Multi-Layer Pipes for Hydrocarbons Conveyance

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Summary: The replacement of metals with plastics in piping systems is a well established practice in a vast range of public and industrial applications. However, difficulties still exist, mainly related to the limited chemical resistance of the polymers commonly used in pipe manufacturing to some conveyed fluids. This prevents using plastic pipes in important applications such as the transport of liquid hydrocarbons, particularly in oil fields. The use of chemically resistant polymers, such as fluorinated polyolefins, is precluded by high cost and poor mechanical properties. Co-extrusion of multi-layer pipes carrying an internal chemically resistant liner can be a viable alternative capable to extend the use of plastic pipes to refining and chemical industries. An experimental PE/PA multi-layer pipe has been developed whose resistance to diffusion and mechanical properties have been tested. Tests in real oil fields confirm the good performance of the new pipes.

Keywords: hydrocarbons; plastic pipes; polyamide (PA); polyethylene (PE); swelling

Introduction

Plastic piping systems are increasingly used in public and industrial water supply systems and for sewage transportation. An important application of plastic pipes is for rehabilitation of degraded pipes when the cost of replacement is prohibitive. In almost all such systems the plastic pipes operate at near room temperature, moderate internal pressure and in contact with water. In the chemical industry, when fluids other that water are to be transported, specifically those with solvent action, the chemical stability of the polymers can be endangered. This is particularly true in petrochemical applications when liquid hydrocarbons are to be transported in polyolefin pipes. In above-ground systems the aggression to the polymer can be favoured by the temperature rise caused by exposure to sunlight. However, the advantages of plastic pipes, e.g., reduced weight, limited transportation and installation costs, toughness and

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strength are such that the use of steel or cement pipes is progressively shrinking. The relatively low costs of high density polyethylene (HDPE) makes this materials the preferred choice, but the chemical affinity of this polymer with low molecular weight olefins has severely limited the use of HDPE pipes hydrocarbons service.

The most important mechanical requirement of a pipe wall is strength. When fluids are in contact with the wall material, the short and long term effect on pipe strength must be addressed. The first phenomenon to take care of is diffusion through the wall thickness. In the steady state, if we assume the diffusion coefficient to be independent of concentration, we can write the mass balance for a cylinder in radial direction (second Fick's law [1]) as:

$$\frac{d}{dr}\left(r \cdot \frac{dC}{dr}\right) = 0 \qquad (1)$$

where C is the concentration of diffusing substance. In practice, the diffusion of very soluble chemicals in crystalline or semi-crystalline polymers may deviate from the Fickian model, particularly due to time dependent rearrangements of the crystalline regions in response to swelling stresses. However, non-fickian processes may be disregarded for what concerns the applications this paper is focused on. By solving equation 1 with proper boundary conditions for a bi-layer pipe and assuming that solubility in each layer does not depend on concentration, it can be shown that the presence of an internal layer with a low diffusion coefficient strongly reduces the amount of permeant in the outer (structural) layer, thus reducing the effect of swelling and chemical de-rating of the whole pipe.

In this paper a new class of thermoplastic bi-layer pipes capable to overcome some of the limitations of HDPE is presented and characterized.

Materials

In this work a 70/30 Nylon 6/HDPE blend has been used as the internal layer and a HDPE (PE 80 or PE 100 bimodal resin) as the structural layer. Being PA and HDPE not compatible polymers, a thin adhesive layer, made of functionalized Linear Low Density Polyethylene, was used to prevent delamination of the two walls. Theoretical predictions for bi-layer pipes still hold, provided the adhesive layer is made very thin. Experimental tests were carried out on three-layer pipes produced with a Nextrom co-extrusion line: samples for laboratory tests

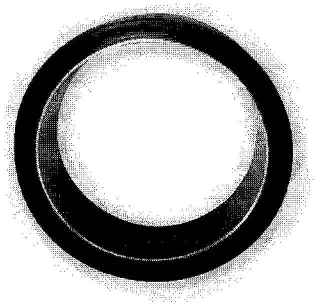

Figure 1. Cross section of a multi-layer pipe for flow lines applications. The internal layer is clearly visible.

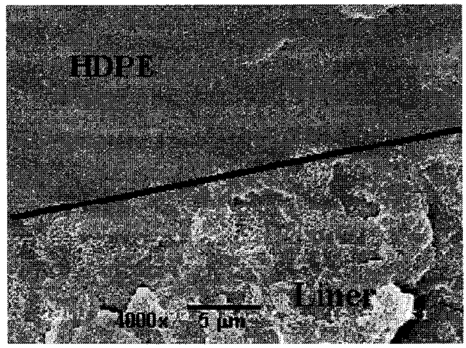

Figure 2. SEM image across the HDPE/Tie-layer/Liner region; the line is the boundary between outer (top) and inner walls (bottom).

had an outside diameter (OD) of 32 mm, a total thickness of 3.2 mm and an inner layer thickness < 1 mm, while field tests samples had OD=90 mm, total thickness=7.6 mm and inner layer thickness< 1 mm.

The pipe cross-section is shown in Figure 1; the black, thick external layer is the load bearing wall whereas the thin internal layer is the low-diffusion wall. The enlarged view in Figure 2 shows that a very good adhesion between outer and internal wall was achieved; the two walls were so intimately bonded that the tie-layer could not be observed.

Laboratory tests

Long Term Hydrostatic resistance

Chemical resistance is not the only factor affecting the pressure rating and the lifetime of thermoplastic pipes. Mechanical properties of the polymers, additives and processing conditions strongly influence the mechanical performance of pipes [2]. An overall figure of merit for plastic materials for pipe applications can be obtained from creep rupture tests. In a creep rupture test a pipe is kept under a constant hoop stress until, at a given temperature, failure occurs (either fragile or ductile). The test procedure is standardized in ISO 9080 and ASTM D 2837. From a complete series of creep tests one obtains the lower confidence limit of the predicted hydrostatic strength (σ_{LPL}), which can be used to define the maximum operating stress at a specific temperature and for the required life time.

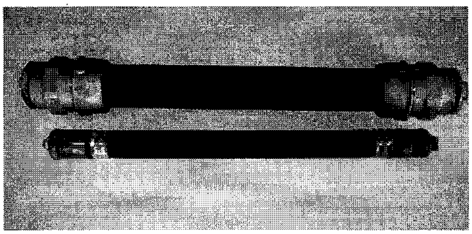

Figure 3. The 32 mm and 50 mm OD pipe samples used for pressure tests.

Test Method

The determination of the time to failure of the pipes was carried out using an IPT 1575 apparatus for burst tests. Pipe samples, filled with the chemical being studied, were sealed at both ends (Figure 3) and placed in an air circulated thermostatic chamber. The internal sample pressure was kept constant with compressed nitrogen. The internal liquid was replaced every two weeks to make sure that its composition remained constant throughout the test. The outer diameter of the specimen was measured daily. The time to failure was taken when either rupture or radial swelling higher than 5 % occurred.

A regression analysis was performed by a numerical code which tries to fit different models to experimental data and identifies, according to a statistical algorithm, inflections in the creep rupture curves. The time to failure, t_R , was given by a 3-parameter model:

$$\log(t_R) = c_1 + \frac{c_2}{T} + \frac{c_3}{T} \cdot \log(\sigma) \qquad (2)$$

where c_1, c_2 and c_3 are the fit parameters, T is the temperature (K) and σ the hoop stress (MPa).

Results

Pressure tests were carried out at 60 and 80°C. In Figures 4-5 the results of the regression analysis (running tests are not included in the regression analysis) are shown for crude oil (Upper Gulf Coast) and Fuel C (50% Toluene + 50% Isooctane). For crude oil no inflection was detected at 80 °C after 17,000 hours (~2 years). The estimated σ_{LPL} hoop stress at 20°C for a service life of 25 years is ~7 MPa.

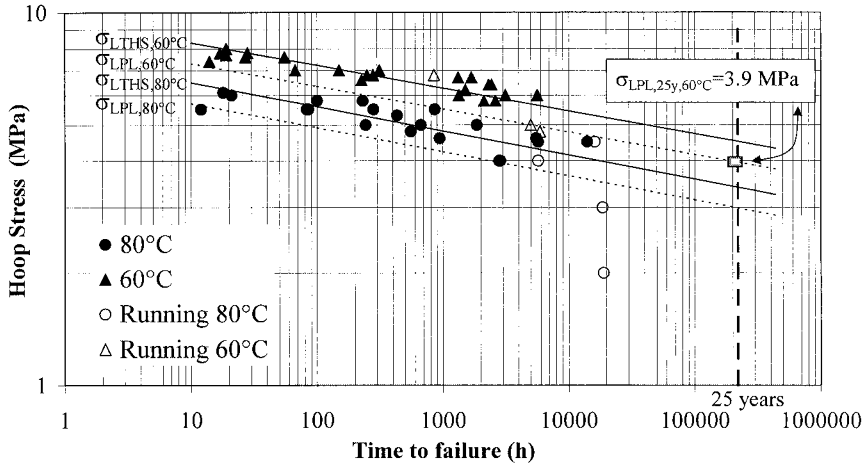

Figure 4. Time to failure for 32 mm OD multi-layer pipes exposed to crude oil; σ_{LTHS} is the Long Term Hydrostatic Strength, i.e., the predicted mean strength at the temperature T and time t; σ_{LPL} is the 97.5% Lower Confidence Limit of σ_{LTHS}.

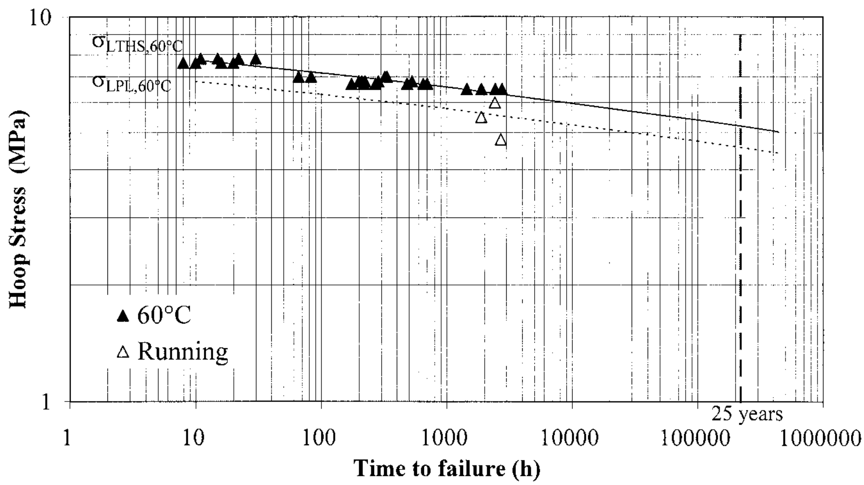

Figure 5. Time to failure for 32 mm OD multi-layer pipes exposed to Fuel C; for σ_{LTHS} and σ_{LPL} (see also caption to Fig.4).

Adhesion in multi-layer pipes

As already outlined, the chemical resistance of the intermediate adhesive layer is of

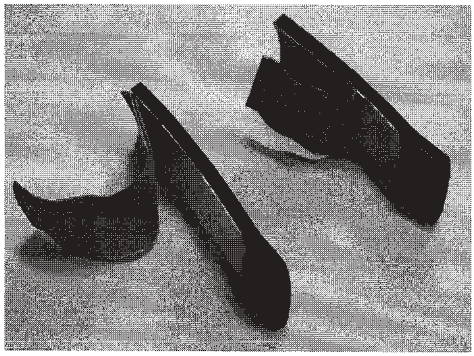

Figure 6. Specimens to test adhesion between inner and outer layers (peeling).

paramount importance. Prolonged exposure to different fluids usually decrease the adhesion strength by 1) formation of voids (blisters) or cracks in the tie layer; 2) reduction of the shear modulus of the adhesive layer through plasticization and 3) desorption of the adhesive. A generally accepted method to assess the chemical resistance of adhesive layers consists in carrying out long-term peel tests after exposure to aggressive fluids.

The adhesion strength of different tie-layers after exposure to Yibal crude oil, water and M15 (42.5 % Toluene + 42.5% Isooctane + 15% Methanol) fluids, at various temperatures, was investigated.

Test Method

Specimens were immersed in the test liquid at various temperatures and tested according to ISO/UNI 36 (see Figure 6). Specimens were periodically removed from the test fluid and peeled with a dynamometer equipped with special jaws. The adhesive strength was averaged over 25 mm length.

Results

The tie-layer used for the marketed multi-layer pipes did not show any loss in strength after exposure for one year at 50 °C; a slight increase was rather observed, possibly due to enhanced diffusion of the adhesive into pipe walls (see Figure 7).

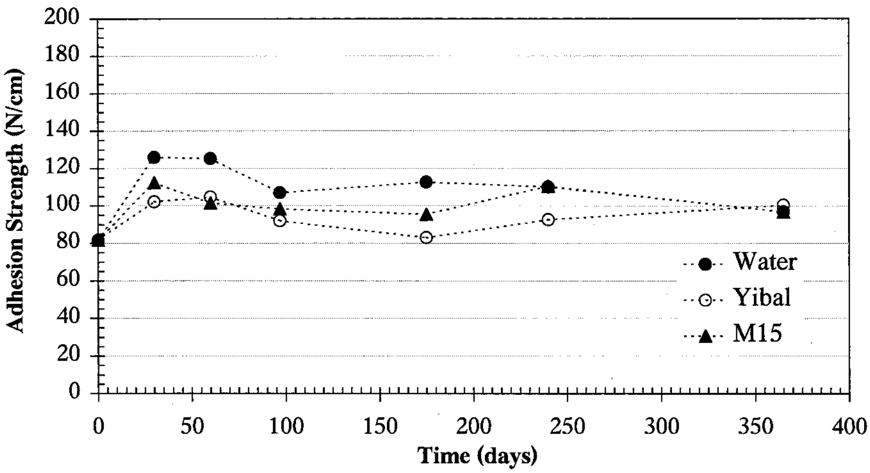

Figure 7. Adhesion strength vs. exposure time for different fluids at 50 °C.

Tensile properties of multi-layer pipes

Finally, tensile test were carried out to ascertain that the diffusion, although limited by the internal layer, did not cause any serious decay of the mechanical properties of the pipes. Samples were filled with crude, plugged and placed in an air circulated oven and periodically tested for swelling and strength.

Test Method

Tensile tests were carried out on 32 mm OD HDPE mono-layer and three-layer pipes 150 mm long. Samples were clamped with special grips and tested according to ASTM D638 M (results of five measurements were averaged).

Results

In Figure 8 the strength of multi-layer pipes exposed to Upper Gulf Coast crude oil at 80 °C is compared to that of a HDPE mono-layer pipes exposed at the same temperature to air. The value of strength at 5% strain has been considered as representative of pipe behaviour because above this strain value the system loses its structural function. The two data sets coincide thus

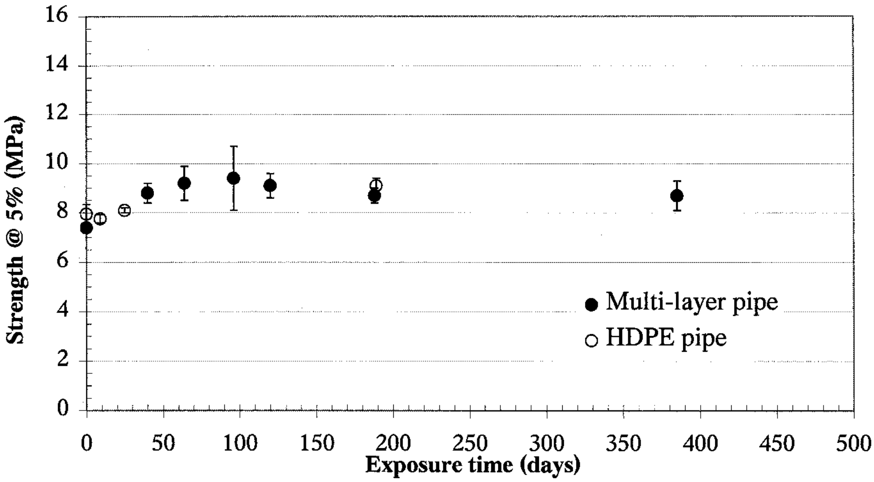

Figure 8. Strength at 5% strain vs. exposure time at 80°C for multi-layer pipe (in crude oil) and for mono-layer pipe (in air).

confirming that even a prolonged exposure of the layered pipe to crude oil did not cause any decay of strength (swelling was not observed as well).

Field tests

Extensive field tests have been carried out in oil fields in West Texas and New Mexico on several 90 mm OD multi-layer pipes. The lines were installed both above, Figure 9, and under-ground and operated at ambient temperature at pressures of 3-20 bar. The oil cut varied from 20% to 45% depending on formation. The lines were connected to the existing systems through stainless steel transition fittings and high-resistance cross-linked polyethylene electro-fusion couplings, Figure 10.

Some of the lines were sampled after 10 months of continuous service. Thermal, mechanical and rheological tests showed that the structural (outer) layer did not suffer any significant damage due to the harsh service conditions.

The use of multi-layer pipes virtually eliminated the paraffin build-up, even in cold weather. This is essentially due to a limited affinity of the liner to paraffins. The conveyed fluid naturally flows and the need of hot oiling or chemical treatment is eliminated. In one field,

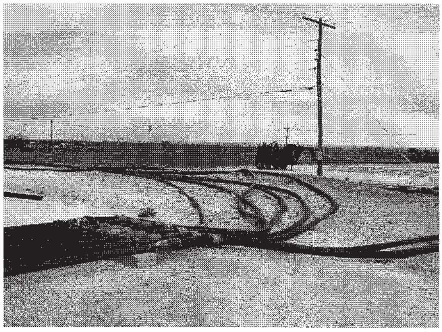

Figure 9. Multi-layer flow lines.

Figure 10. Manifold connection.

neither chemical treatments nor hot oiling were needed for a period of one year on 76 different oil wells; this resulted in savings for over € 200,000 .

Conclusion

A new class of composite piping systems has been developed along with proprietary compounds, process conditions and materials selection criteria. All this now allows the production of PE-like pipes capable to fulfil some of the requirements for oil extraction, conveyance of automotive fuels and wastes and hazardous materials treatment.

The experimental analysis showed that the main advantages offered by multi-layer pipes are:

i) Virtually "zero permeability" to hydrocarbons.

ii) Reduced paraffin build-up and consequent substantial savings in the operating costs.

Also, an increased pressure rating in hydrocarbons service with respect to HDPE pipes is arising from ongoing tests, which are currently being carried out on different geometries, materials and fluids at the NUPI Technology Center in Imola BO – Italy in order to expand the field of application of this new technology.

Through co-extrusion technology, the basic properties of polyethylene (chemical resistance, permeability to hydrocarbons, friction coefficient and creep resistance) can be improved, thus giving the multi-layer pipes a remarkable cost/performance ratio.

[1] J. Crank, *"The Mathematics of Diffusion"*, 2nd Edition, Clarendon Press, Oxford 1955, p.44.
[2] U. Andersson, *"Which factor control the lifetime of plastic pipes and how the lifetime can be extrapolated"*, in: *Plastics Pipes XI Conference Proceedings,* St Edmundsbury Press, London 2001, p.311.