

The butt-fusion welding of PVDF and its composites

Part 1 *The butt-fusion of PVDF pipe systems*

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A wide range of mirror plate butt welding conditions were used to join PVDF pipe to pipe and to an injection moulded fitting. The microstructures of the welds were characterized by microtomy and by transmitted light microscopy, and the mechanical properties by tensile testing. The results show that high integrity pipe to pipe joints can be produced for a relatively wide range of welding conditions, and that the integrity of pipe to fitting joints may be reduced because of the adverse influence of the moulded part on weld bead geometry.

1. Introduction

This paper reports on a survey of the effects of varying welding conditions on the mechanical properties of butt fusion welds in thermoplastic polyvinylidene fluoride (PVDF). PVDF, which is easily moulded and extruded, has become increasingly popular since its initial appearance in the early 1960's when it was used primarily as a highly chemically resistant coating. It is increasingly used for the fabrication of pipeline systems intended for chemical plant applications.

The integrity of the joints in a system is of prime importance, as weak joints can dramatically reduce the working performance of the system, and render any inherent advantages of the base material ineffective. This paper is therefore primarily concerned with the properties of welded joints between sections of PVDF pipe and between pipe and injection moulded fittings.

The pipe used had an outside diameter of 63 mm and a wall thickness of 2.6 mm, and had been extruded from SOLVAY'S SOLEF X10N general purpose grade. This has a melt flow index of 10 to 20 g (10 min)⁻¹ under 10 kg at 230°C, and it has been reported as being suitable for welding using hot gas, spigot and socket, and butt fusion welding. The pipe was cut into 50 cm sections and welded on a Haxey mk II welding machine, using

a thermostatically controlled PTFE backed hot plate. The welding machine employed on-axis hydraulic pressure supplied by a compressed air line which could be accurately controlled. Soak, welding and cooling times of 30 sec, 5 min and 10 min, respectively, were used. Four dumb-bell shaped tensile bars were cut at 90° intervals around each weld and tested on an Instron tensile testing machine at a constant crosshead speed of 0.5 cm min⁻¹. The weld bead was left on in all cases. The tensile strengths of all welded bars were compared with the strengths of otherwise identical unwelded bars, the ratio of the former to the latter being known as the weld factor. This follows the classification first defined by Menges and Zohren [1]; however, in those instances where a specimen did not fail at the weld, but in the gauge region away from the weld, the weld factor was then defined as equal to one, as the weld was manifestly as strong as the unwelded material.

The welding pressure (P_w) was held constant at one of a series of predetermined values and welds made at a number of different temperatures (T_w). These ranged from 180°C, just above the nominal melting point of PVDF, to 250°C, some 30°C below the point at which initial degradation begins. This was also near the upper working limit of the commercial hot plate used.

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2. The structure of PVDF

PVDF is a semi-crystalline polymer with repeat unit $-(\text{CH}_2-\text{CF}_2)-$, containing about 60% fluorine by weight. It is highly resistant to chemicals and is not degraded by irradiation [2], properties which lead to its initial uses as dispersion coatings and in the aerospace industry in the 1960's. The discovery that it has the highest pyroelectric constant of any known polymer [3], and also a very high piezoelectric constant [4, 5] has resulted in its widespread use in systems which involve transducers, especially as recent developments [6] have resulted in increased electrical responses. Its ease of moulding, coupled with superior mechanical and chemical properties, have been increasingly exploited in the chemical industry, where it is now an accepted engineering material [7]. A number of commercial pipeline systems are available which can be joined using most of the commonly known methods, and an area of increasing interest is in the development of components manufactured from reinforced PVDF.

The crystalline structure of PVDF can be modified between four principal forms. The most common of these is the α -form, also known as form II; then there are the β and γ forms, I and III, respectively, and recently a fourth form, σ or form IV, has been isolated. The currently accepted solution is that the cell of form II is orthorhombic with a TGT \bar{G} configuration [8, 9]. Form I is also orthorhombic, but with an all-trans configuration [8, 9]. Form III was first discovered by Cortili and Zerbi [1] and Natta *et al.* [11], and shortly afterwards its production was reported by Doll and Lando [12]. Recent X-ray data suggests that the unit cell of form III is orthorhombic and polar [13] with a chain sequence of T₃GT₃G. Form IV, discovered comparatively recently, is a polar version of form II, and is obtained as a result of the orienting action of high electric fields.

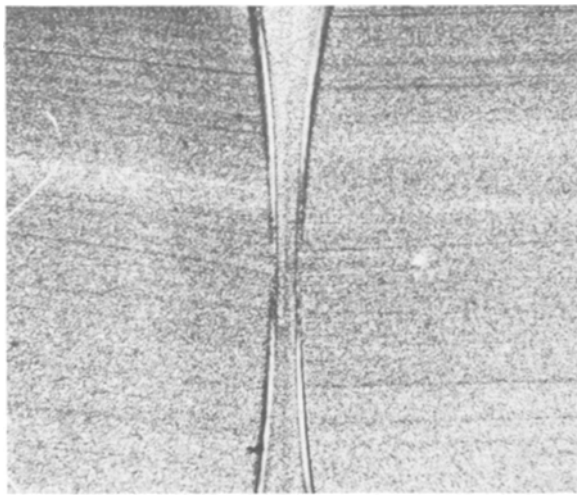
The study of the morphology of PVDF has produced some highly interesting and at times, unusual results. When the polymer is crystallized from the melt under atmospheric pressure, two discrete types of spherulite are formed; the larger of the two is form II, but some controversy exists over the composition of the smaller type, which are less common and generally seen only at high temperatures. The first report of this spherulite type, by Gianotti *et al.* [14], suggests that they are form III; but a more detailed study by Prest and Luca [15] favours form I as the more likely struc-

ture. This matter is as yet unresolved, although some results [16] tend to confirm the form III suggestion. However, Lovinger [17] notes that the morphological features are occasionally disturbed, and also that there has been the possibility of another phase being present. Hence, this species is currently referred to as "mixed spherulites". As the polymer crystallizes from the melt, two types of crystalline transformation can occur. In the first type form II is initiated at the growth fronts of crystallizing mixed spherulites [16, 18]. This phenomenon is not unique to PVDF, and has been seen in other thermoplastics, such as isotactic polypropylene and polyamides. However, the second type of transformation is of greater interest and is apparently only found in PVDF. The transformation, which takes place in the solid state, is of form II spherulites to a higher melting form which was initially thought to be form I [14], but now appears to be form III [15, 17]. Prest and Luca [15] suggested that the transformation starts at the nuclei of already existing form II spherulites and proceeds radially outwards. The recent work by Lovinger [17] disagrees with this, preferring the explanation of an initiation at the peripheries of form II spherulites and a growth inwards towards the nuclei, but there is also evidence of limited nucleation initiation at very high temperatures.

3. Microstructure of butt-welds

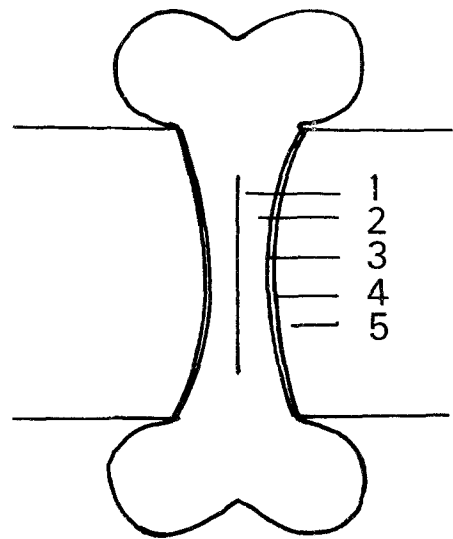
Thin sections (approximately 7 μm thick) were taken across butt fusion welds in a plane normal to the weld surface and parallel to the pipe axis, using a sledge microtome. The sections were examined in transmitted light under crossed polars. Welds formed at varying welding conditions were examined in order to obtain a classification of weld microstructure.

A typical micrograph of a weld region is shown in Fig. 1, taking as an example a weld temperature and pressure of 200°C and 1.2 bar, respectively. Some features are immediately apparent. The weld region is well defined and its perimeters are marked by a sharp contrast in microstructure. A thin dark line runs down the middle of the weld, along the contact plane of the two weld surfaces. Just inside the weld region perimeter line on each side is a thin region of different microstructure to the bulk material. Between this region and the central weld line the material appears to be of essentially the same structure to the bulk pipe material, and most of the weld region is comprised of this



(a)

500 μ m

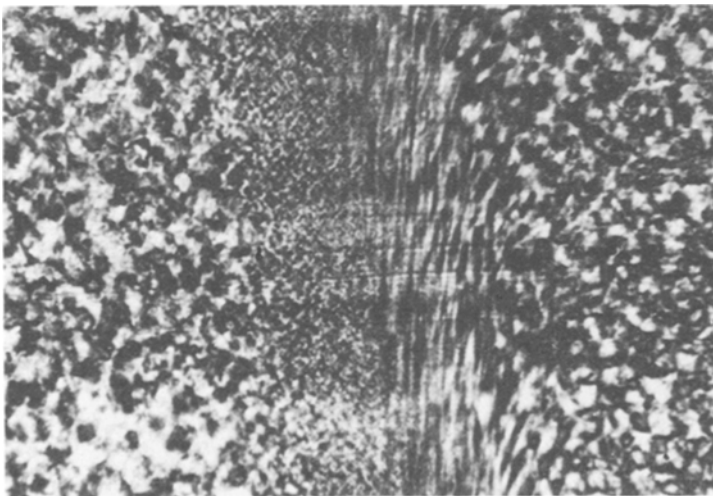


(b)

Figure 1 Light micrograph of a microtomed section taken across a mirror plate butt-weld produced at a welding temperature and pressure of 200°C and 1.2 Bar, respectively, with adjacent schematic diagram of the butt-weld and distinctive regions of different morphologies.

material. A higher magnification micrograph of part of a weld (Fig. 2) shows some of these characteristic features in greater detail, taking for example a welding temperature and pressure of 200°C and 0.6 bar, respectively. Four distinct zones can be identified from left to right across the micrograph; the first zone, which corresponds to material inside the weld, consists of a large scale

crystalline structure, similar to the structure of the bulk pipe material, which can be seen in the fourth zone (far right hand side). These two zones are denoted zone 2 and zone 5, respectively, with the central skin (not seen on this micrograph) denoted zone 1. In between zones 2 and 5 are two adjacent and distinct zones, 3 and 4, which comprise the perimeter line that defines one limit of the weld



2

3

4

5

20 μ m

Figure 2 Light micrograph of a microtomed section taken across a mirror plate butt-weld produced at a welding temperature and pressure of 200°C and 0.6 bar, respectively.

region; this line is clearly seen in Fig. 1. Zone 3, to the right of the large scale structured zone 2, consists of much smaller scale spherulitic growth. It is likely that these spherulites, crystallizing from slightly below the melt temperature, are of form III, and are nucleated at the peripheries of the bulk weld material (zone 2) following the mechanisms suggested recently by Lovinger [17] for form II to form III transformations. Zone 2, crystallizing from the melting point or above, would be expected to consist of form II spherulites [16, 18]; this explains the similarity in structure with zone 5, the bulk pipe material, which is known to consist of form II material. It should also be noted that the form II to form III transformation takes place in the solid state, at a temperature of about 155°C, and this is consistent with the likely temperature of zone 3, due to the steep temperature gradient away from the welding surface which has been found for other thermoplastics [19].

The small scale structure of zone 3 changes abruptly to the highly aligned structure of zone 4, situated at the extreme outer limit of the weld region. The structure of this zone, which has been identified in other butt fusion welded thermoplastics, is of particular interest, as in many weld failures it contains the fracture path, the crack initiating at the intersection of this zone with a pipe surface. At the time that the weld is formed this zone consists of softened material, below the melting point, which is subjected to large shearing stresses as the welding surfaces are brought together under pressure. As the weld cools, the preferred molecular orientation develops in this zone in a direction parallel to the welding plane and orthogonal to the subsequent applied tensile stress. Examination of Fig 2 shows this alignment very clearly. The material is at a temperature of around 147 to 150°C, the softening point of PVDF, which correlates with the suggestion that zone 3, the next zone in towards the welding surfaces, is at the form II to form III transformation temperature of 155°C.

Zone 1, the dark line seen in Fig. 1 running centrally down the length of the weld from one surface to the other, has been identified as a characteristic feature of butt fusion welds in other thermoplastics [19]. It marks the plane of contact of the two welding surfaces. As a finite time (of the order of 3 sec, but possibly longer) elapses between the removal of the hot plate and the mating of the two surfaces, a skin forms on each

surface, made of rapidly cooling material exposed to the air. The line is more pronounced in an area around the centre of the pipe walls, some distance in from each surface, and may be explained in terms of material flow during welding. The skin would be expected to form equally over the entire pipe wall welding surface, and is in the process of formation as the two surfaces are brought together; at this point, the two skins come into contact to form zone 1. Immediately to either side of zone 1 is zone 2, in the main weld region; this consists of cooling, but still very hot, material. As the pressure is held on this hot material flows symmetrically towards the two (inner and outer) pipe surfaces, flowing along the sides of the essentially stationary skin. However, the material flow follows a mass gradient which increases from the centre outwards, that is, minimum flow occurs in the centremost region. This effect is enhanced by the fact that the hottest material will be pushed up into the weld bead. So, away from the central region there is a flow of hot material past the skin, whilst in the central region there exists essentially static material slightly cooler than that in the outer regions. Away from the central region the hot flowing material may be of a sufficient temperature to melt all or part of the skin, whilst in the central region this will not be the case. This effect is likely to be more pronounced at higher welding temperatures, which would tend to minimize zone 1 formation. It should also be noted that the principal factor in controlling the initial skin thickness is the time taken to bring the welding surfaces together after removal of the hot plate. This time is of particularly critical importance at low temperatures; in this case, a thick skin is likely to form, and the material on either side (zone 2) is unlikely to be at a sufficiently high temperature to melt a significant part of the skin. This results in poor bonding.

The overall dimensions of the weld region are only slightly affected by changing the welding temperature, although the total width of the weld region increases with increasing temperature. For example, at the same welding pressure the total width of a 220°C weld is about 30% greater than the lower temperature 200°C weld. The widths of zones 2, 3 and 4 are in the same proportion in both welds, but in the higher temperature weld the width of zone 1, the central skin, is proportionally less, for reasons discussed above. Most of the increased width, as the welding temperature is

raised, is to be found in zone 2, the large scale structured bulk weld material. At higher temperatures, the flow of material into the weld bead increases, but this can be compensated for by lowering the soak time. In PVDF, a significant increase in melt flow is not noticeable until the welding temperature rises above 240°C.

The effect of welding pressure on weld dimensions for a set welding temperature is more marked, with the width of the weld region decreasing with the increasing pressure. Region 3 is relatively constant, while region 4 increases as a consequence of increased material flow and the main effect being the reduction in the width of region 2.

4. Deformation of pipe to pipe butt welds

The tensile testing of dumbbell shaped bars containing a butt fusion weld in a plane orthogonal to the applied stress results in two distinct failure modes:

- (i) failure at the weld;
- (ii) failure away from the weld in the gauge length region.

Failure mode (i) is characterized by a small elongation to break, of the order of 15%, but sometimes less than 10%; Failure mode (ii) is characterized by ductile drawing accompanied usually by stress whitening, and an elongation to break of around 50%, occasionally reaching 70%. We will henceforth refer to mode (i) as "weld failures" and mode (ii) as "ductile failures".

In similar tests on butt fusion welds in other thermoplastics, it has been generally found that if the weld bead is left on, weld failures predominate [19–21]. The failure is initiated at the region where the bead rolls back onto the pipe surface. The molten bead does not bond well with the comparatively cold pipe, such that the pipe/bead interface acts as a notch, and hence a stress concentration effect occurs at this point. The tip of

this notch is located at the outer edge of the weld region, which is a zone of high molecular orientation, and it appears that a crack is initiated at the notch tip and then propagates down through the oriented zone. The stress concentrating effect caused by the notch is large enough to hide any other failure mechanisms in other thermoplastics, and this had led to the practice of machining off the weld bead prior to testing. In this work the weld bead was left intact for two reasons:

- (i) preliminary testing indicated that weld failures were not necessarily the predominant failure mode, even with the bead left on;
- (ii) in practical situations the weld bead would always be left on.

The deformation for a typical weld failure was linear elastic up to a stress of 32 MPa, 65% of the fracture stress. The specimen then yielded slightly before failing abruptly at about 50 MPa, with an accompanying strain to failure of just under 15%.

In the case of typical ductile failures a distinct yield point at about 50 MPa was identified; the material behaved elastically up to 25 MPa, corresponding to a strain of 4%. Yielding occurred at a strain of 15%, essentially the failure strain in weld failure specimens. The specimen then cold draws and eventually fails at a strain of 45%. In some samples necking occurred, the neck initially forming near the shoulder at one end of the gauge length and propagating towards the weld. Failure invariably occurs before the neck reaches the weld, with a gradual decrease in stress.

5. The effect on tensile strength of varying the welding conditions

The weld factors for all different conditions used are given in Table I. Inspection of this table shows us that for any given welding pressure a range of temperatures exists at which high quality welds can be obtained (welds having weld factors greater

TABLE I Weld factors of pipe to pipe butt fusion welds

Welding temperature (°C)	Welding pressure (bar)				
	0.0	0.3	0.6	0.9	1.2
180	0.94 ± 0.1	0.97 ± 0.03	0.88 ± 0.09	0.88 ± 0.01	0.90 ± 0.05
200	0.97 ± 0.07	1.00 ± 0.02	0.99 ± 0.03	0.92 ± 0.08	0.91 ± 0.07
210	0.94 ± 0.07	1.00 ± 0.0	0.99 ± 0.04	0.92 ± 0.04	0.91 ± 0.1
220	0.98 ± 0.02	0.99 ± 0.01	1.00 ± 0.0	0.94 ± 0.09	1.00 ± 0.01
230	0.99 ± 0.01	0.98 ± 0.08	0.97 ± 0.07	0.98 ± 0.02	0.88 ± 0.03
250	1.00 ± 0.0	0.93 ± 0.07	1.00 ± 0.0	0.95 ± 0.1	0.95 ± 0.1

than or equal to 0.98). At the lowest pressure used, 0.1 bar, good welds were obtained at and above 220°C. At these temperatures the welding faces are sufficiently molten to flow under only minimal pressure. When the temperature is lower than this, however, a surface skin will form too quickly to allow adequate bonding to take place, and the lack of pressure will result in little molecular flow from one surface to another. As the temperature is increased the time taken for a skin to form increases, thus allowing considerable flow to take place, such that at the upper bound temperature of 250°C the weld factor is equal to unity, that is, the weld is equal in strength to the base material. The weld factor decreases steadily with decreasing temperature down to below 220°C whereupon it drops markedly. At 0.3 bar, as in the 0.1 bar specimens, good welds can be obtained over a 30°C range of temperatures. However, a notable difference between the two was seen in the limits of this range: a lower temperature could be used (200°C), but the upper temperature of 250°C produced a weld factor of 0.93, which is unacceptable in practical situations. The good results at lower temperatures appear to be due to an optimal temperature–pressure combination, the pressure being high enough to compensate for the less molten state of the polymer, resulting in adequate flow. 0.3 bar appears to be the optimum welding pressure for PVDF; below this pressure the possibility of inadequate weld surface contact arises, a problem which can lead to the entrapment of air bubbles and consequent weld weakening. This has been seen in other thermoplastics [22]. Above 0.3 bar, it is difficult to spot any definite trends in temperature dependence. At 0.6 bar good welds can be obtained, especially at higher temperatures, but the lower bound (180°C) result is disappointing, and is repeated at 0.9 bar, with only a slight improvement at 1.2 bar. At low temperatures, then, apart from the isolated case of 0.3 bar, good welds are not produced. At 0.9 bar a large number of substandard welds were produced, with occasional high weld factors at intermediate temperatures. The same is true for 1.2 bar welds, which overall had even fewer high integrity welds, the 220°C weld being a notable exception. In general, then, we can say that with careful control of the other welding parameters, good welds can be obtained as long as the welding temperature is equal to or greater than 200°C, that is, 20°C above the

melting point of the polymer. If the temperature is too close to the melting point, a surface skin will form such that molecular flow between the welding surface will be inhibited and poor bonding will result. Another problem is that it has been found in industrial applications, particularly on site, that the air temperature can affect the weld surface cooling rate — in particular, very cold conditions can lead to a rapid skin formation, and in practice higher temperatures than are customary are used.

In the second part of the experiment, the effect of welding pressure was investigated by holding the welding temperature constant and performing a set of welds over a range from 0.1 bar to 1.2 bar. As is the case for the temperature dependence of the weld factor, no clear cut trends for the pressure dependence are apparent. At lower welding temperatures, up to 210°C, good welds were not obtained at the lowest pressure used; the optimum pressure appears to be 0.3 bar. At the highest pressure, 1.2 bar, poor welds were invariably produced, with one anomalous result at 220°C. This poor performance at high pressure can be explained in terms of the flow of molten material at the weld faces in a direction orthogonal to the applied pressure, that is, into the weld beads. The high pressure results in considerable shearing of the material and, on cooling of the weld, the material at the edges of the weld is aligned in the weld surface plane. This plane is orthogonal to the tensile test axis and thus acts as a low strength region likely to fail when the weld is stressed. Overall the tensile test results were consistent with the observations on the microstructure of the butt-welds, in that the most satisfactory tensile properties relate to welds which exhibit a narrow zone 4, and a zone 1 which only extends part way through the thickness of the join between the two pipe ends. The dependence of weld factor on welding temperature and pressure is illustrated graphically in Fig. 3. As well as the mean weld factor for each welding condition, the scatter bars have been included in each case. Inspection of the graphs shows a considerable scatter in some cases. There does not appear to be any dependence of the scatter on welding conditions, as has been seen, for example, in saddle fusion joints in polyethylene by Dillon and Bevis [23]. In a practical design situation particular note must be taken of the lower bound value; in many cases this will be due to a flaw introduced during the welding process, rather than a material

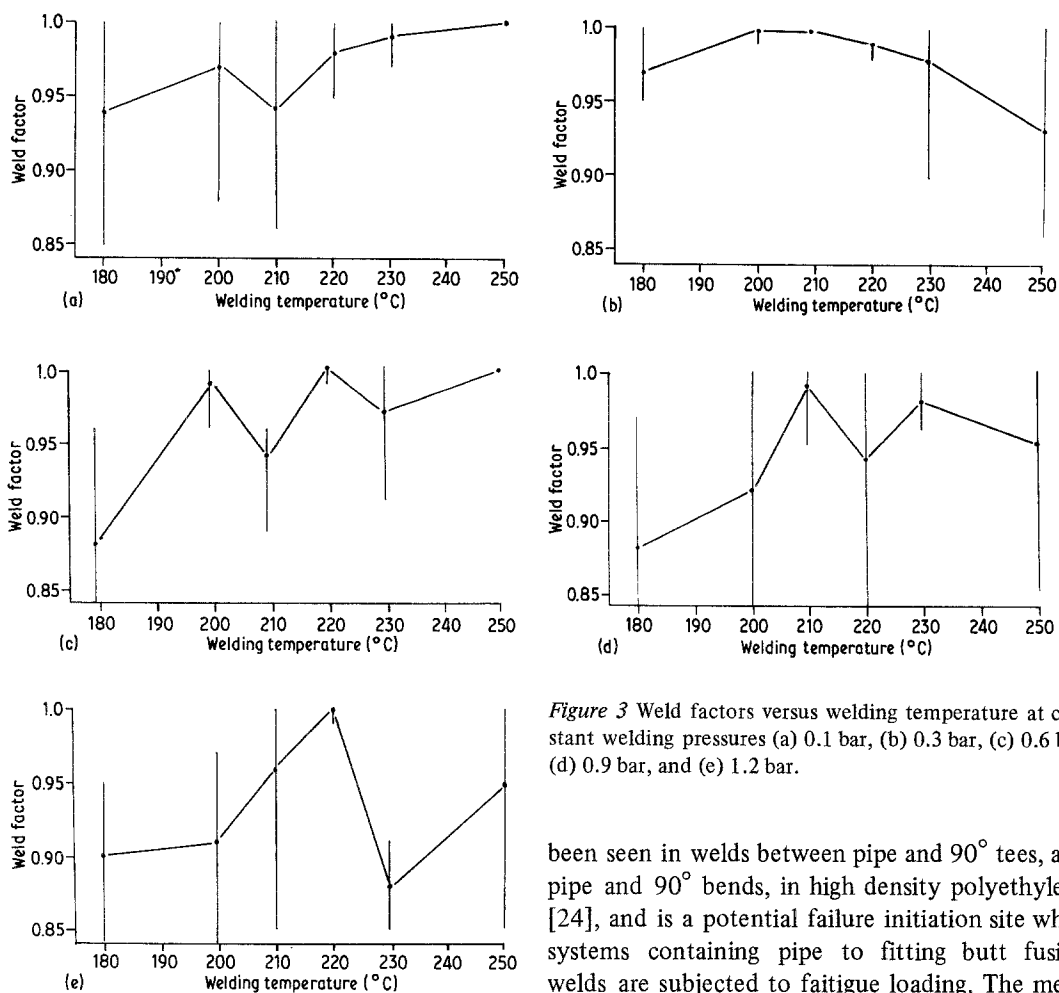


Figure 3 Weld factors versus welding temperature at constant welding pressures (a) 0.1 bar, (b) 0.3 bar, (c) 0.6 bar, (d) 0.9 bar, and (e) 1.2 bar.

property, and the utmost care must be taken to minimise any potential sources of such flaws.

6. Deformation of pipe to fitting welds

An injection moulded 63 mm outside diameter 90° equal tee was butt fusion welded to a length of extruded pipe with complementary dimensions. Four tensile bar specimens taken at 90° intervals around the weld were produced in an identical manner to the pipe to pipe specimens described above. The location of the bars was determined such that two of them contained the internal weld lines of the fitting, present due to the fitting design. The weld was made at a welding temperature of 205°C and a welding pressure of 0.3 bar, using a soak time of 30 sec and a welding time of 5 min. A visual inspection of the weld showed that the internal weld lines on the fitting side of the specimen intersected the weld bead at 90° and at the points of intersection a small irregularity or “blip” appeared. This kind of irregularity has also

been seen in welds between pipe and 90° tees, and pipe and 90° bends, in high density polyethylene [24], and is a potential failure initiation site when systems containing pipe to fitting butt fusion welds are subjected to fatigue loading. The mean weld factor was 0.96. This compares with a weld factor of 1.00 for a pipe to pipe weld made at the same conditions. Three of the four bars failed in a ductile manner, away from the weld region. The fourth bar, one of the two containing the fitting internal weld line, and weld bead blip, failed at the weld in a brittle manner. The bead fractured at the blip, but it was not possible to ascertain if this was the fracture initiator. The drop in weld factor can be attributed to a number of effects; the difference in melt flow index of the two grades of polymer used in the pipe and fitting, and the subsequent difference in flow properties at the time of welding; frozen in stresses in the fitting, caused by uneven mould shrinkage between regions of differing thickness; and a possible stress concentrating effect of the fitting internal weld lines, which may not in themselves have been large enough to initiate failure, but in conjunction with the other factors mentioned above will have had an overall weakening effect. In principle it should be possible to gain improvements on the results gained for the

fitting to pipe welds, by more appropriate selection of the PVDF grade used for moulding the fitting, and the use of alternative processing conditions and mould designs to reduce the influence of internal weld lines on the external butt weld.

7. Concluding remarks

A systematic study of the tensile properties and microstructure of butt fusion welds in PVDF pipes has shown that a broad band of welding conditions may be used successfully. These results indicated that PVDF is exceptionally suitable for hot-plate welding, and may provide a suitable base for developing a stronger material with good welding characteristics.

PVDF has been found to be attractive primarily because of its excellent resistance to chemical and irradiative attack, and, whilst its mechanical properties are good enough to have it classified as a high performance engineering thermoplastic, it is clear that its uses would be extended if its specific strength and stiffness could be improved significantly. A large body of experience shows that the most effective method of attaining these improvements is by incorporating cylindrical fibres into the matrix, and in Part 2 the compounding and processing of fibre-filled PVDF materials is considered, using carbon fibres, rather than glass, because the boron component in the latter acts as a catalyst for the degradation of PVDF with hydrogen fluoride gas as a product.

The feasibility of incorporating fibre-filled PVDF components into a typical system, such as the pipeline system referred to above, is also considered in Part 2, and includes the butt fusion welding of carbon filled PVDF compounds, both to themselves, and to equivalent components made from the unfilled material.

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