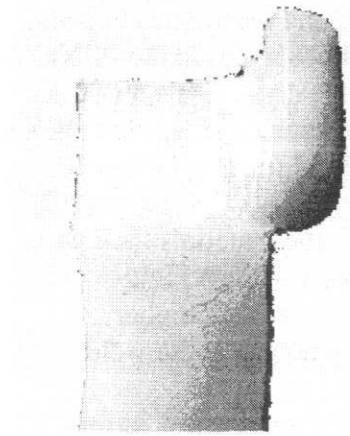

Figure 8. Failed butt weld between PEXa and MDPE 110 mm pipes after constant-load testing at 80 °C.

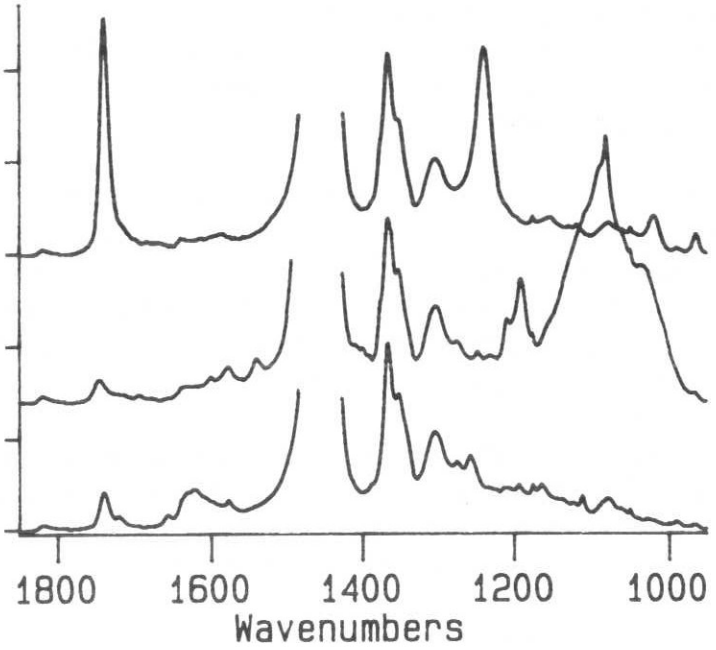

Figure 9. Part of the infrared spectra of PEXa (below), PEXb (middle) and PEXc. Bending vibrations at around 1,450 cm^{-1} omitted.

Butt welding of PEXa to MDPE

PEXa pipe (110 mm) was also butt welded at 210 °C and 0.18 MPa to MDPE pipes. The PEXa pipe does not form a bead. Dumb-bell samples were cut from the welded pipes and tested[25] at 4.0 MPa and 80 °C in a detergent solution (Arkopal N110) under constant load. Although the welds looked good, the failure times were very short (only a few hours). Figure 9 illustrates, that contrary to the situation for electrofusion welding of PEXa, the failed surface of the PEXa pipe end shows mainly adhesive failure. Only the vicinity of one of the beads of the MDPE (!) has adhered to the PEXa pipe.

DISCUSSION

That PEX can be welded to uncrosslinked PE was already proven more than 25 years ago. In 1971, Vakula et al[26] have found that 100 micrometers thick gamma radiation crosslinked LDPE foils can be welded to uncrosslinked LDPE foils, provided the degree of crosslinking is not too high. This is supported by Table IV, which shows results of peel testing on PEXc foils welded to MDPE foils. PEXb foils welded to MDPE foils show cohesive failures as well. PEXa and PEXc foils can even be welded to themselves, but PEXb foils not.
Even xylene extracted PEXa foils (effectively 100% crosslinked samples) can be welded. Consequently the presence of residual uncrosslinked molecular chains in PEXa is not a necessary requirement to obtain a good weld quality of foils.
SEM images show a very good compatibility between PEXa and MDPE (or PE100) in welds, both as foil and as electrofusion welded pipe. The lamellar crystals of MDPE or PE100 and PEXa are near enough to each other in the weld plane, to make the formation of mixed crystals conceivable. The impossibility to image molecular chains directly prevents delivery of direct proof of the mixed crystal hypothesis.

Peel testing of welded foils can only give a first indication of the possibility for welding PEX materials. Peel testing of electrowelded PEX pipes is a more severe test. Table 5 shows that

under these practical conditions only PEXa pipes have a satisfactory electrofusion quality. The strength of electrofusion welds of PEXb and PEXc pipes is not acceptable.
These differences cannot be explained by the mixed crystal hypothesis alone. As determined by DSC measurements, PEXa, PEXb, PEXc and MDPE show only marginal differences in melting and crystallisation behaviour. Therefore, it is not expected that this will lead to large differences of these materials to form mixed crystals on the welding plane. Differences in the degree of crosslinking of the three PEX types (Table I) does not play a part either.
The most likely explanation for the differences in weld quality is related to the adhesion theory and more specifically to differences in composition. Infrared Spectroscopy (Figure 9) shows, that while PEXa exhibits an infrared spectrum very similar to uncrosslinked PE, PEXb contains a rather high concentration of silicon containing groups, which are residues of the crosslinking process and that PEXc contains ethylenevinylacetate (EVA), which was confirmed by the manufacturer.
These polar "impurities" may have a deteriorating effect on the quality of electrofusion welds produced with PEXb and PEXc pipes. This is in line with results of Potente[17], who found that even a low content of calcium stearate (0.4%) has a detrimental effect on the weld quality of PE.

Butt welding of PEXa pipe was unsuccessful. Due to frozen-in extrusion stresses in the PEXa pipes set free during heating, inward (towards the pipe bore) deformation of the pipe wall at the molten ends occurs. Consequently, the pipe ends are not square to the centre line of the pipes any more and although MDPE easily compensates for this by viscous flow, PEXa does not. This leads to a non-uniform welding pressure and consequently to poor weld quality except for those locations, where the welding pressure was indeed high enough. This effect does not occur during electrofusion welding of PEXa pipes, because then, only a thin surface area of the pipe is molten and there is only negligible stress release in the pipe.

CONCLUSIONS

The degree of crosslinking between 70 and 90% does not affect the weld quality of PEXa foils and the residue of uncrosslinked chains in PEXa is not a necessary requirement to obtain a good weld strength. This supports the mixed crystal hypothesis, which postulates that the crosslinked chains themselves can form mixed crystals on the welding plane. On the other hand, this hypothesis could not be proven directly, due to a lack of adequate high resolution imaging techniques.
Electrofusion welding of PEXa pipes provides good results, but electrowelding of PEXb and PEXc pipes does not, probably due to polar additives and residues of the crosslinking process respectively.
Butt welding of PEXa pipes to MDPE pipes is difficult, not because of fundamental problems with welding of PEXa, but due to the release of extrusion stresses which is typical for butt welding and which does not play a part in electrofusion welding.

ACKNOWLEDGEMENTS

A large part of the paper is based on an investigation which was carried out between January 1994 and December 1996 on behalf of the DVGW in Bonn (Germany). Another part was carried out on behalf of EnergieNed in Arnhem (The Netherlands) under Contract No 96.G.A02.022. The financial support of these organisations is gratefully acknowledged.
The authors wish to thank Mr. R.B. Zefrin, Mr. M.G. Smeltink, Mr. F.G.E.B. Weyn and Mr. R. Rouwenhorst at GASTEC for careful microscopic, spectroscopic and mechanical

measurements and welding. Mr. H. Nijland at the University of Groningen, The Netherlands is thanked for Field Emission Scanning Electron Microscopy.

REFERENCES

[1] Scholten F.L., Rijpkema H.J.M., "Field Failures in Polyethylene Gas Pipes - Analysis versus Lifetime Prediction", Proc. Plastics Pipes VIII, Eindhoven, The Netherlands, Sept. 1992, The Institute of Materials, London.
[2] Scholten F.L., Zefrin R.B. and Smeltink M.G., "Evaluation of European (GERG) PE materials", Proc. IEA Int. Conf. on Natural Gas Technol., Berlin, Sept. 1996, BGW/DVGW, Bonn, Germany.
[3] Scholten F.L. and Wolters M., "GERG Materials Bank of PE gas pipe grades - recent developments", Proc. Int. Gas Res. Conf., San Diego, USA, 8-11 Nov. 1998, The Gas Research Institute, Chicago, USA.
[4] Fleig W., gwf/Gas-Erdgas, 131, 10/11 (1990), 477 (in german).
[5] Bowman J., "Fusion joining of cross-linked polyethylene pipe", Paper 13 in "Advances in joining plastics and composites", The Welding Institute, Bradford, Yorkshire, UK, June 1991.
[6] Bowman J., "Advances in Joining Plastics and Composites", TWI, Bradford, 1991.
[7] Harget D.C., Skarelius J., Imgram F., Crosslinked Polyethylene - extending the limits of pressure pipe system performance", Proc. Plastics Pipes VIII, Sept. 1992, Eindhoven, The Netherlands, The Institute of Materials, London.
[8] Scholten F.L. and Oesterholt D.J.A., "Schweisseignung und Kerbunempfindlichkeit von Rohren aus vernetztem Polyethylen (PEXa), GASTEC report GDT/MAT96319/Sch/052.V, December 1996 (in german).
[9] Wesemann U., gwf-Gas/Erdgas 138 (1997), 285-288 (in german).
[10] Brinken F., "A theoretical approach to the practical problem of jointing different PE grades", Plastic Pipes V, 8-10 Sept. 1982, York, The Institute of Materials, London (not included in the Proceedings).
[11] Kaelbe D.H., "Physical Chemistry of Adhesion", Wiley-Interscience, New York (1971).
[12] Voyutskii S.S., "Autoadhesion and Adhesion of High Polymers", Interscience, New York.
[13] Anand J.N., Karam H.J, J. of Adhesion 1, (1969), 16.
[14] Anand J.N., Dipzinski L., J. of Adhesion 2, (1970)16.
[15] Potente H. und Reinke M., Maschinenmarkt, 87, (1981), 172 (in german)
[16] Potente H., Kunststoffe, 67, (1977), 98 (in german).
[17] Potente H., Kunststoffe, 70, (1980), 193 (in german).
[18] Kimura H., Uematu M., "Autoadhesion of solid high polymers", Plastic Fabrication and Uses, 6 (2), (1969), 21-30.
[19] Lustiger A., "Tie molecules in Polyethylene, Final Report", Gas Research Institute, Chicago, USA, GRI-85/0129, (1985).
[20] Richtlinie DVS 2203, Teil 1, Germany.
[21] Olley R.H., Bassett D.C., Polymer, 23, (1982), 1707.
[22] Rego Lopez J.M., Gedde U.W., Polymer, 29, (1988), 1037.
[23] Conde Braha M.T., Iragorri Sainz J.I, Gedde U.W., Polym. Bull., 22, (1989), 280.
[24] Bonten Ch., Proc. ANTEC98, Atlanta, GA, USA, p. 1072-1077, Soc. Plastics Engineers, Brookfield CT, USA.
[25] Scholten F.L., Pisters J. and Venema B., Polym. Testing, 8, (1989), 385.
[26] Vakula V.L., Mishustin V.I., Gorchakova V.M. and Voyutskii S.S., "The effect of radiation-chemical crosslinking of Polyethylene on its capacity to form autoadhesion bonds during seam welding", Polym. Sci. USSR (1972), 105-113, translation from: Vysokomol. soyed. Ser. A, 13, No 1, (1971), 92-98.