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Weldability of Dissimilar Thermoplastics—Experiments in Heated Tool Welding

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In the welding of thermoplastics, there are various effects that contribute to the adhesion, such as flow processes, viscoelastic contact and diffusion. Where different thermoplastics are welded together, the heat applied has to suit both materials, and this can be done with two separate heating elements. For the different heating required for the two pieces being joined, it would not be possible to fix the temperatures of the heated tools with the viscosities and surface tensions of the melts. Characteristic for the adhesion is the polar part of the surface tensions of the solids. However, during cooling, stresses are formed in the weld zone which means that the ratio of the coefficients of thermal expansion must also be considered when assessing the weldability.

1. INTRODUCTION

Welding is coming to be used increasingly as a means of joining not only plastics of the same type but dissimilar thermoplastics as well. Heated tool welding of dissimilar thermoplastics is of particular interest when it comes to welding moulded articles in series production. It can frequently replace more expensive joining processes. Rear car lights in PMMA and ABS are a familiar example here.¹ The new method makes for considerable simplification in assembly—lights were previously held together by means of screws and additional sealant material was used in many cases. A welded rear light, on the other hand, requires no additional fastener elements and is completely adequate for this loading case. In addition, welding makes for greater freedom in design.

In the past weldability has been assessed on the basis of processes which involve a pronounced flow of molten plastic during the jointing process, such as friction welding or ultrasonic welding. Very few studies are available

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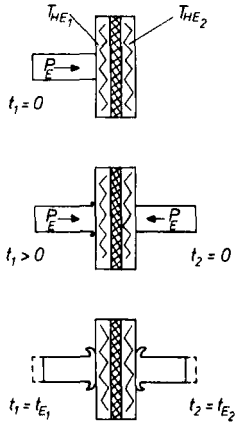
on heated tool welding in this context. Kalev and colleagues² used different heated tool temperatures for the two joint components and in this way were able to achieve welded joints between dissimilar amorphous plastomers. Fractures in the base material only occurred in joints where one of the components was PMMA.

In the long run the question of weldability can only be resolved by experiment. Nevertheless, it is still a good idea to establish criteria which can be applied to give a rough assessment of material pairings.

2. HEATING WITH TWO HEATED TOOLS

In heated tool welding the joint components are supplied with the heat necessary to produce a plastic (*i.e.*, weldable) zone through contact heating with a heated metal tool. Apart from the temperature of the heated tool and the heating time the so-called heating pressure at the start of the heating process and the selected melt-off path play a role here.

Roberg³ points out that surfaces which have been plasticised to differing degrees do not form a bond because the more highly plasticised material deforms on the cooler material and no convolution of molecules occurs.



$\frac{P}{E}$ = Heating-up pressure
 t_E = Heating time
 T_{HE} = Heated tool temperature

FIGURE 1 Heating for welding with two heated tools.

When it comes to welding dissimilar plastomers the materials to be bonded will generally have dissimilar flow properties at a given temperature.

In order to achieve a weld, though, the two joint components need to be heated up so as to give a plastic weld zone but not so far as to bring about thermal deterioration. One way of achieving this is to use two heated tools, as shown in Figure 1. The two heated tools are insulated from each other and have individual temperature control. This means that an appropriate heated tool temperature can be selected for the two joint components as a function of the plastomers involved. Furthermore, the machine can also be set to give non-identical heating-times. In Figure 1, for example, the second joint component comes into contact with the heated tool at a later stage than the first component, such that $t_{E2} < t_{E1}$ applies for heating times in this case. Being able to heat the joint components independently of each other constitutes an essential condition for the welding of dissimilar plastics—disregarding welds involving plastomers of similar types or with similar heating properties.

The machine used in the experiments can be set to give two independent heated tool temperatures, θ_{HE1} and θ_{HE2} , and two heating times, t_{E1} and t_{E2} .

3. EXPERIMENTAL PARAMETERS AND MATERIALS

According to Röber,⁴ the molten plastic components have to be slid along each other during welding for complete contact to be made. Pieschel⁵ investigated flow processes in heated tool butt welding. Working on from the velocity fields he established, Potente⁶ went on to compile the so-called theory of minimum flow velocity. This is the minimum velocity at which the molten plastic must flow into the weld bead in order to ensure sufficient strength in the joint plane. This minimum value, which must be exceeded, is material-dependent. Potente⁶ was able to show that an interrelationship does exist between flow velocity and both heating conditions (heated tool temperature, heating time) and joining pressure.

The essential process parameters for the heating and joining processes can therefore be brought together in a reference index—the mean flow velocity, v_m . With allowance for a mean apparent viscosity of η_m , the following mean flow velocity is obtained⁶:

$$v_m = \frac{8 P_s L_o^2}{\pi \eta_m d}$$

where η_m = mean viscosity

P_s = joining pressure

L_o = width of melted-down zone

d = thickness of joint components

Now dissimilar plastics also have dissimilar thermal and rheological material data. In addition, the process outlined calls for different heated tool temperatures and heating times. Thus when flow velocities are calculated, two divergent values will always be obtained in this case. The values v_1 and v_2 are thus to be established as reference values for the welding experiments.

Welding experiments were carried out using a series of dissimilar plastics combinations. Both amorphous and semi-crystalline plastics were taken into consideration as follows:

amorphous: PVC, PMMA, ABS, PS

semi-crystalline: PP, HDPE

The combinations investigated were as follows:

PMMA-PS; PMMA-PVC; PMMA-ABS

PVC-ABS; PVC-PP; PVC-PS

HDPE-PP; HDPE-PS; PP-PS

ABS-PS; ABS-HDPE; ABS-PP

4 mm thick plates were used as joint components.

In the welding experiments the heated tool temperature and the heating time were varied for each of the joint components independently. Table I gives the ranges selected for the individual materials.

4. ADHESIVE STRENGTHS OBTAINED

The welded test-pieces were put through the short-time tensile test. Strips 25 mm in width were sawn out of the plates for this purpose. The drawing

TABLE I
Variation of welding parameters

Material	Heated Tool Temperature	Heating Time
	θ_{HE} ($^{\circ}$ C) from . . . to	t_E (sec.) from . . . to
HDPE	230-280	20-90
PP	240-280	20-90
PVC	200-210	20-90
PMMA	200-270	20-90
ABS	200-280	20-90
PS	200-260	20-90

Heating pressure p_E , welding pressure p_S and the melt-off path limited by stops, s_A , remained constant. The values were: $p_E = 15 \text{ N/cm}^2$; $p_S = 30 \text{ N/cm}^2$; $s_A = 0.6 \text{ mm}$.

rate in the tensile tests was 4 mm/min. Fracture generally occurred in the seam plane, *i.e.* this was so-called adhesion fracture. Only with the combinations PVC-PMMA and ABS-PMMA were fractures found in the base material. With the combinations ABS-PS mixed fractures also occurred, running from the seam plane or a point near the seam into the base material. The individual joint factors are given in Table II. These are the values obtained with optimum parameters, expressed in terms of the short-term tensile strength of the weaker joint component.

TABLE II
Joint factors for welds involving dissimilar plastomers

PMMA-PS	0.87	PP-PS	0
PMMA-PVC	0.99	HDPE-PP	0.59
PMMA-ABS	0.85	HDPE-PS	0.04
PVC-ABS	0.57	ABS-PS	0.64
PVC-PP	0	ABS-HDPE	0
PVC-PS	0	ABS-PP	0

Where the value "0" appears in Table II, this means it proved impossible to form a weld within the parameter variation range investigated, such as the two joint components could be taken out separately from the machine after completion of the welding process. It is interesting to note that for the combinations PS-PVC, PS-PP, ABS-PP and ABS-HDPE a welded joint had formed upon removal from the machine but during subsequent storage (*i.e.*, cooling) the joint split open of its own accord, along the seam line, without any external mechanical influence.

5. ADHESIVE STRENGTH AS A FUNCTION OF WELD PARAMETERS

The weld parameters were combined into a flow velocity in the manner set out in Section 3. For welds involving identical materials the flow velocity can be applied in parameter optimisation. Figure 2 shows that this index has to exceed a certain minimum value if good weld joints are to be achieved.

Figure 3 gives the strengths obtained for the material combination HDPE-PP as a function of the two flow velocities. It is seen that specific minimum flow velocities have to be exceeded in the case of both joint components in order to arrive in the optimum strength range. For HDPE, for instance, flow velocity must be at least 6 cm/s and for PP, at least 1.2 cm/s. It is striking that at very high flow velocities strength begins to fall again. This is attributable to the fact that virtually all the molten plastic is squeezed out of the

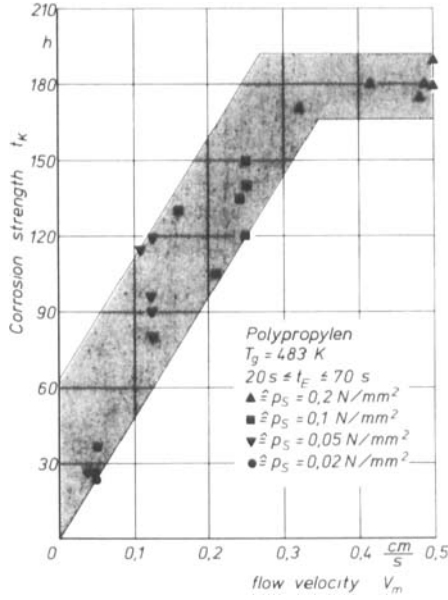


FIGURE 2 Dependency of corrosion strength on flow velocity (Ref. 9).

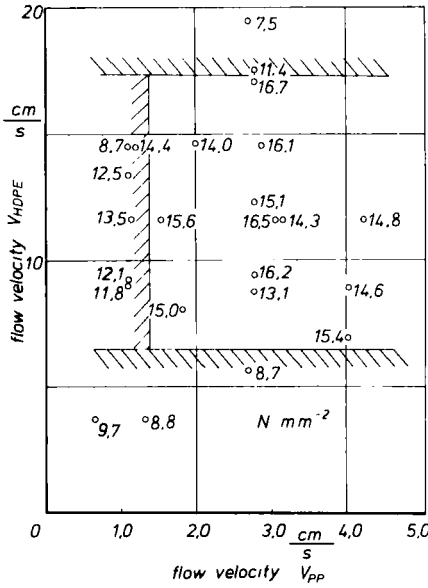


FIGURE 3 Short-time tensile strengths with different welding parameters for HDPE/PP.

joint zone at this stage. This becomes particularly pronounced where the joint components have dissimilar flow properties.

For purposes of establishing optimum weld parameters, a limited number of experiments will generally suffice to find an appropriate parameter range here.

6. SIGNIFICANCE OF THE VISCOSITY AND SURFACE TENSION OF THE MOLTEN PLASTIC FOR ADHESIVE STRENGTH

For side valency forces to act effectively close contact or interpenetration of the joint components is necessary. Formation of the interface takes place during the molten phase. It thus has to be considered whether improvements in seam quality could not be brought about through alignment of certain melt properties (*e.g.*, surface tension or viscosity).

Surface tension was therefore established in accordance with Roe. For the plastomers LDPE, HDPE, PS and PP it was found that surface tension is linearly dependent upon temperature within the temperature range measured (Figure 4).

It is seen that the curves over temperature follow a relatively flat course. If identical surface tension is to be achieved in both molten plastics this will,

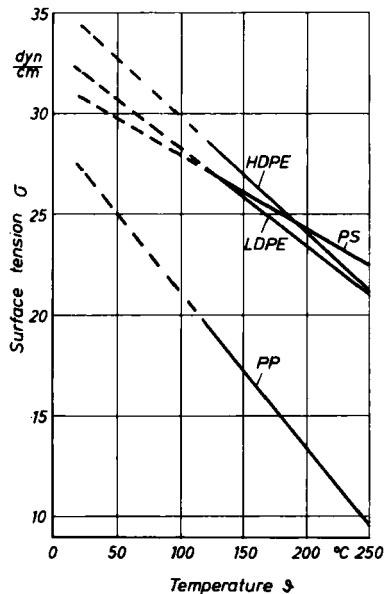


FIGURE 4 Surface tension of thermoplastics as a function of temperature.

as a rule, call for large-scale differences in temperature. For the combination HDPE-PS the components have identical surface tensions at about 190°C. At this particular temperature, though, it was impossible to achieve a joint because the material was insufficiently plasticised. In addition, at higher temperatures only minimal strengths were attainable.

In the HDPE-PP bond, for example, 59% of the base material strength of the weaker joint component was achieved. It is clear from Figure 4 that alignment of the two surface tensions through temperature adjustment is only possible with great difficulty. Figure 5 shows short-time strength as a

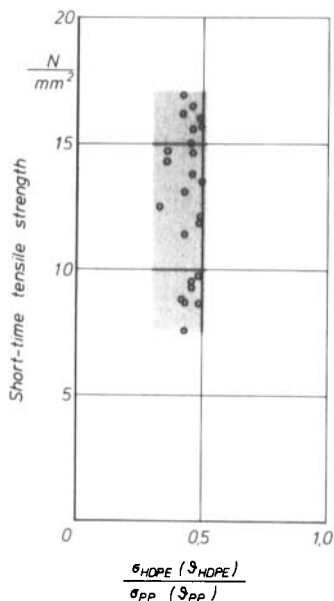


FIGURE 5 Dependency of seam strength on the surface tension of the molten plastic.

function of surface tension ratio for the particular contact temperatures with the heated tool. Identical surface tensions, *i.e.*, $\sigma_{HDPE}/\sigma_{PP} = 1$, were not achieved. Despite parameter variation, as is evident from the different strengths, all the values lie within a relatively small band between $\sigma_{HDPE}/\sigma_{PP} = 0.3$ and 0.5. Weldability cannot therefore be read off from the surface tension ratio of the molten plastics. In optimising weld parameters consideration must also be given to the viscosity of the plasticised zone.

Particularly where materials with markedly different heating and flow properties are involved, each material must receive independent and individually-tailored heating treatment. If, for formation of a contact plane,

the two polymers are to have virtually identical flow properties, it has to be considered whether viscosity could not be used as a meaningful reference index here. As the viscosity dependence on temperature shows, parameter optimisation through viscosity alignment would seem to be difficult on account of the resultant large-scale differences in temperature. If we then turn to the contact temperature again, experimental results have indeed confirmed this. Figure 6 shows that the viscosity ratios for the combination

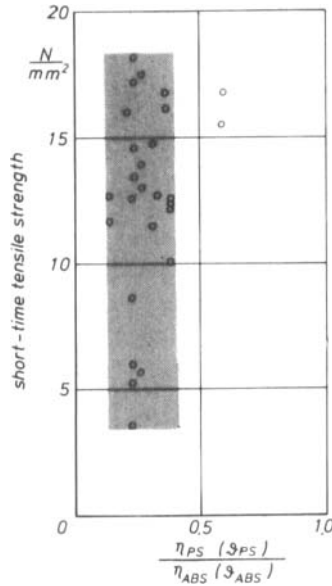


FIGURE 6 Dependency of seam strength on viscosity.

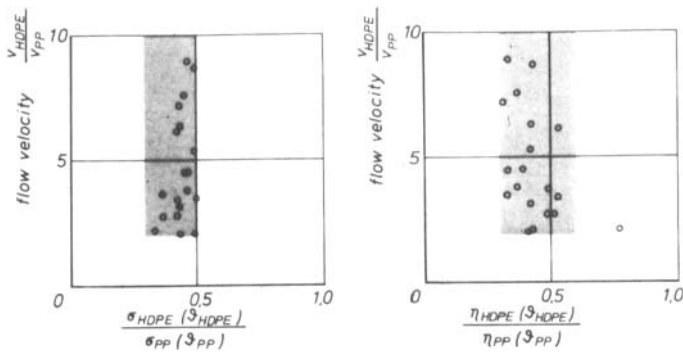


FIGURE 7 Flow velocities at different viscosities and surface tensions.

ABS-PS were in the main between 0.13 and 0.40. Identical viscosity values in the contact plane have therefore not been possible here under the practical welding condition range.

Figure 7 shows flow velocity dependence on surface tension and on viscosity.

It is seen that within a relatively narrow range of surface tension and viscosity ratios there can be a pronounced change in the flow velocity ratio. Seam strength is, however, dependent on flow velocity. Hence, the parameters viscosity and surface tension of the molten plastic cannot be applied for suitably tailored heating of the two joint components. Optimum parameters are better determined in a flow velocity diagram.

7. CHARACTERISATION OF MATERIALS THROUGH POLAR SURFACE TENSION COMPONENTS

Potente and Krüger¹¹ were able to show in the case of adhesive strength of paints on polymers that correlation of total surface tension with adhesive strength does not point to any clear-cut dependence here. It was, however, very easy to point a clear influence of the polar components of solid-state

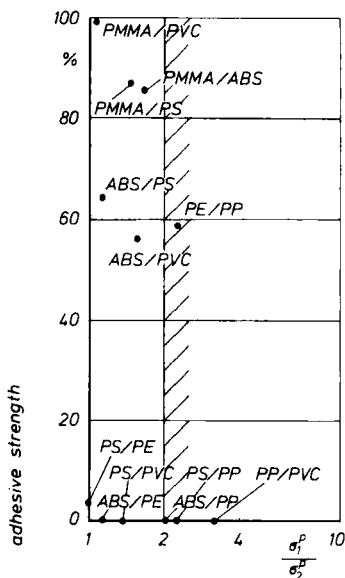


FIGURE 8 Adhesive strength as a function of polar surface tension components.

surface tension. The specific interfacial energy tends to zero where

$$\frac{\sigma_1^p}{\sigma_2^p} = 1, \quad \frac{\sigma_1^d}{\sigma_2^d} = 1$$

In respect of surface energy, two identical substances are then present, *i.e.* giving maximum adhesion. Accordingly, as the quotients move further away from 1, adhesion must be reduced. The polar components were established in accordance with Rabel.¹² A total of 12 material combinations are given in Figure 8, with adhesive strength expressed in terms of the base material strength of the weaker joint component. It is noticeable that the maximum does not always clearly coincide with the ratio "1.0". There are values with both higher and lower strengths in close proximity to 1.0. This implies that polar surface tension components alone are not sufficient for assessing the attainable strength and that additional parameters have to be applied. It was precisely with combinations of "zero" strength, which came close to $\sigma_1^p/\sigma_2^p = 1$, that a welded joint was removed from the machine only to split open of its own accord along the seam during subsequent cooling. This means that thermal influences on seam strength also need to be characterised in welding.

8. INHERENT STRESSES DUE TO THE COOLING PROCESS

Stresses develop in the weld seam during cooling. We can work on the basis that bond points develop between the materials upon contact and that these are constantly being created or destroyed during the whole jointing process. As cooling progresses so molecule mobility decreases. If the two materials contract at markedly different rates, then the differential longitudinal deformation gives rise to elastic or plastic deformation at the point of adhesion—this, though, is only possible to a very limited extent. At low adhesion strengths, therefore, a considerable proportion of the adhesion effect can be lost by bond points being destroyed during cooling.

Inherent stresses influence the strength of the weld joint yet these are not taken into account in adhesion theories. An attempt was made to estimate the extent of cooling stresses with the aid of a computer program.

The joint components under observation were two plates, divided up into uniform parallel layers (Figure 9). The stress which is created through the individual layers mutually hampering each other's expansion effort is only discussed for the Z coordinates in the following.

The computed results provided by the program have to be viewed with certain reservations when it comes to their applicability. These reservations stem firstly from the fact of the properties of a real weld deviating from those

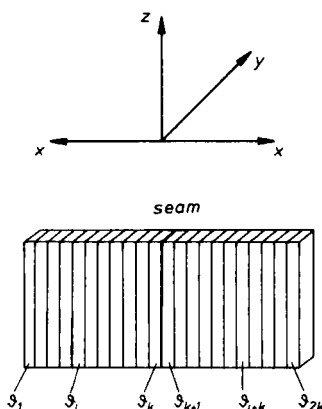


FIGURE 9 Layer model for heated tool butt welding.

of the models used in program compilation, particularly, and secondly from the fact that certain process conditions were not covered by the program. These include flow processes, temperature fluctuations in the heated tools, material value functions only described approximately, assumption of complete adhesion in the seam plane as well, etc. The program does, however, provide a means of estimating the general directions in which the materials to be welded will mutually influence each other.

In the presentation of results it is to some extent assumed that a stress develops in the weld seam plane, which is equivalent to the arithmetical mean of the neighbouring layer stresses. This applies with the condition that a transitional zone develops in the seam area, consisting of a mixed phase. In the calculation proper, where stress is calculated for one layer element at a time, there is a jump in stress in the interface between the two materials.

Figure 10 shows calculated stress curves as a function of time. A step occurs in the stress profile for the seam plane ($x_1 = x_2 = 0$) with increasing cooling time. In addition, the polymer combination ABS-PMMA gives a relatively high stress peak in the immediate proximity of the seam (1-2 mm). This stress peak can be explained from the calculation process by the fact that the increase in shear modulus is particularly pronounced in this area.

Figure 11 gives the (calculated) mutual stress influence in the seam area. It is clear that for an ABS-PMMA weld the inherent stresses that develop in the ABS in the weld seam zone are higher than they would be for an ABS-ABS combination. The reverse applies in the case of the PMMA.

By selective modification of the material value functions it was possible to assess their influence on the build-up of stress. The influence was simulated with the material combination ABS-ABS, with one of the joint components

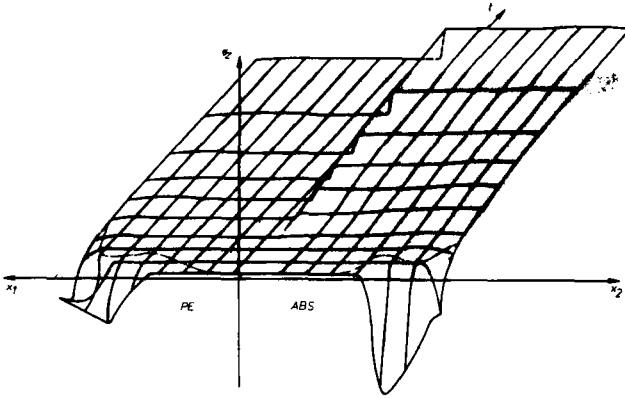


FIGURE 10 Stress profile in the seam area during cooling.

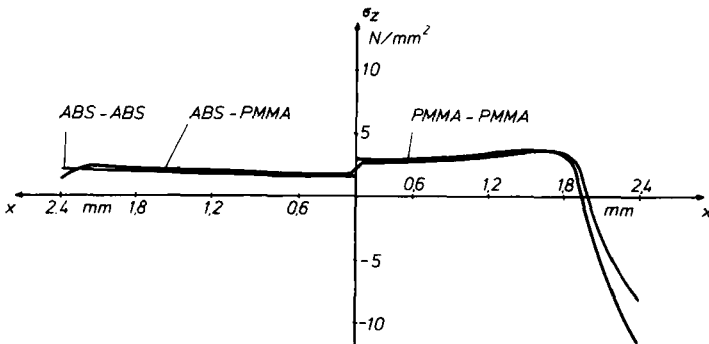


FIGURE 11 Inherent stress in the weld seam area for ABS-ABS, PMMA-PMMA, ABS-PMMA.

having modified characteristic data. If the rise in specific volume in the solid-state range is increased, for example, this then leads to a sharper increase in stress in the seam (Figure 12). If the rise in shear modulus in the solid-state range is increased, this also produces a clearly sharper rise in stress as cooling progresses compared with stress development in an ABS combination made up of two non-influenced materials.

A higher shear modulus and steeper gradient on the volume characteristic curve in the solid-state range show a clear increase in seam stress upon cooling, with shear modulus having the greater influence here. An increase

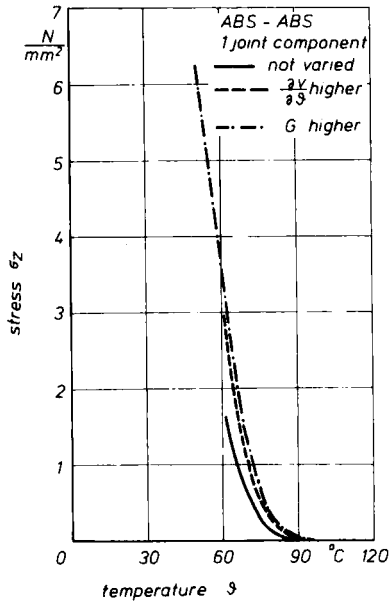


FIGURE 12 Stress in the seam plane with modified shear modulus and thermal expansion.

in heating time gives a considerable reduction in the build-up of stress in the seam. This is explained by the fact that a longer heating time increases the heat content of the workpiece and thus means that the influence of relaxation in stress build-up becomes greater.

9. MICROSCOPIC SEAM ANALYSIS

The interface between the two joint components is always in evidence on electron micrographs. For HDPE and PP, for example, chemical etching processes were applied which preferentially attack the amorphous phase. Figures 13, 14 and 15 show an HDPE-PP welded joint in different magnifications. Figure 13 gives a general view of the weld zone with the weld bead which is very pronounced in this case.

Figures 14 and 15 show the interface between HDPE and PP again, at two different magnifications, with the interface running in a straight line. All in all, the preparation method gives a clear joint between HDPE and PP. This excludes the possibility of any interlocking in the crystalline phases of the materials. It is not possible to establish in this way whether an interface also develops between the amorphous phases or whether a mixed phase occurs.

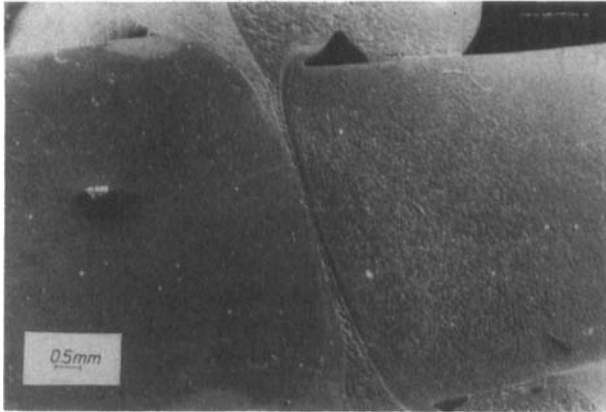


FIGURE 13 Scanning electron micrograph (HDPE-PP).

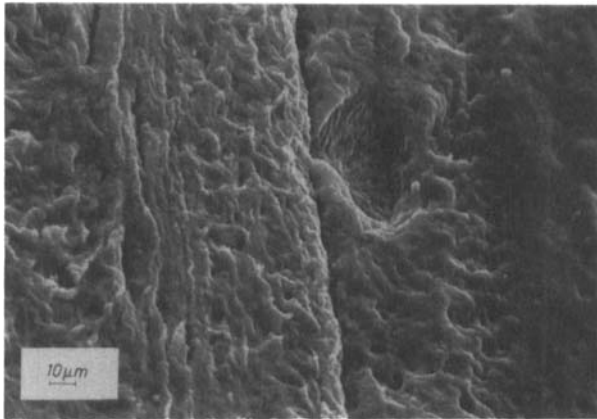


FIGURE 14 Scanning electron micrograph (HDPE-PP).

10. SECONDARY ION MASS SPECTROMETRY (SIMS)

Tensile tests led in the main to adhesion fractures. The electron micrographs do not reveal any particles of the other component on the fracture surfaces. An interface can always be seen in the welded joints themselves. In the light of the theory of diffusion, it now has to be investigated whether traces of the other joint component perhaps remain adhered to the fracture surfaces in the sub-microscopic range.

With SIMS the surface under investigation is bombarded with ions. The

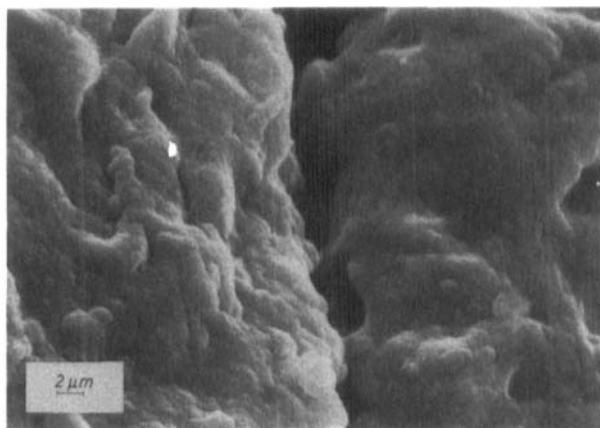


FIGURE 15 Scanning electron micrograph (HDPE-PP).

ions trigger off *inter alia* chemical reactions and scatter. The emission products (secondary ions) are analysed in a mass analyser. Since there is a chemical analysis process, polymers were selected that had very different structures, *i.e.* the combination PMMA-PVC. This is also a very high strength joint which means that it would be here, if anywhere, that traces of the other joint component would be chemically detectable on the fracture surface.

Bar-shaped test-pieces were sawn out of the welded plates for this purpose. Fracture was brought about in a high vacuum shortly before the analysis so as to largely exclude any contamination of the surfaces.

Figures 16 and 17 show the spectra of both the fracture surfaces. Between

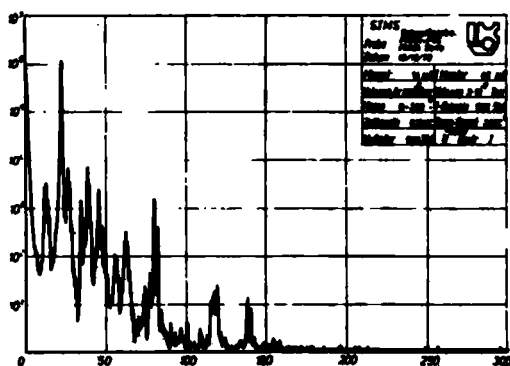


FIGURE 16 Secondary ion mass spectrometry, PMMA side of PMMA-PVC bond.

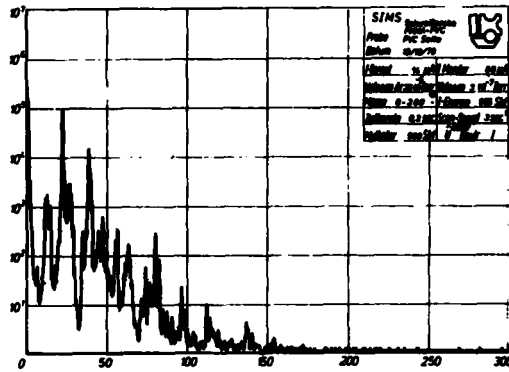


FIGURE 17 Secondary ion mass spectrometry, PVC-side of PVC-PMMA bond.

the mass count 100 and 150 responses which are characteristic for PVC additives have occurred in each case.

The response at mass count 82 points to Cl compounds in the PVC. It would therefore seem that the two materials do mutually influence each other in the seam plane—albeit in the submicroscopic range.

11. ASSESSMENT OF WELDABILITY

To achieve good seam strength consideration must be given firstly to process-specific influences.

The use of two independently controllable heated tools permits a sufficiently plasticised zone to be obtained in both the joint components. It would not seem possible to select welding parameters on the basis of the material data viscosity and surface tension of the molten plastic. In addition to visual assessment of bead formation it would also seem wise to establish optimum flow velocity ranges that cover the process parameters.

If the weldability of a specific material combination is to be assessed, consideration must then be given to material-specific influences as well. To ensure low cooling stresses in the seam there should no longer be any sharp rise in shear modulus at low temperatures (*i.e.*, in the solid-state range). The polar components of (solid-state) surface tension are characteristic of the specific adhesion between two materials. Furthermore, the coefficients of thermal expansion give an initial approximation as to the extent to which bond points are destroyed again upon cooling. These two criteria are given in Table III for the welded material combinations.

From Table III it is clear that the quotients of both parameters should be as close to 1.0 as possible. With $\alpha_1/\alpha_2 \geq 1.20$, for example, no seam strength

TABLE III

Seam strength as a function of material data

Combination	α_1/α_2	σ_1^P/σ_2^P	Relative Strength
			%
PMMA/PVC	1.04	1.07	99
PVC/ABS	1.08	1.57	57
PMMA/ABS	1.13	1.67	85
PMMA/PS	1.15	1.48	87
HDPE/PP	1.18	2.29	59
PVC/PS	1.20	1.39	0
ABS/PS	1.30	1.12	63
ABS/PP	1.59	2.03	0
PVC/PP	1.72	3.18	0
ABS/HDPE	1.88	1.12	0
PP/PS	2.07	2.29	0
PS/HDPE	2.44	1.00	4

can be expected any longer. The combination ABS-PS marks an exception here, though the ratio σ_1^P/σ_2^P at 1.12 is relatively close to 1.0.

At values of $\sigma_1^P/\sigma_2^P \geq 2.0$ adhesion can no longer be achieved unless the ratio of coefficients of heat expansion is very close to 1.0 (e.g., with HDPE-PP).

In overall terms, good strengths were achieved in welding dissimilar plastomers for

$$\alpha_1/\alpha_2 < 1.20 \quad \text{and} \quad \sigma_1^P/\sigma_2^P < 2.0$$

No adhesion can be expected for

$$\alpha_1/\alpha_2 > 1.20 \quad \text{and} \quad \sigma_1^P/\sigma_2^P > 2.0$$

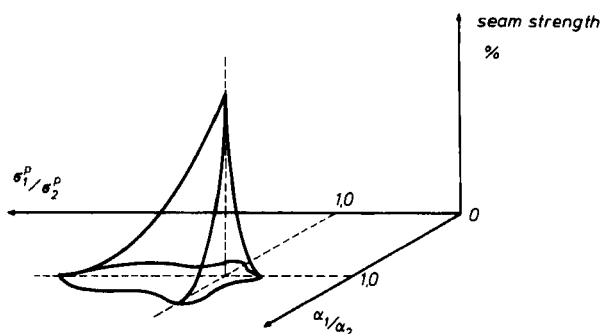


FIGURE 18 Relative seam strength as a function of surface energy and thermal expansion quotients (in qualitative terms).

If only one of the two quotients is greater than the given limits good adhesion may be still possible. Figure 18 shows, in qualitative terms, the dependence of relative seam strength on material data.

References

1. N. N. *European Plastics News* **4**, 16, (1977)
2. L. Kalev, K. Alexiev and L. Kamenova, *Internat. Inst. of Welding*, IIW-Doc. XVI-263-75.
3. P. Roberg, *Kunststoff Rundschau* **15**, 101 (1968).
4. H. Röber, *Schweißtechnik (DVS)*, Vol. **47** (1966).
5. D. Pieschel, *Dissertation RWTH Aachen* (1975).
6. H. Potente, *Kunststoffe* **67**, 98 (1977).
7. H. Potente and K. Gabler, *DFG Nr. Po 171/9*.
8. R. J. Roe, *J. Phys. Chem.* **72**, 2013 (1968).
9. R. J. Roe, V. L. Bacchetta and P. Wong, *Library of Congress*, Doc. No. 9668.
10. R. J. Roe, V. L. Bacchetta and P. Wong, *J. Phys. Chem.* **71**, 4190 (1967).
11. H. Potente and R. Krüger, *Farbe + Lack* **84**, 72 (1978).
12. W. Rabel, *Farbe + Lack* **77**, 997 (1971).