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IMPERMEABLE COMPOSITE PIPES FOR ETHANOL TRANSMISSION

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Abstract. Organic solvents have no effect (long-term or short-term) on the glass fibers used in the manufacture of composite pipes. The resin matrix, however, shows strong interaction with some organic solvents. The resin-solvent interaction governs the performance of composite pipes in contact with organic solvents. The large amount of solvent that is picked up by the resin matrix reduces the ability of the composite to perform in structural applications. The market clearly needs a low cost solution that would allow the use of composites in high pressure pipelines for the transmission of solvents, especially the transmission of ethanol. Such a solution would open huge opportunities for composite pipes in a variety of load-bearing applications.

The solution proposed in this paper is low cost, simple and straightforward. It consists essentially in making all pipeline components – pipes and fittings – impermeable to the solvent. The impermeable composite prevents the ingress of solvents into the structural wall of the pipe component. The solvents kept out of the laminate cannot swell the resin and cannot do any structural harm to the composite. The proposed solution is market-ready and does not require any extensive and expensive testing and product development. The pipe components made with this new technology easily meet and exceed the requirements of product standards like AWWA C950, ISO 14692 and API 15HR.

Introduction - Composites have been used for many years in the pulp bleaching and oil industries to carry contaminated process water, effluent and a variety of highly corrosive chemical solutions. However, due to its high permeability, composites are not considered in applications involving high pressure pipelines used to carry gases and solvents. This paper will propose that the insertion of a metal foil in the liner of the composite structure will make the pipe component impermeable to the gases and to the solvents. The impermeable liner prevents the escape of gases and keeps the solvents away from the load-bearing structural plies of the composite. This simple and direct solution allows the use of composite pipes in the transmission of gases and solvents. The impermeable pipes and components are especially of interest in the transmission of ethanol.

The glass fibers used in the manufacture of composites do not absorb or otherwise interact with organic solvents. It can be safely assumed that organic solvents have no long-term effect on the glass fibers. The same cannot be said of the resin matrices, however, which are permeable to and absorb large quantities of solvents. The performance of composites in contact with organic solvents is governed by the resin matrix. The amount of solvent that permeates and eventually saturates the resin is determined by the solubility parameters of the resin and solvent, and other factors like temperature, laminate layup, degree of cure, etc. The solvent that is picked up swells the resin and strains the composite, reducing its ability to perform under loads in structural applications. Loss of structural capability is the bad news regarding the effect of solvents on composites. The good news is that the organic solvents are not reactive with the resin (or the glass fibers) and for that reason they do not cause long-term damage. Whatever damage the solvents do to composites they do in the short-term. The deterioration ceases when the saturation level is reached.

The suitability of a given resin for use in a given solvent is a go, no-go proposition that can be resolved by conducting short-term immersion tests of resin castings in the contemplated solvent. In this paper we will be concerned primarily with the transmission of ethanol. However, the concepts discussed herein are general and applicable to other solvents and to gases as well.

Solvent classification - Inasmuch as composites are concerned, the organic solvents can be classified in three categories.

- *Low absorption* - The solvents in this category do little harm to composites and are in fact not a deterrent to structural applications. The most notorious representative of this category is water, which saturates the resin at

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low levels of absorption, usually in the 1% range. The low strains caused by such small absorption do little structural harm to the composite and allow its use in demanding load bearing applications such as the high pressure pipes so common in the oil industry. The use of high pressure composite pipes in the oil industry is a widespread "regular" application which is familiar to everyone. Low absorption solvents like water, therefore, are not a deterrent to the use of composites in load bearing structural situations.

- *Medium absorption* - The level of swelling caused by the solvents in this category is moderate and may allow the application of composite in non-load bearing applications such as underground storage tanks and low pressure pipes. There is a variety of organic solvents falling in the category. The most notorious are, maybe, ethanol and methanol, which saturates the resin at circa 10% absorption. The 10% saturation observed in ethanol/methanol should be compared with the 1% saturation observed in water.

- *High absorption* - The swelling caused by the solvents in this category is too high, leading to resin cracking and the failure of the composite even in non-structural applications. Acetone is a good example of a solvent in this category.

There are many low pressure non-structural applications of composites in ethanol. Examples are the widespread underground storage tanks and distribution pipelines used in filling stations. The Underwriters Laboratories have tested and approved specific resins for use in the storage and distribution of ethanol and methanol in such applications. However, these are non-structural or at best low pressure applications that do not require the ultimate structural performance and ultimate mechanical properties of the composite. This scenario changes completely in demanding structural applications such as high pressure pipelines.

The high pressures stretch the composites to their limit. Ethanol does not interact chemically with the polyester or epoxy resins that are used in the manufacture of the composite pipes. Rather, ethanol has a solvent effect on these resins. As the resin picks-up the ethanol, it swells, expands and loses mechanical properties in the process. The degree of deterioration depends on the amount of ethanol that is absorbed. Small amounts of solvent pick-up are acceptable and even desirable in some applications as the solvent may plasticize and improve the performance of the resin matrix. For example, the polyester resins immersed in water will pick-up and saturate when the level of 1.0% absorption is reached. This low absorption is considered acceptable and is not a concern in engineering applications. Other solvents, however, are picked-up in such high quantities as to crack the resin and rule out the use of composites altogether, even in non-structural applications.

A good starting rule to decide the suitability of composites in load-bearing applications with solvents is to discard their use if the saturation level exceeds 5% of the resin weight. That was the rule used in screening the resins for application in ethanol transmission lines. We tested several products in our portfolio, ranging from the best, high cost UL-approved resins for ethanol use, to the lowest cost least likely products. The tests consisted in immersing post-cured 2,0 mm thick resin castings in ethanol at room temperature and monitor the weight gain. The results are shown in table 1.

Resin	Initial weight	Post-cure	Absorption Δm (%)						
			30 days	60 days	90 days	120 days	180 days	210 days	240 days
DCPD	98,3306	90C	6,38	11,58	13,79	14,12	14,50		
TERE	95,5145	90C	0,74	1,72	2,53	2,90	3,72	4,22	4,89
TERE	92,0003	120C	0,34	1,02	1,58	1,79	2,31	2,62	3,00

Resin	Initial weight	Post-cure	Absorption Δm (%)						
			270 days	300 days	330 days	360 days	390 days	420 days	450 days
DCPD	98,3306	90C	14,50						
TERE	95,5145	90C	5,60	6,66	8,14	9,48	10,08	10,49	10,64
TERE	92,0003	120C	3,37	3,79	4,32	4,95	5,74	6,70	7,58

Resin	Initial weight	Post-cure	Absorption Δm (%)						
			480 days	510 days	540 days	570 days	600 days	690 days	710 days

DCPD	98,3306	90C	14,50						
TERE	95,5145	90C	10,71	10,75	----	10,69	10,69	10,74	10,74
TERE	92,0003	120C	8,19	8,68	----	9,32	9,85	10,30	10,62

Table 1 Ethanol pick-up evolution by a high end TERE and a low end DCPD polyester resin.

Table 1 indicates a high absorption level (circa 11%) of ethanol at saturation for the high-end UL approved terephthalic resin. This level exceeds the 5% limit that we consider reasonable for structural use. The UL 1317 standard allows the use of TERE resins in non-structural applications such as underground ethanol storage tanks. However, for high pressure pipelines the 11% absorption is deemed too high and TERE resins should not be used. As a side note the reader may see from table 1 that the difference between the low-end DCPD resin and high-end terephthalic polyester is not in the final saturation level, but in the time to saturation.

The coefficients of diffusion are related to the times to saturation. The coefficients of diffusion for the resins tested are calculated as:

TERE:

$$D = \frac{\pi^2}{4} \times \frac{(thickness)^2}{time} = \frac{\pi^2}{4} \times \frac{2^2}{710} = 0{,}014 \frac{mm^2}{day}$$

DCPD:

$$D = \frac{\pi^2}{4} \times \frac{2^2}{120} = 0{,}082 \frac{mm^2}{day}$$

The solution - The previous section indicated that there is no resin available in the market to produce high pressure composite pipes for the transmission of ethanol. Even the best UL approved products cannot be used. Still, there is a clear market need for a technical solution that would allow the structural use of composites in the transmission of ethanol. Such a solution would open huge opportunities for composite pipes and tanks in a variety of load-bearing applications involving not only ethanol but other organic solvents as well. Ethanol transmission is the most notorious and immediate application. Brazil has at this time large ongoing projects to build thousands of miles of pipelines to bring ethanol from remote sugar cane producing provinces to export or consumer outlets. The transmission of ethanol is a clear and immediate opportunity for composite pipes. Another interesting application would be in gas transmission pipelines, as we have indicated. However, a solution is needed to solve the high ethanol absorption problem.

The solution that we propose is very simple and straightforward. Our solution consists essentially in making pipes, fittings and joints having a low cost impermeable liner that prevents the solvent from entering the structural wall of the composite. If the solvent cannot get in, it cannot swell the resin and it cannot do any harm to the composite. As far as the pipe/tank/fitting/joint is concerned, the scary solvent application is the equivalent to the benign and usual water situation which is familiar to all design engineers and is accounted for in the available design codes.

Our solution is market-ready and does not require extensive and expensive testing. The pipe components are qualified by existing test methods to meet the requirements of product standards like AWWA C950, ISO 14692 and API 15HR. The qualification tests are performed on water-filled test specimens. The use of water-filled test specimens is acceptable since, as we said earlier, the impermeable liner keeps the solvent away from the structural layers of the composite. In many instances the qualification routine is not really necessary, since the pipe manufacturer would in fact be offering a “new product” that is essentially the same regular, pre-qualified product from his regular portfolio, plus the additional impermeable liner.

Figures 1, 2 and 3 show the manufacturing process. The impermeable metal foil is helically wound on a rotating mandrel prior to the lamination of the structural plies.

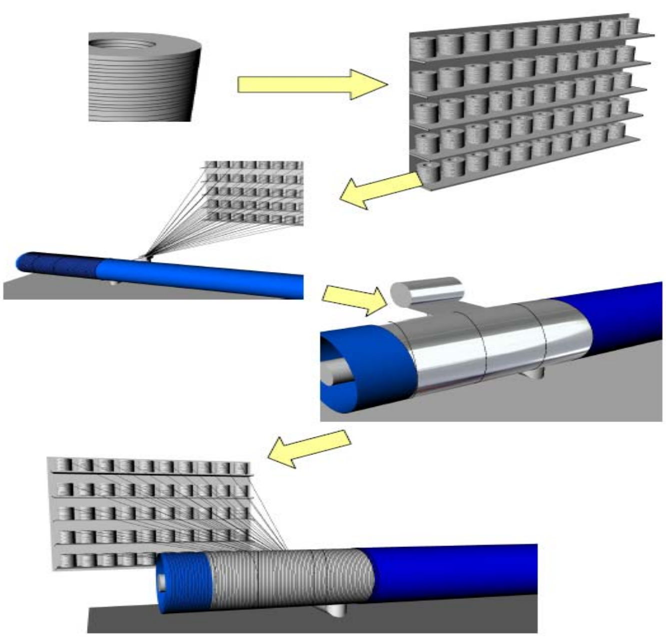

Fig. 1 - The pipes are made in the usual way. The impermeable metal foil is helically wound on the rotating mandrel prior to laminating the structural plies

Market acceptance - The end-users will realize that the “new impermeable pipes” are in essence the same “standard products” that have been proven in many “non-solvent” applications. Market acceptance is not expected to be a major hurdle. Once the end-users realize that the impermeable liner prevents the solvent from reaching the structural layers of the composite, they understand that this “new product” is in fact the same “old product”. The “new product” should perform like the “old product”. The difference being, of course, in the impermeable liner that keeps away the dreadful solvent.

Economics – The impermeable liners in composite components bring with them a very significant economic benefit. Since the resin never comes in contact with the solvent/ethanol, it is possible to make the composite using low cost resins throughout. This is a major factor in cutting cost, even in non-structural applications like underground fuel storage tanks. Expensive novolac type vinyl ester resins are no longer required.

Conclusion – The inclusion of impermeable liners in pipes, tanks, fittings and joints allows the use of low cost composites in structural applications involving solvents. Such applications have never before been contemplated. A window of opportunity opens up for storage tanks and pipelines for solvents, gas and ethanol transportation.

Fig 2. Shows the metal foil wrapped over the mandrel

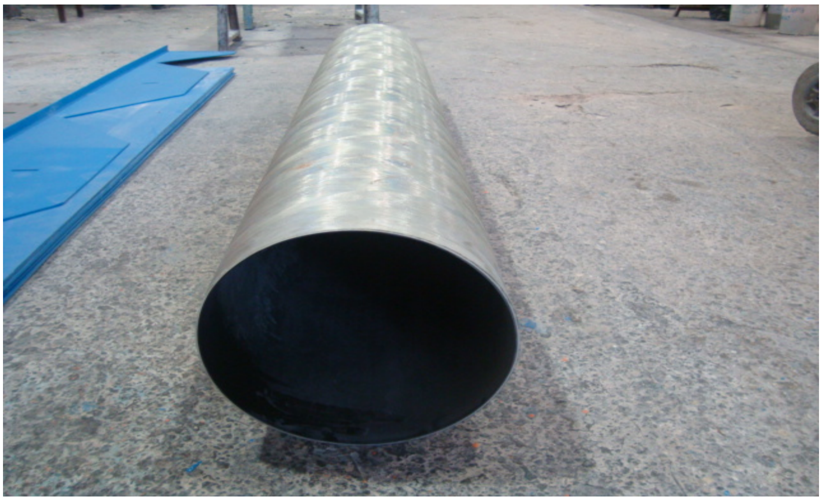

Fig. 3 The pipe shown in this picture has the following layup:

- Conductive inner layer. The dark color is imparted by the graphite loading. Conductivity is a requirement for hydrocarbon solvents.
- Impermeable liner of tape wound Aluminum foil.
- Filament wound ± 55 angle-plies.

8. References

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