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Silane compounds in hot-water pipe and cable technology

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The problems of technique and equipment used in the crosslinking of polyethylene polymer are discussed. The practice of organosilicon chemistry for crosslinking of polyethylene chains is also considered. The use of a Cavity Transfer Mixer (CTM) for control of silane-based crosslinking is described and the properties of the resultant polymers are tested. Use of this crosslinking method via the CTM produces polyethylene with improved hot-water characteristics.

Keywords: Polyethylene, vinyl silanes, crosslinking, extrusion, Cavity Transfer Mixer (CTM), physical properties

INTRODUCTION

The family of vinyl silanes are well-established as primer or surface-coating materials which will bond to polar surfaces (glass fibre, silica fillers, etc.), whilst leaving the vinyl group free for bonding into an organic medium. These additives can be used as direct coatings for glass fibre, or as particulate filters for use in composite polymeric materials, whilst precoated materials are also commercially available under various trade names. Some important commercially available silane coupling compounds are cited in Table 1.

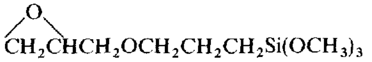
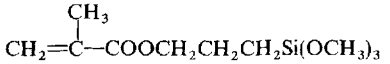
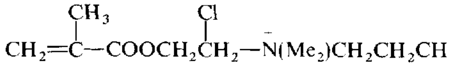
The facile condensation reactions which are exploited in surface bonding can also be used to advantage in homogeneous polymeric systems where the vinyl addition reaction is used to graft the silane on to the polymer backbone and the condensation reaction, between two such grafted silane compounds, can usefully control molecular weight build-up. The different rates of these reactions, and hence the changes in physical properties of the polymer, are controlled by the selective addition of organotin catalysts.

The effect of changes in molecular weight on the way in which the polymer can be made to flow means that organosilane chemistry can be used to change the processing characteristics and thereby play a novel role in the development of new manufacturing techniques for plastics products.

The requirement for a polymer to be melt-processable, yet resistant to deformation in a high-temperature service application, places conflicting demands on the thermal characteristics of that polymer. The conventional approach to resolving this dilemma is to effect a dramatic increase in the molecular weight of the polymer after fabrication, and this is achieved in practice by introducing additional chemical bonds which are intermolecular (crosslinking) to create a polymer network of potentially infinite molecular weight. Prior to crosslinking, any polymer structure has a viscous character which can be enhanced by the action of heat, but the action of crosslinking eliminates this viscous flow. Thus a crosslinked polymer cannot be remelted at temperatures below the onset of degradation.

The saturated hydrocarbon polymers which comprise the family of polyethylenes have a flexible molecular backbone which promotes melt flow in some grades at temperatures little higher than 100°C. These polymers are cheap, easily fabricated and widely used, but the low reactivity expected of a saturated paraffin is a deterrent to the implementation of network-forming reactions. In particular, the practical requirement for unsupported products dictates that the crosslinking chemistry should only operate at the lower temperatures after freezing the polymer in the desired profile, and this places severe constraints on the options available. This paper shows how a sequential series of reactions can be exploited to accomplish the required changes and how an adventitious silanol condensation is used to effect the final crosslinking.

Table 1 Some commercially available silane coupling agents[a]

Organofunctional group	Chemical structure
Vinyl	$CH_2{=}CHSi(OCH_3)_3$
Chloropropyl	$ClCH_2CH_2CH_2Si(OCH_3)_3$
Epoxy	 $\overbrace{CH_2CH}^{O}CH_2OCH_2CH_2CH_2Si(OCH_3)_3$
Methacrylate	 $CH_2{=}\overset{CH_3}{C}{-}COOCH_2CH_2CH_2Si(OCH_3)_3$
Primary amine	$N_2NCH_2CH_2CH_2Si(OC_2H_5)_3$
Diamine	$H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$
Mercapto	$HSCH_2CH_2CH_2Si(OCH_3)_3$
Cationic styryl	$CH_2{=}CHC_6H_4CH_2NHCH_2CH_2NH(CH_2)_3Si(OCH_3)_3 \cdot HCl$
Cationic methacrylate	 $CH_2{=}\overset{CH_3}{C}{-}COOCH_2\overset{Cl^-}{C}H_2{-}N(Me_2)CH_2CH_2CH_2Si(OCH_3)_3$

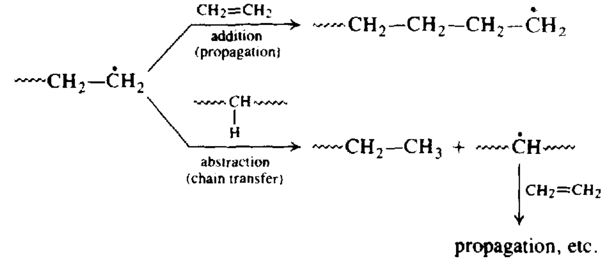
[a]Adapted from Plueddemain, E P, *Silane Coupling Agents*, Plenum Press, New York, 1982.

In this way the continuous production of crosslinked polyethylene pipe or cable becomes a feasible proposition. However, the techniques necessary for achieving this in practice have emerged only from the systematic evaluation of the technology required to effect mixing and reaction. This paper also considers the problems involved and discusses the techniques and equipment required for the execution of organosilane chemistry in a high-molecular-weight polyethylene-type medium.

POLYETHYLENES

Materials

The polyethylenes (PE) are a family of saturated hydrocarbon polymers containing substantially the recurring unit $(CH_2{-}CH_2)_n$ but having different grades distinguished by the quantity and type of branching present. Those grades obtained by free-radical polymerization possess branches of various lengths as a result of radical chain transfer competing with chain propagation (Scheme 1).



Scheme 1

Such branching reduces crystallinity and, in consequence, density to give the so-called low-density polyethylenes (LDPE) of widespread familiarity. These have densities within the range 0.916–0.930 g cm^{-3} as distinct from the values between 0.945 and 0.965 g cm^{-3} for the high-density polyethylenes (HDPE) which are obtained virtually free of side-chain branching (i.e. essentially linear polymers) by polymerization via coordination catalysis. Polymers at the lower-density end of this latter range (which have improved stress cracking resistance) are sometimes called 'medium-density' polyethylenes.

A third type of polyethylene, first introduced in 1977, employs coordination catalysis for reaction control but introduces α-olefins, such as butene, etc., as co-monomers with ethylene at levels of around 8–10%. By this means short-chain branches of known length are introduced to produce the so-called 'linear low-density' polyethylenes (LLDPE).

Polyethylene is processed mainly into three groups of extruded products: cables, pipes and sheets/films. From polyethylene's earliest manufacture, cables have been an important application, whilst polyethylene pipes for cold-water services have been widely used for nearly as many years. Being thermoplastic with comparatively low melt viscosity and good thermal stability at about 150–180°C for LDPE and LLDPE, and about 175–200°C for HDPE, polyethylene is comparatively easy to extrude, but the same factors mean that applications are limited by a comparatively low upper limit on service temperature. This applies to both continuous use under stress at up to 100°C for hot-water pipes and to occasional excursions to significantly higher temperatures, but without applied stress due to temporary electrical overload of a cable.

The need for a cable material which had all the advantageous properties of polyethylene such as low power factor, high voltage breakdown, toughness, low water absorption, etc., but with a higher temperature performance led to the development of crosslinked polyethylene cables. Unusually, there are commercially three quite different methods of crosslinking polyethylene, each one finding applications which suits its particular advantages.[1] These are as follows:

(1) Peroxide crosslinking;
(2) Radiation crosslinking;
(3) Silane grafting—moisture crosslinking.

Following development of a dynamic mixing device, the Cavity Transfer Mixer (CTM), to enable extruders producing pipe for cold-water services to the UK industrial standard BS 1972 to use carbon black masterbatch,[2] a programme of work was carried out to determine if the mixer could be used for grafting directly injected silane on to the polyethylene in the melt stage. This would enable adaptation of existing polyethylene pipe extrusion lines to produce crosslinked polyethylene pipes suitable for hot-water applications, whilst cable extrusion lines might similarly be adapted.

Crosslinking extrusion processes

Extruded thermoplastic polyethylene cables and pipes are conventionally made on lines consisting of an extruder, die, sizing/cooling tanks, haul-off and reeling equipment (Fig. 1). The process is basically a comparatively simple one of melting the PE pellets, pumping the melt through a die to form the product and cooling the product to shape. Crosslinked products require one or more steps of precompounding and post-extrusion processing to achieve crosslinking.

All of the three industrially applied crosslinking technologies (radiation, peroxide and silane grafting) were developed primarily for the cable industry. Although the same methods are all used for crosslinked polyethylene pipes, a direct application from cable technology is not possible. In addition to the harsher service conditions from the combined effects of temperature, pressure and hot water, extra demands on processing are made as, unlike in cable manufacture, there is no internal wire support during post-extrusion operations. As a result, a variety of specialized processes have been developed for crosslinked polyethylene pipe manufacture.

Silane crosslinking

A comprehensive literature review has been produced by Munteanu.[3] In 1968, Midlands Silicones (Dow Corning) patented the ‘Sioplas’ process for crosslinking polyethylene using silanes.[4] It is essentially a two-step process (Fig. 2a). The first step is the grafting of a vinyl silane on to the polyethylene backbone. This is a classical free-radical chain reaction involving a peroxide catalyst. The peroxide employed is proprietary but dicumyl peroxide is known to be widely used. The chain is initiated by a hydrogen-abstraction from the polyethylene (Figure 2a). It follows that the ease of abstraction will depend on the type of hydrogens available (e.g. primary, secondary or tertiary) and that differences in the frequency and length of branching, amongst the different types of polyethylene, will ensure different proportions of these hydrogen types. Thus the grade of polyethylene used would be expected to have an important bearing on the process of grafting and its influence merits investigation in this current study.

The competition from side-reactions in any radical process merits critical attention, two reactions which can compete with grafting being crosslinking and vinyl homopolymerization (Fig. 2b, Eqns [1] and [2] respectively).

Whilst a degree of optimization of grafting efficiency can be achieved by attention to the type and concentration of initiator and monomer, a key factor in suppressing such side-reactions is to ensure a rapid and effective solution of the monomer in the polymer. From a chemical viewpoint, some excess of the monomer, if properly dissolved, could be tolerated since this can promote grafting at the expense of crosslinking and is not detrimental to the next stage of the two-step process. However, the volatility and flammability of materials such as trimethoxyvinylsilane ($CH_2{=}CHSi(OMe)_3$) at typical polyethylene melt temperatures would make the processing hazardous if sufficient unreacted silane remains in the material as it leaves the hot extrusion die.

This second step is the controlled introduction of crosslinks after fabricaton of the grafted

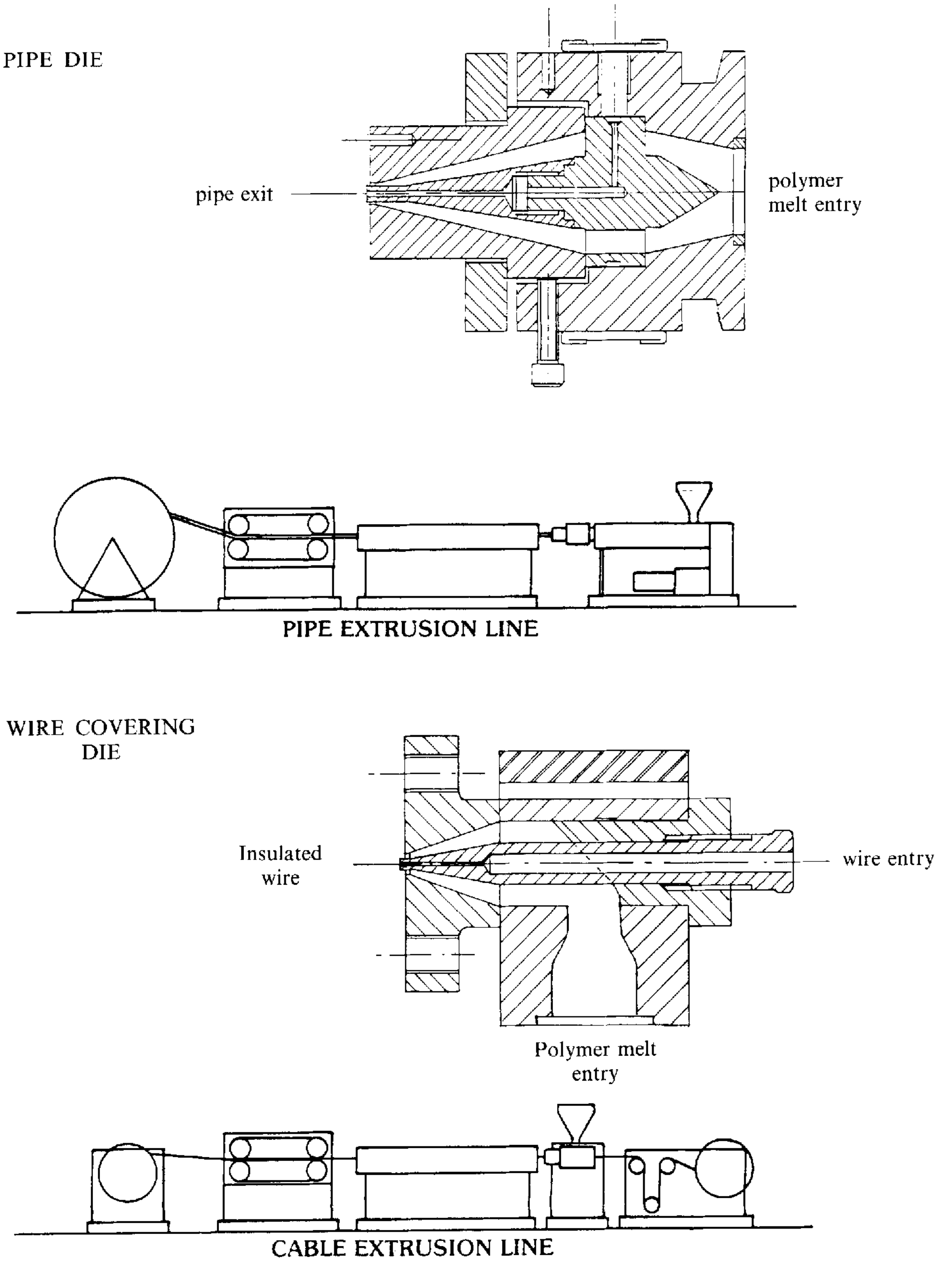
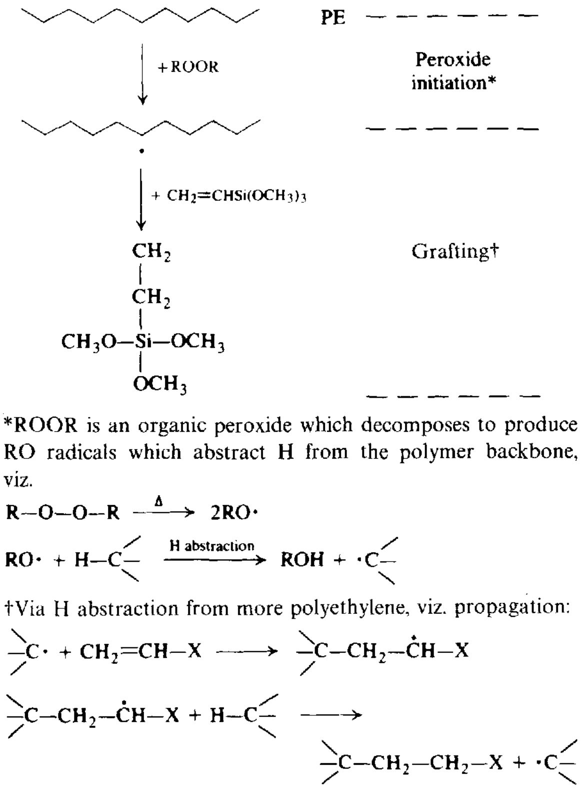


Figure 1 Extrusion of thermoplastic pipes and cables.

polymers. It should be recognized that the graft as first obtained is thermoplastic and can be shaped on conventional plastics machinery to a finished product such as cable, pipe injection moulding, etc. The second step is to modify the properties of the fabricated product by a controlled hydrolysis reaction, i.e. by exposing the product to moisture. By employing a trialkoxyvinylsilane as the graft monomer, hydrolysis and silanol condensation produce the crosslink (Figure 2c).



*ROOR is an organic peroxide which decomposes to produce RO radicals which abstract H from the polymer backbone, viz.

$R{-}O{-}O{-}R \xrightarrow{\Delta} 2RO\cdot$

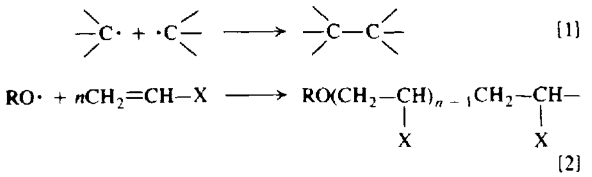
$RO\cdot + H{-}C\lessgtr \xrightarrow{\text{H abstraction}} ROH + \cdot C\lessgtr$

†Via H abstraction from more polyethylene, viz. propagation:

$\gtrless C\cdot + CH_2{=}CH{-}X \longrightarrow \gtrless C{-}CH_2{-}\dot{C}H{-}X$

$\gtrless C{-}CH_2{-}\dot{C}H{-}X + H{-}C\lessgtr \longrightarrow \gtrless C{-}CH_2{-}CH_2{-}X + \cdot C\lessgtr$

Figure 2a The Sioplas process for crosslinking polyethylenes.



$\gtrless C\cdot + \cdot C\lessgtr \longrightarrow \gtrless C{-}C\lessgtr$ [1]

$RO\cdot + nCH_2{=}CH{-}X \longrightarrow RO(CH_2{-}CH(X))_{n-1}CH_2{-}CH(X){-}$ [2]

Figure 2b Sioplas process—side-reactions.

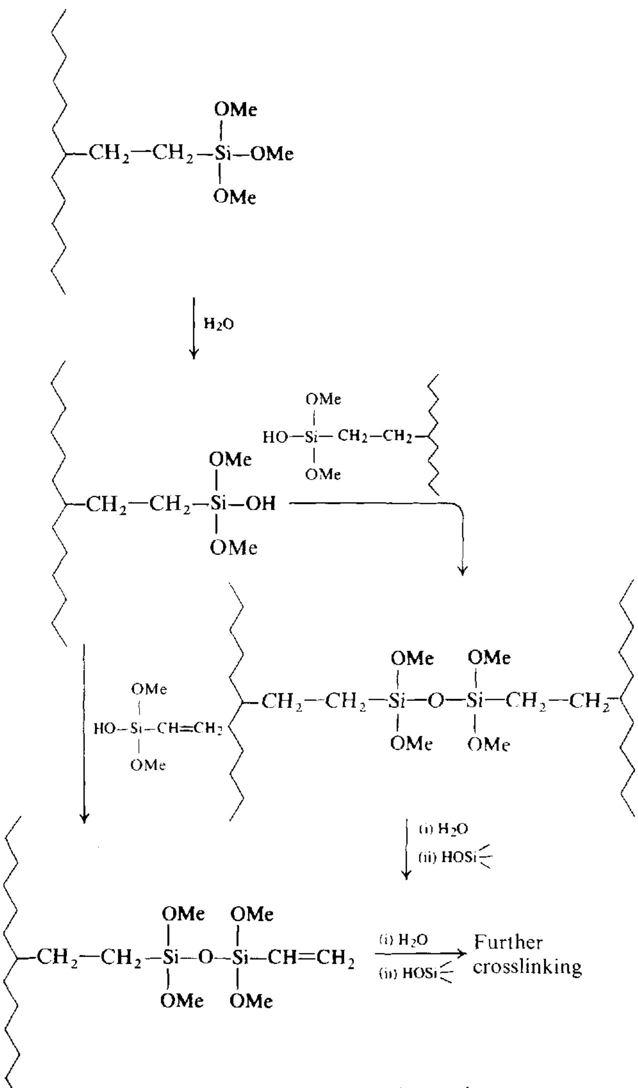


Figure 2c Sioplas process—side-reactions.

The achievement of a rapid bimolecular condensation between silanol groups present at low concentration exploits established catalysis. The use of organotin compounds to catalyse this condensation has been described and studied by Fierens *et al.*[5] The reaction catalysed by dialkyltin dicarboxylates is thought to involve a reaction of the silanol with a silanol–organotin complex as the rate-determining step (Fig. 3). The dialkyltin dicarboxylates studied included the dibutyltin diacetate, dilaurate and di-(2-ethylhexanoate), but it is the latter longer-chain dicarboxylates which are more commonly encountered in commercial organosilicon polymer formulations, since these have the preferred solubility characteristics.

The time taken to crosslink depends on the thickness and the temperature.[3] In the examples described below extruded pipe was steam autoclaved at 110°C for 4 h.

The siloxane Si—O—Si bridges form a crosslinked network which is expected to be substantially different in character from that produced by peroxide or radiation crosslinking. The latter processes produce C—C bridges, each forming an isolated link between two polyethylene chains. On the other hand the trifunctional character of the trialkylsilane graft will

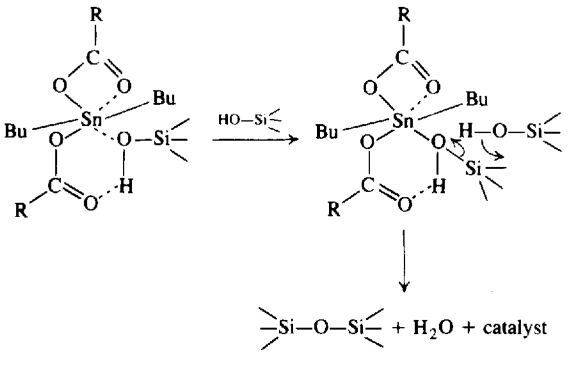


Figure 3 Proposed complex formation in the dibutyltin dicarboxylate-catalysed silanol condensation.

ensure that more than two chains are bound together at a single site (e.g. Fig. 4). How many such chains may be bound to one crosslink cluster is not known with certainty, but even with only a two-thirds contribution from each graft, at least four chains can conceivably be joined.[3] This probably accounts for the differences which occur between the two crosslinking methods in relating properties with degree of crosslinking assessed by gel content following solvent extraction of uncrosslinked material.[6] In practical terms the silane cure gives a tightly bound network which appears to be equal to C—C bound networks in performance in hot-water pipe applications.

CAVITY TRANSFER MIXER (CTM)—DIRECT SILANE INJECTION TECHNOLOGY

In 1974, BICC UK and Maillefer jointly patented the 'Monosil' process[7] (Fig. 5a), in which silane, peroxide and tin catalyst are added with the polyethylene into the feed zone of a cable extruder, eliminating the need for grafting in a precompounding stage. For this process a special extruder is used with a combination of screw design and temperature control to achieve the required conditions necessary for complete mixing followed by grafting. Claims are made[8] that in comparison with the two-step process, the Monosil process has lower capital and material costs and equal output rate, whilst in comparison with steam continuous vulcanizing (peroxide) it has lower capital costs, equal raw-material costs and 2½ times the output rate.[8]

The manufacture of crosslinked polyethylene hot-water pipes by feeding the three constituents (silane, peroxide and tin catalyst, as in Fig. 5a) into existing polyethylene pipe extruders appeared to be a suitable way of both using currently idle plant and expanding the market for polyethylene pipes. However, there are technological as well as patent restraints against applying the Monosil process to existing extruders. Although direct injection of silane into the melt may appear to be a simple alternative,

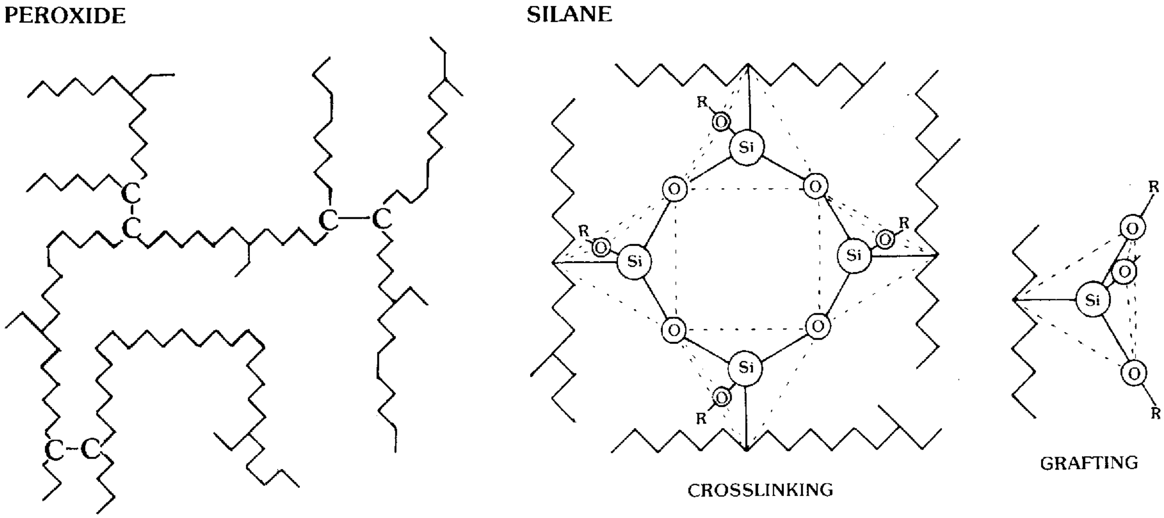


Figure 4 Possible differences between peroxide and silane crosslinking networks.

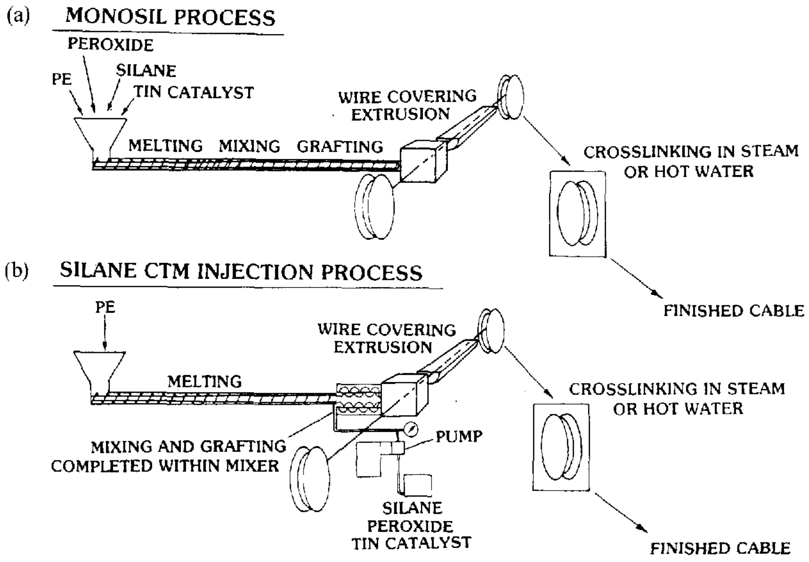


Figure 5 The Monosil and silane CTM processes.

the slow laminar mixing by an extruder screw will produce zones of high additive concentration for periods long enough for crosslinked nib formation.

Mixing in polymer melts—the Cavity Transfer Mixer

A possible technique was to inject the grafting additives into a sufficiently efficient mixing device which could be added as an extension to existing extruders. Mixing performance of the Cavity Transfer Mixer (CTM) in comparison with other mixing devices[9] indicated its potential suitability for this application.

The general arrangement is shown in Fig. 5b. A three-component mixture of silane, peroxide and tin catalyst is injected at a constant rate by a metering-type piston pump into the polyethylene melt as it enters the CTM. During passage through the CTM, materials are mixed into the polymer melt, free radicals are formed, and the silane grafted on to the polyethylene. The rate of injection, set by the adjustable pump stroke, is determined by the rate of loss in weight of the silane mixture from a container on a digital top-loading balance with a suitable response time.

As there have been numerous screw mixing devices and static mixers available for many years, it is reasonable to question why a CTM need be used. To provide an answer it is necessary to consider the requirements for good distributive- (or blending-) type mixing. Edwards and Shales[10] have shown that laminar flow mixing in single-screw extruders is even worse than that predicted by established extrusion theory. A theory for efficient viscous fluid mixing by Spencer and Wiley[11] with later work by Ng and Erwin[12] indicates an alternative mechanism which can be used.

Distributive mixing

As mixing of two viscous fluids proceeds, there is an increase in interfacial area, so that the final interfacial area divided by the original interfacial area can be used as a quantitative measure of the mixing which has taken place. This can also be expressed as the original striation thickness divided by the final striation thickness, the two expressions being related by Eqn [3].

$$\text{Degree of mixing} = \frac{A_f}{A_0} = \frac{t_0}{t_f} \qquad [3]$$

where

A_f = final interfacial area,
A_0 = original interfacial area,
t_0 = original striation thickness,
t_f = final striation thickness.

For the normal extruder screw, a striation of molten masterbatch at point A (in Fig. 7) will

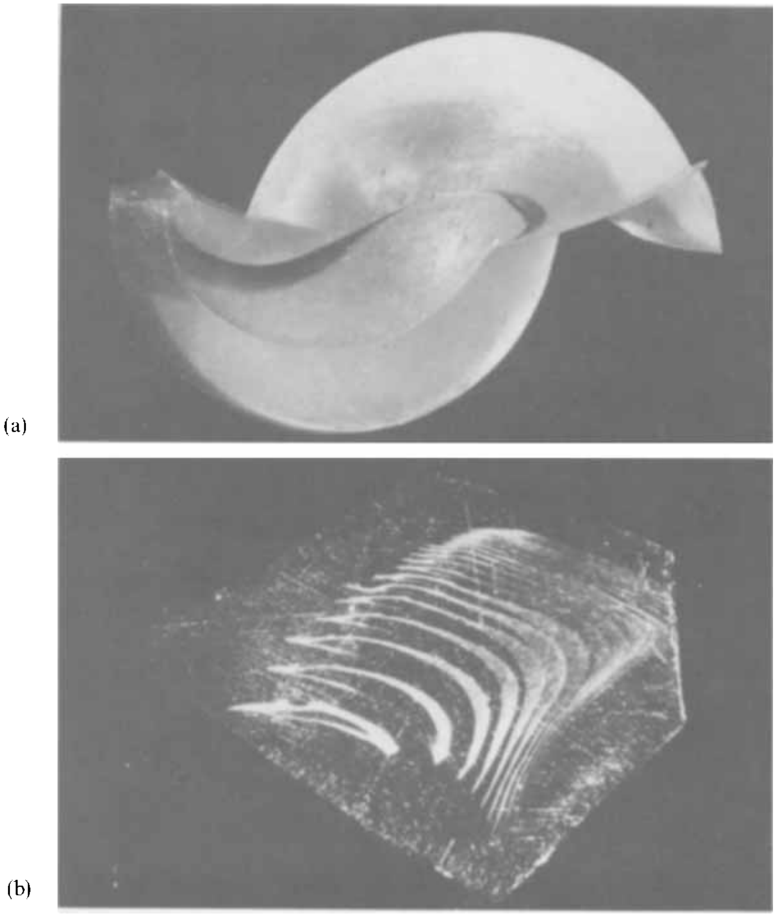


Figure 6 Silicone casting showing: (a) circulatory flow at injection; (b) sheared striation formation.

experience shear deformation which will increase the surface area by the amounts shown for the increasing amounts of shear strain caused by rotation of the screw. The striation becomes aligned in the direction of shear and when exposed graphically the relationship is linear. In the theory of Spencer and Wiley,[11] illustrated in model experiments by Ng and Erwin,[12] mixing will be much more effective if the striations are re-positioned at a more favourable angle.

In terms of a mixing device, the requirement is for the laminar mixing action to be interrupted by regular cutting and turning actions. This is carried out in Fig. 6 where the striations have been cut into ten equal pieces and re-positioned at right angles to the direction of shear. Assuming this has been carried out by mixing stages along the original length of screw, plotting increase in interfacial area against shear strain shows that mixing is no longer simply proportional to the length of the screw, and theoretically can be an exponential relationship. Consequently, a very short mixing device using this principle can achieve the same degree of mixing as an impossibly long conventional extruder screw.

The Cavity Transfer Mixer has a matching rotor and stator having staggered rows of approximately hemispherical cavities, such that cavities on one side overlap those on the other to form a continuous path. The stator forms an extension to the barrel and the rotor an extension to the screw, so that laminar shear occurs within the cavities with a chopping and turning action during transfer from one cavity to another (Fig. 8). Theoretical work by Bromilow and

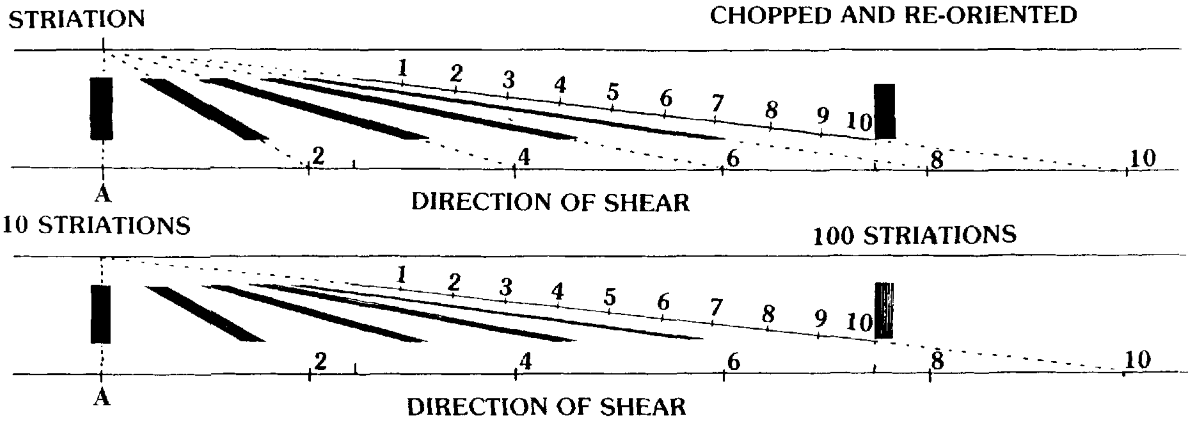


Figure 7 Interruption of laminar mixing action by regular cutting and turning actions.

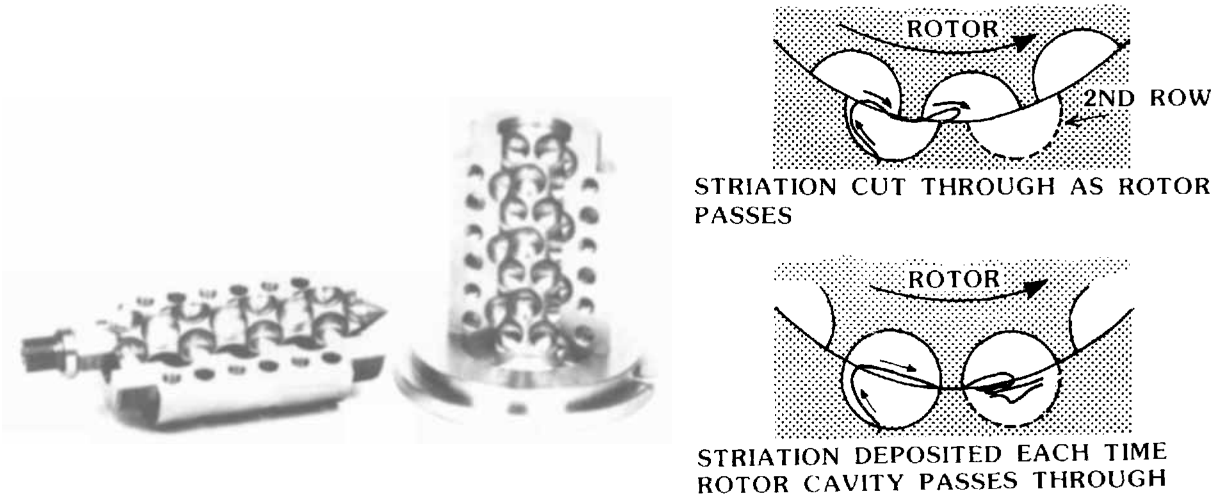


Figure 8 The Cavity Transfer Mixer (CTM) and action (38 mm extruder).

Hulme[13] showing that the mixing pattern gives an exponential mixing relationship has been verified by practical experiments using microscopy to measure striation thicknesses in material removed from the CTM cavities[1] (Fig. 6).

The CTM as a reactor

An all-important requirement for silane grafting is that mixing should be very rapid to ensure completion during the peroxide induction time to avoid reaction within the silane instead of between silane and polyethylene; otherwise the degree of grafting will be reduced with respect to silane homopolymerization (e.g. Fig. 2b), and hard nibs will be formed. It is also important that the mixer should be streamlined with no corners for stagnation and nib formation.

In addition to efficient distributive mixing there are a number of advantages for the overlapping hemispherical cavity arrangement, as follows.

(1) At any point during rotation, each cavity is open to three opposite cavities with a large overlapping area being possible. This minimizes pressure drop, and cross-sectional area variation-induced pressure pulses have a small amplitude at a high frequency.
(2) Land lengths (i.e. the regions of close contact between rotor and stator) are minimal so that high-shear regions are minimised thus reducing the likelihood of hot spots forming from the resulting shear heating.
(3) The configuration is streamlined with no corners for stagnation to occur.

(4) The CTM appears to be self-cleaning in operation, and when stripped down is easily cleaned or polished with rotary tools.

In carrying our a chemical reaction involving a continuous viscous fluid mixing process, the result will depend on a number of variables such as rate of addition, mixing, diffusion, residence time, temperature, pressure, etc., of which there is limited theory.[14]

EQUIPMENT

In the initial work a single strand of polyethylene of 8 mm diameter was extruded and tested to cable specifications. This was followed by development work for production of pipe for hot-water applications in which a pipe die with associated downstream ancillaries were used to produce hot-water pipes to DIN 16-893 specification.

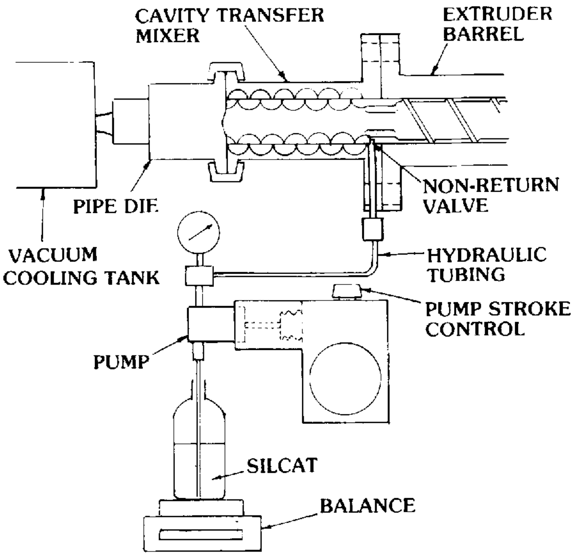


Figure 9 Laboratory arrangement for silane injection.

Cable-type extrusion

A 38 mm extruder was used having a conventional 24D screw with equal length feed, compression, and metering zones (Fig. 1), a nominal channel depth ratio of 3:1 and a feed zone channel depth of 6.35 mm. The extruder was fitted with a Cavity Transfer Mixer as shown in Fig. 8, having electrical resistance heating but without cooling. The three-component silane additive was injected from a burette via a metering pump, pressure-measuring manifold and non-return injector into the adaptor region between screw and rotor (Fig. 9). The injector was fitted into a conventional half-inch (12.7 mm) UNF pressure transducer port.

Bleed holes were available from stator cavities at three approximately equidistant points along the CTM, samples being taken by removing and replacing the plugs one at a time. A single 8 mm diameter strand die was fitted to the mixer outlet.

Pipe extrusion

The same extruder and CTM were used, but the silane mixture was injected from a triple-headed pump (to minimize pulsations) from a container mounted on a digital top-loading balance. An in-line tube die was fitted to the CTM and pipe-cooling carried out in a vacuum cooling/calibration water tank, which was followed by a conventional caterpillar haul-off. The final pipe size was 20 mm OD with 2.0 mm wall (DIN 16-893). The general arrangement is shown in Fig. 9.

It is important that exposure of silane mixture to the atmosphere is minimized to ensure that premature reaction with atmospheric moisture is avoided. The container was therefore kept sealed when injection was not being carried out, and for longer runs a dry nitrogen atmosphere was provided.

PROCEDURE

Cable-type extrusion

By using a simple strand die (8 mm diameter), an extruded product similar to a cable insulation without a central conducting wire was produced. The exclusion of wire pay-out, crosshead die assembly, etc., eliminated variables which at this stage of the development would have made experimental work unnecessarily complicated.

Strands were extruded under the conditions of polymer type, silane concentration and screw speed under investigation with monitoring of processing conditions, extrudate appearance and the retention of samples for xylene extraction and hot deformation tests. After setting the screw speed, the extruder output rate was measured by cutting and weighing samples at one-minute intervals. Injection of a prepared mixture of silane, peroxide and tin catalyst was then started with the pump stroke adjusted to the appropriate setting from a calibration graph for the concentration of silane required. As grafting increased the melt viscosity, which consequently marginally reduced the output rate, this was measured again and the injection pump adjusted against measurements of rate of emptying of the burette. Following establishment of steady conditions, samples were taken for assessment of crosslinking both during grafting in the mixer and after reaction with water.

For solvent extraction tests on the grafted polymer, one sample was transferred immediately to a desiccator. As soon as possible afterwards, shavings were taken in the dry nitrogen atmosphere of an 'Atmos bag' using a trimming knife and the shavings subjected to xylene extraction using a Soxhlet refluxing method with a procedure similar to that described in ASTM D2765-68. This determined the gel level of the grafted polymer extrudate before crosslinking with water. A second sample was stored in a labelled polyethylene bag and shavings prepared later were boiled in water under reflux for 4 h. These samples were also tested for crosslinking assessment by xylene extraction. A third sample was immediately compression-moulded at 170°C into sheets 1 mm thick. After storage for 24 h in vacuum flasks filled with boiling water, tensile bars to BS 902, Part A2, Type 2 were cut from the moulded sheets and hot deformation tests carried out to IEC 502 1983 in which measurements were made of extension under a load of 20 N cm^{-2} after 15 min at 200°C.

Examination of grafting during material progress through the mixer was carried out by testing polymer issuing from three feed ports located in stator cavities which were opened one at a time for sampling.

Pipes

Pipe extrusion trials included an evaluation of a range of silane–peroxide–tin catalyst systems in combination with several polymers. The setting of the silane level was the same as that used for the strands. The extruded (grafted) pipes were crosslinked by steam autoclaving for 4 h at 110°C. The pipes were tested to DIN 16-892 specifications as follows.

(1) Measure gel content (using xylene extraction from turned washers 0.2 mm thick).
(2) Withstand 1 h under pressure in water at 95°C with a wall stress of 4.8 N mm^{-2}.
(3) Withstand 1000 h under pressure in water at 95°C with a wall stress of 4.4 N mm^{-2}.

For comparison with initial work, the cable specification hot-set tests were carried out, initially using sheet moulded from pipe samples prior to crosslinking, but later with tensile specimens cut directly from the crosslinked pipe.

RESULTS

For the strand extrusion, tests were carried out for three polymers.

(1) Vestolen A4516 (Hüls): A linear-type medium-density PE, normally used for blow-moulded containers. Density 945 kg m^{-3}. Melt Flow Index (MFI) 7 g/10 min.
(2) Unifos DFDS 4444 (Neste): A branched LDPE used for cable extrusion. Density 922 kg m^{-3}. MFI 2.2 g/10 min.
(3) Unifos NEWS 8019 (Neste): A linear LDPE used for cable extrusion. Density 934 kg m^{-3}. MFI 4 g/10 min.

For pipe extrusion, tests were carried out on two medium-density polymers, density nominally 945 kg m^{-3}, one made using Ziegler catalysts and the other by the Phillips process.[15]

DISCUSSION

The initial objective was to produce extrusions which met the extension maximum of 175% of IEC Standard 502 and have minimum residual polymer after xylene extraction of 65%. It was also necessary that these conditions should be met with 2.0% or less silane mixture to be competitive and to operate over a wide range of screw speeds.

The results (Tables 2–4) show that these basic requirements could be easily met with several polymers, but precise trends were difficult to identify. It was considered possible that residence times at high screw speeds could be too short for

Table 2 Vestolen A4516: effect of Silcat® concentrations[a]

Test	Screw speed (rpm)							
	60				105			
Silcat® concn (%)	1.6	1.8	2.0	2.2	1.6	1.8	2.0	2.2
Residue (dry) (%)	5	5	13	15	8	15	10	16
Residue (wet) (%)	67	56	67	71	67	77	71	72
Extn at 200°C (%)	150	67	45	—	75	69	62	—

[a] Silcat® is a proprietary silane, peroxide and tin catalyst mixture supplied by Union Carbide Europe SA.

Table 3 Vestolen A4516+Silcat® at 2%: effect of screw speed

Test	Screw speed (rpm)					
	30	45	60	75	90	105
Residue (dry) (%)	24	16	13	12	7	10
Residue (wet) (%)	80	66	67	75	67	71
Extn at 200°C (%)	26	39	45	41	47	—

Table 4 Unifos 4444+Silcat® at 2%: effect of screw speed

Test	Screw speed (rpm)					
	30	45	60	75	90	105
Residue (dry) (%)	24	15	25	21	19	20
Residue (wet) (%)	75	77	82	77	78	67
Extn at 200°C (%)	62	75	64	50	50	75

completion of grafting whilst at low screw speeds mixing would be too slow, but this did not appear to be generally the case; there were no clear trends.

If we exclude the LLDPE (NEWS 8019), 2% of the silane mixture appears to be a suitable level for all conditions, with 1.8% being a possibility under suitable extrusion conditions. The specifications were met over screw speeds ranging from 30 to 105 rpm with no clear trends, except that at the lower levels of silane addition results were better at the higher screw speeds.

In Table 5, comparisons of bleed port samples show that very little grafting has occurred at the first port, but that it advances rapidly in proportion to the level of silane and the screw speed, so that lower levels benefiting from higher speeds shown in Tables 3 and 4 could be due to this effect. Conversely, a too rapid reaction could be detrimental, as mixing must be substantially complete before grafting starts. (Anomalies between results in Table 5 and those in the preceding tables for die extrudates are attributed to differing shear and heat histories.)

The results for the LLDPE are particularly interesting in that IEC 502 requirements can be met with silane levels at about 1.0% (Fig. 10; Tables 6 and 7). A problem with this polymer is

Table 5 Assessment of rate of grafting

	Screw speed . . .	60 rpm			105 rpm		
Polymer	Bleed port . . . Test	1	2	3	1	2	3
Vestolen A4516, 1.6%	Residue (dry) (%)	2	5	5	1	1	4
	Residue (wet) (%)	35	64	76	10	67	74
	200°C Extn (%)	F[a]	F	45	F	32	35
Vestolen A4516, 1.8%	Residue (dry) (%)	4	9	12	1	7	22
	Residue (wet) (%)	20	47	65	29	78	81
	200° C Extn (%)	F	40	55	F	61	—
Unifos DFDS 4444, 2.0%	Residue (wet) (%)	3	49	75	34	71	82

[a] F, tensile failure.

Table 6 Unifos 6 Unifos News 8019: influence of silane mixture level between 0 and 1.6% at 90 rpm

	Silcat® concn (%)							
Test	0	0.4	0.6	0.8	1.0	1.2	1.4	1.6
Residue (wet) (%)	—	2.1	18.3	39.2	60.3	75	89	61
Extn at 200°C (%)	>200	>200	>200	185	45	40	22.5	20
Permanent extn (%)	—	—	—	18	5	5	0	0

Table 7 Unifos News 8019: influence of screw speed at 1.2, 1.4 and 1.6% silane mixture

	Screw speed (rpm)											
Test	60			75			90			105		
Silcat® concn (%)	1.2	1.4	1.6	1.2	1.4	1.6	1.2	1.4	1.6	1.2	1.4	1.6
Residue (wet) (%)	74	89	66	69	79	78	75	89	61	65	83	66
Extn at 200°C (%)	—	32	59	37.5	26	24	40	22.5	20	32.5	19	—
Permanent extn (%)	—	7.5	10	5	1.25	0	5	0	0	2.5	0	0

that the severe sharkskin which often occurs at high shear rates (e.g. in blown film) in conventional extrusion occurred at all extrusion speeds when grafted at about 1.0% silane level and above. A compromise solution in conventional blown-film extrusion is to use a blend of LLDPE with LDPE, which has subsequently been found to be a compromise solution for silane grafting also.

Results (Table 8) show that adaption of a 'conventional' single-screw extrusion line for production of crosslinked polyethylene pipe suitable for hot-water systems can be carried out by retro-fitting a Cavity Transfer Mixer and injecting a 'one-shot' mixture of silane, peroxide and catalyst. However, although the 1000 h, 95°C, 4.4 N mm^{-2} pressure test requirement can be met, further experimental work is needed to ensure that the 8000 h, 110°C, 2.8 N mm^{-2} pressure test is also met, whilst attention must be paid to toxicity, odour, etc. Compared with cables, hot-water pipes have additional long-term requirements, because of the need to perform under continuous conditions of stress and of temperature with one surface exposed to air (and oxygen) and the other to flowing hot water. For

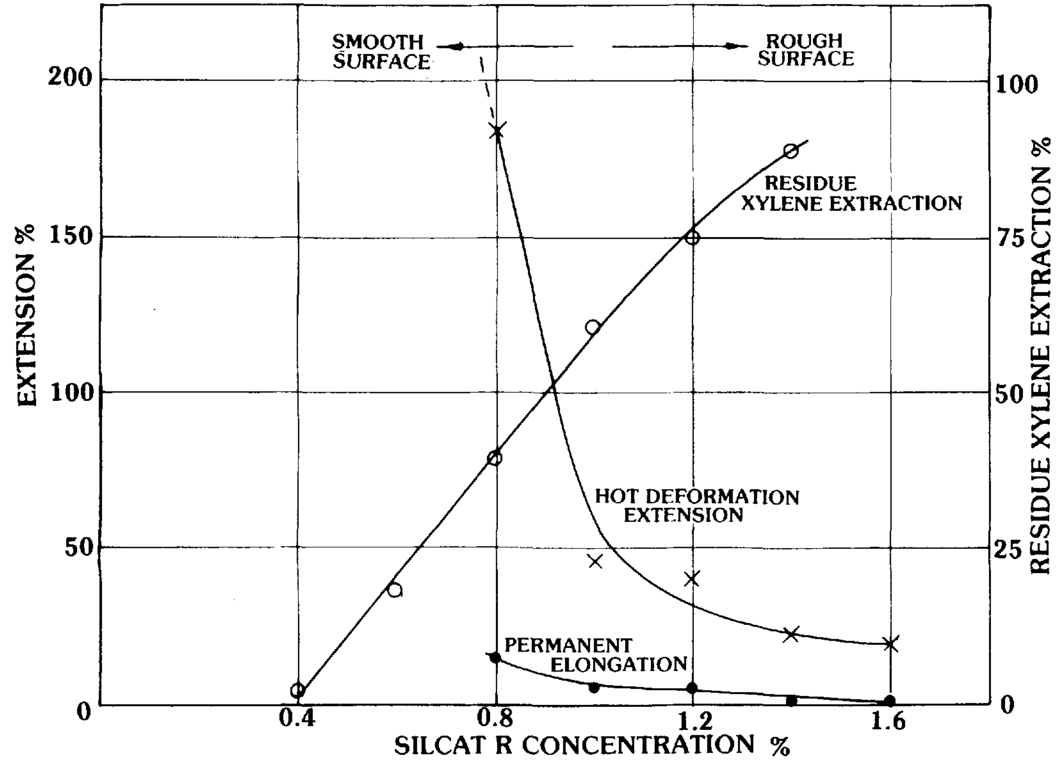


Figure 10 Influence of silane concentration on properties of crosslinked LLDPE.

Table 8 Influence of polymer on pipe properties

Supplier	Process	Density ($g\,cm^{-3}$)	MF (g/10 min)	Gel content (%)	Hot set (%)	Pressure test[a]
A	Phillips	0.950	0.2	49	Fail	Fail
A	Ziegler	0.952	6.5	62.3	38.5	Pass
B	Ziegler	0.945	7.0	72	19	Pass

[a] DIN 16-892, 1 h and 1000 h tests at 95°C.

such conditions stringent demands are made on polymer, crosslinking system and anti-oxidant (which must not be leached by the hot water).

CONCLUSIONS

(1) Crosslinked polyethylene extrusions meeting cable specifications can be produced by injecting silanes into a retrofitted Cavity Transfer Mixer fitted to a conventional single-screw extruder.

(2) The grafting process can be used for LDPE, MDPE and LLDPE polymers.

(3) There appears to be no reason why the system should not be used to retro-fit existing pipe extruders for the manufacture of crosslinked polyethylene pipes for conveying hot water.

(4) The continuous injection-mixing system should be suitable for other polymer/additive reactive combinations to produce upgraded products.

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REFERENCES

1. Roberts, A J and Verne, S *Plast. Rubb. Process. Appln*, 1984, 4(2): 135
2. Gale, G M *Plast. Rubb. Proc. Appln*, 1982, 2(4): 347
3. Munteanu, D Moisture cross-linkable silane-grafted polyolefins. In: *Metal-containing Polymeric Systems*, Sheats, J E, Carraher, C E and Pittman, C U (eds), Plenum Press, New York, 1985
4. Midland Silicones (Dow Corning), US Patent 3 646 155
5. Fierens, P, Vandendunghen, G, Segers, W and van Elsuwe, R *React. Kinet. Catal. Lett*, 1978, 8(2): 179
6. Thomas, B *Annual Nat. Conf. Cross-Linking Network Formation in Polymers*, PRI, London, Oct. 1982, p 11
7. BICC Ltd and Maillefer S A US Patent 4 117 195
8. Maillefer S A *Ecubiens*, Lausanne, April 1976
9. Gale, G M *41st ANTEC of the SPE*, 1983, p 109
10. Edwards, M F and Shales, R W Mixing in single screw extruders. In: *Making the Most of the Cavity Transfer Mixer*, Rapra Technology Ltd, Oct. 1986, pp 2.1–2.8
11. Spencer, R S and Wiley, R M *J. Colloid Sci.*, 1951, 6: 133
12. Ng, K Y and Erwin, L *37th ANTEC of the SPE*, 1979, 25: 241
13. Bromilow, T M and Hulme, A T Towards a mathematical model of the Cavity Transfer Mixer. In: *Making the Most of the Cavity Transfer Mixer*, Rapra Technology Ltd, Oct. 1986, pp 3.1–3.15
14. Ottino, J and Chella, R *Polym. Eng. Sci.*, May 1983, 23(7): 357
15. Kresser, T O J *Polyolefin Plastics*, Van Nostrand Reinhold, New York, 1969