

Development and Analysis of New Filament Wound Composite Pipes Made of Glass Fiber Reinforced 3P Resin

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Summary: Filament wound composite pressure pipes made of newly developed 3P, various hybrid and reference resin materials and glass fiber filaments were investigated. 3P resins consist of soluble silicates, polyisocyanates and other additives, they are flame and chemical resistant, and capable of curing under wet conditions. Tensile strengths, tensile moduli and effective moduli values obtained from ring stiffness tests were evaluated. Properties of pipe types made of new resin materials were compared to those made of reference resins. A special tensile specimen fabricating process and a cross sectional area calculating method was presented. The calculation method is capable of handling the geometric inaccuracies of specimen prefabrication steps e.g. cutting. Evaluated material properties were discussed by defining dimensionless performance factors. Pipes were classified according to these performance factors and the suitability of the new resin materials for composite pressure pipe manufacturing was established. The best newly developed matrix materials were the 16905 type vinylester-3P hybrid and 16907 type vinylester-urethane hybrid resins, because of their outstanding mechanical properties.

Keywords: composite; failure; filament winding; mechanical properties; ring test

Introduction

Major benefits of polymer composite pipes over metals include considerably higher strength-to-weight ratio, better chemical resistance, lower maintenance costs, lower weight, easier handling, cheaper transportation and installation. Lifetime management of pipelines is one of the most important issues in the hydrocarbon, and chemical industries, because continuous production is essential in these fields^[1]. Glass fiber reinforced unsaturated polyester and vinylester pipes have been applied successfully for transporting industrial and domestic wastewater or various chemicals

for decades^[2]. They offer a corrosion and maintenance free alternative to steel pressure pipes. Although conventional polyester pipes proved to be acceptable, in special cases more chemically resistant materials are needed. Vinylester based pipes exhibit high chemical resistance, but they are expensive. Even severely corrosive media can be transported and stored safely and economically using pipes made of a wide range of recently developed 3P resins (an acronym of Polyisocyanate – Polysilicate – Phosphate resins) and 3P based hybrid resins^[3,4]. 3P resin materials are flame resistant, which is necessary in many applications and they are cheaper than other chemical and flame resistant pipe materials. 3P and 3P-hybrid resins are all products of Polinvent Ltd. Hungary.

Composite pipes can be manufactured mainly by filament winding, rotational casting and pultrusion technologies and they can be operated under gravity or as

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pressure pipes. Pultruded circular closed profiles exhibit superior strength in the axial direction but poor properties in the circumferential direction because of their high content of unidirectional continuous reinforcement structure. These profiles are suitable for tensile and bending loads. Rotational cast composite pipes are quasi-isotropic and have relatively low chopped reinforcement content, resulting in relatively low strength. Filament wound composite pipes can be manufactured with up to 70 weight percent reinforcement content. Changing the winding angle the performance of the pipe can be fitted to the loads^[5,6]. It can be stated that filament winding is the most suitable and widespread technology for high performance polymer composite pressure vessels.

New materials for pressure vessels have to be extensively tested and approved because of the high stresses and dangerous media. Behaviour of filament wound pipes under biaxial loading was investigated by a number of authors^[7–10]. Martens and Ellyin^[7] found, that changes in the Poisson's ratio of the pipe material is the best indicator of failures during monotonic and repeated (fatigue) loading. They also stated, that the ratio of the biaxial load components influences the type of failure.

As transported media are mainly aqueous liquids the water uptake properties of the pipes have to be taken into account^[11–13]. Perreux and Suri^[12] modelled the kinetics of water absorption in glass/epoxy composite pipes. They investigated the influence of moisture content on pipe failures under biaxial loading. They found, that the damage rates increased as a function of moisture content.

Farshad and Necola^[13] studied the long-term properties of rotational cast glass reinforced polyester pipes under wet conditions. From the results of 1000 hour creep tests they concluded, that the strength of the pipes was reduced by 40% due to the moisture, and long-term loading. Extrapolating the 1000 hours results, 65% reduction in strength was predicted for the 50-year lifetime.

Montestruc et al.^[14] examined the fire resistance of polymer composite pipes, and developed a new test method. They found, that the application of an intumescent coating, and the increase of the thickness of the fire resistant foam insulation improve the fire resistance significantly.

In the case of a 3P-resin based pipe the application of these expensive protective layers can be avoided, because of the fire resistance of the matrix and reinforcement material.

The aim of this study is to present the first part of a comprehensive testing procedure. In this state of the research the tensile properties, the ring stiffness and deformability properties of 3P-resin based pipes were compared to those of reference types. Tensile tests were carried out on specimens taken from the axial direction of the pipes and ring compression tests were chosen for radial loading. On the basis of the evaluated mechanical properties dimensionless performance factors were calculated and used for the evaluation and comparison of the complex mechanical behaviour of different composite pipes.

Experimental

Materials, Manufacturing Technology

The matrix materials of the examined composite pipes were various 3P, 3P hybrid, other hybrid and reference resins (Table 1.) 3P resins are based on Na-water-glass, isocyanates and other additives, capable of curing under wet conditions, even in water. Because of this behaviour they are suitable for underwater construction and rehabilitation applications, for example sewage system rehabilitations^[2]. Another very important property of 3P resin is flame resistance, which is extremely advantageous for almost all applications in the chemical industry. The two main components of 3P resins are immiscible, and form a heterogeneous emulsion. The dimension of the water-glass droplets in the emulsion and the properties of the cured resin highly depend on the intensity of mixing. Because

Table 1.Applied materials, heat treatment and basic geometry of test pipes, D_i - inner diameter, s - wall thickness

| | Code | D_i [mm] | s [mm] | Heat treatment | Matrix material |
|--------------------------------------------|------|------------|----------|-----------------------------------------|--------------------------------------------------------------------------------------------------|
| First series (newly developed resins) | 1PI | 301 | 5,4 | 3 zone furnace - 60, 80, 90 °C, 120 min | 16905 Vinylester-3P hybrid resin with soluble-glass (Polinvent Ltd. Hungary) |
| | 2PI | 124 | 7,3 | 3 zone furnace - 60, 80, 90 °C, 120 min | |
| | 3PI | 301,5 | 6,2 | 3 zone furnace - 60, 80, 90 °C, 120 min | HL30 P 3P resin (Polinvent Ltd. Hungary) |
| | 4PI | 126 | 8,1 | 3 zone furnace - 60, 80, 90 °C, 120 min | |
| | 10PI | 250 | 7,6 | none | |
| | 11PI | 125 | 6,2 | none | |
| | 12PI | 250 | 8,7 | none | |
| | 13PI | 125 | 3,9 | none | |
| | 14PI | 500 | 15 | none | |
| | 16PI | 500 | 10 | none | |
| | 15PI | 301 | 6,6 | 3 zone furnace - 60, 70, 80 °C, 110 min | HL30 P IN 3P resin initiated with Fivenox B50 G (dibenzoylperoxide 50%) (Polinvent Ltd. Hungary) |
| | 17PI | 300 | 9 | 3 zone furnace - 60, 70, 80 °C, 110 min | |
| | 5PI | 300 | 5,9 | 1 zone furnace - 120 °C, 60+110 min | 16907 Vinylester-urethane hybrid resin (Polinvent Ltd. Hungary) |
| | 6PI | 124,5 | 7,2 | 1 zone furnace - 120 °C, 60+110 min | |
| | 8PI | 251,2 | 12,2 | 1 zone furnace - 120 °C, 60+110 min | |
| | 7PI | 126,2 | 7,2 | none | Derakane 411-350 Vinylester reference resin (Ashland Ltd.) |
| Second series (mainly reference resins) | 20PI | 124 | 8,8 | 1 zone furnace - 100 °C, 40 min | VUP-4812 Polyester-urethane hybrid reference resin (Vianova Ltd.) |
| | 21PI | 128,2 | 8,2 | 1 zone furnace - 100 °C, 40+40+40 min | Daron XP Vinylester-urethane hybrid reference resin (DSM Ltd.) |
| | 26PI | 125 | 7,5 | 1 zone furnace - 100 °C, 40 min | 17907 Vinylester+polyester-urethane hybrid resin (Polinvent Ltd. Hungary) |
| | 27PI | 124,8 | 7,1 | 1 zone furnace - 150 °C, 60 min | 17264 Vinylester with blocked isocyanates (Polinvent Ltd. Hungary) |
| | 31PI | 128,5 | 6,3 | 1 zone furnace - 100 °C, 180 min | |
| | 28PI | 128,2 | 6,9 | 1 zone furnace - 150 °C, 60 min | 17644 Increased viscosity vinylester with blocked isocyanates (Polinvent Ltd. Hungary) |
| | 32PI | 126 | 6,5 | 1 zone furnace - 100 °C, 180 min | |
| | 29PI | 126 | 6,7 | 1 zone furnace - 100 °C, 40 min | Dion Vinylester reference resin (Reichhold Ltd.) |
| | 35PI | 125 | 7,2 | 1 zone furnace - 60 °C, 60 min | |
| | 30PI | 124,8 | 7,1 | 1 zone furnace - 100 °C, 40 min | Derakane 411 Vinylester reference resin (Ashland Ltd.) |

of the heterogeneous structure, the water-glass droplet size distribution has a strong influence on the viscosity of the emulsion. Attention must be paid to mixing because filament winding requires relatively low viscosity.

Hybrid resins differ from conventional thermoset matrix materials in the way of crosslinking. In hybrid resins crosslinking takes place in at least two ways (mainly by polyaddition and radical polymerization) simultaneously or in succession. Hybrid

resins with different, designed composition can offer various combinations of advantageous properties of the base resins. Different pipes made of hybrid resins and standard industrial reference resins with various geometries and heat treatments were tested (Table 1.). As the manufacturing and the examination of the test-pipes were carried out in two independent series, the pipe-types are arranged in two groups in Table 1. Newly developed matrix materials were characterized in the first series and mainly reference resins in the second.

The reinforcement material used for the composite pipes was commercially available E-glass fiber filament (Owens Corning R25 HX14). Test pipes were manufactured with filament winding technology. Resin impregnated rovings were wound on cylindrical mandrels under 50 degrees to the longitudinal axis of the pipes. Each test pipe was manufactured with the same winding programme, they differ from each other only in their wall thickness, inner diameter and heat treatment (Table 1.).

Testing Methods

Mechanical properties of the new type composite pipes were examined in two ways. Specimen-level tensile tests were executed in longitudinal direction of the test pipes and ring compression tests (ring stiffness, and ring strength) were carried out in radial direction. ÖNORM B 5161 Austrian standard was used for determining the parameters and conditions of each executed investigation.

Specimens for tensile tests were cut from the pipes in the axial direction, using a diamond cutting tool. The prefabricated 300 x 30 mm bars needed further preparation for the tests, because they did not have flat areas for mounting into the gripping head of the tensile testing machine (Fig. 1.). The solution for this problem was bonding glass-polyester tabs at both ends of the specimens with chopped glass fiber filled epoxy adhesive. The gap between the cylindrical surface of the specimen and the flat tabs were filled with a proper amount of adhesive.

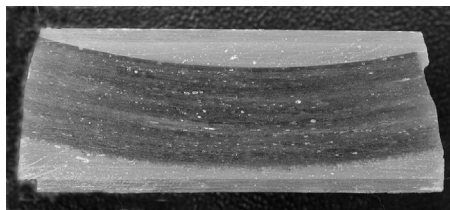


Figure 1.

Cross sectional shape of the tensile test specimens taken from the axial direction of pipes, with bonded tabs.

The following calculation method was used for determining the cross sectional areas of the tensile specimens (Fig. 2.):

$$A = \frac{l_1 + l'_2}{2} \cdot s \quad (1)$$

$$l_1 = \frac{2 \cdot \pi \cdot r_i \cdot \alpha_1}{360} \quad (2)$$

$$l'_2 = \frac{2 \cdot \pi \cdot r_o \cdot \alpha_2}{360} \quad (3)$$

$$\alpha_1 = \arccos\left(\frac{2 \cdot r_i^2 - a_1^2}{2 \cdot r_i^2}\right) \quad (4)$$

$$\alpha_2 = \arccos\left(\frac{2 \cdot r_o^2 - a_2^2}{2 \cdot r_o^2}\right) \quad (5)$$

where: l_1 –length of the inner arc, l'_2 –length of the outer arc, s –wall thickness of pipe, r_i –inner radius of pipe, r_o –outer radius of pipe, α_1, α_2 –central angles, a_1 –inner width of specimen, a_2 –outer width of specimen.

The cross section was estimated with a trapezoid, with parallel side lengths equal to the calculated arc lengths (l_1, l'_2). This method is capable of taking the inaccuracies of cutting into account, because it does not requires equal central angles for each arc. The inner radii of the test-pipes were measured before cutting the specimens, the thicknesses and widths of the specimens were determined after the tests in the fracture area.

The tensile tests were carried out on a Zwick Z050 type universal computer controlled tensile testing machine at a tensile rate of 2 mm/min. The elongations were monitored with a Zwick BW40220 videoextensometer. This special elongation measurement method was chosen because

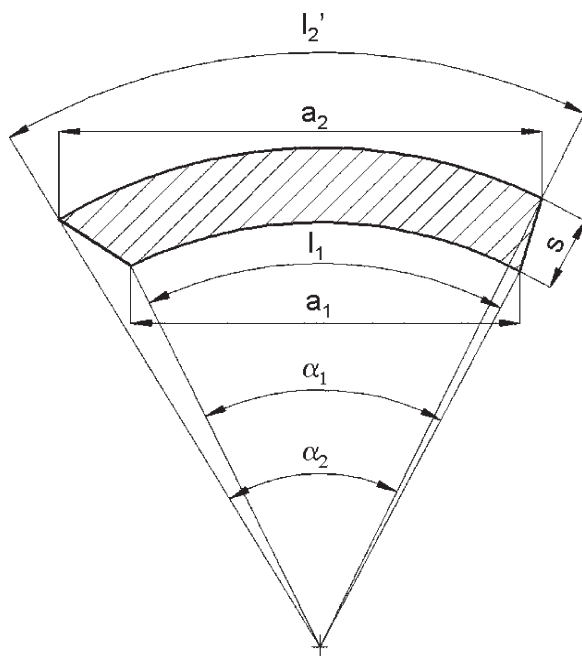


Figure 2.

Geometrical properties of tensile specimen cross section.

it has higher accuracy than the elongation determination using the crosshead travel monitor of the testing machine. Videoextensometer ignores the undesired deformations in the area of clamping, by measuring the changes in the distance between two marks (lines) printed on the specimen. Tensile strengths and elastic moduli were evaluated from five specimens of each material.

Ring compression tests were carried out on specimens cut from the test-pipes. The length (l) of the specimens was equal to their inner diameter (D_i) if $D_i \leq 300$ mm, and 300 mm if $D_i > 300$ mm. Compression was applied between rigid flat parallel steel plates on a universal computer controlled testing machine.

For ring stiffness determination, ring specimens were compressed in three different positions in radial direction until their deformations reached 3% of their nominal diameters ($D_n = D_i + s$). After compressing a specimen in one position, it was left uncompressed for 15 minutes and then it was compressed again in a rotated

(120°) position. Ring strength tests were executed until 9 and 15% deformation of the nominal diameter or until the failure of the specimen. 9% relative deformation is the maximum operating deformation, and 15% is the limiting deformation of the pipes. Applied test rates were calculated according to the standard mentioned above:

$$v = \frac{D_n \cdot 0,03}{2} \text{ mm/min } (\pm 10\%) \quad (6)$$

where: D_n is the nominal diameter of the pipe.

The effective elastic moduli of the various composite pipe materials were evaluated using the following equation:

$$E_{eff} = 0,223 \cdot \frac{D_n^3}{s^3 \cdot l} \cdot \frac{\Delta F}{\Delta f} \quad (7)$$

where: ΔF –the change in the measured compressive force, Δf –the change in the vertical deformation of the ring specimen.

Glass and ash content of the examined composite materials were determined by

heating the specimens at 800 °C for 1 hour according to ISO 3451-1:1997. Glass content of the tested materials could not be determined exactly because 3P and 3P hybrid resins contained water glass. Silicates have melting points similar to the glass fibers so they could not be distinguished from each other by heating.

Results and Discussion

As the manufacturing and the examination of the test-pipes were carried out in two series, one part of the results are arranged in separate diagrams. Figs. 3, 4 show the tensile strengths of the tested pipe materials. The results are in the same order of magnitude, but the average of the first series is the half of the average of the second series.

In the first series the effect of different geometries on the strength seemed to be serious. The four best pipe types (2PI, 4PI, 6PI, 7PI) were 125 mm in nominal diameter, and pipes made of the same materials and with the same heat treatments exhibited different strengths. In the

second series the differences were much lower because the nominal diameters of the pipes were 125 mm in all cases. In addition to the effect of different diameters another difference was observed after the tests. Although the nominal winding angle of each pipe was 50° to the longitudinal axis of the pipes, the angles scattered in a wide range between 40° and 75°. Due to the inaccurate manufacturing, the pipes with 125 mm diameter had significantly lower winding angles (Fig. 5). Applying a correction on the data of the first series, where the effects of the different winding angles were stronger, a much more even distribution was experienced (Fig. 6). The corrected parameters were obtained as follows:

$$C_{\sigma} = \frac{\sigma_b}{\cos \alpha}, \quad (8)$$

$$C_E = \frac{E}{\cos \alpha} \quad (9)$$

where: σ_b – tensile strength of the tested material, E – elastic modulus of the tested material, α – the winding angle to the longitudinal axis of the pipe

In the most important cases (1PI-2PI, 3PI-4PI, 5PI-6PI-8PI) where similar mate-

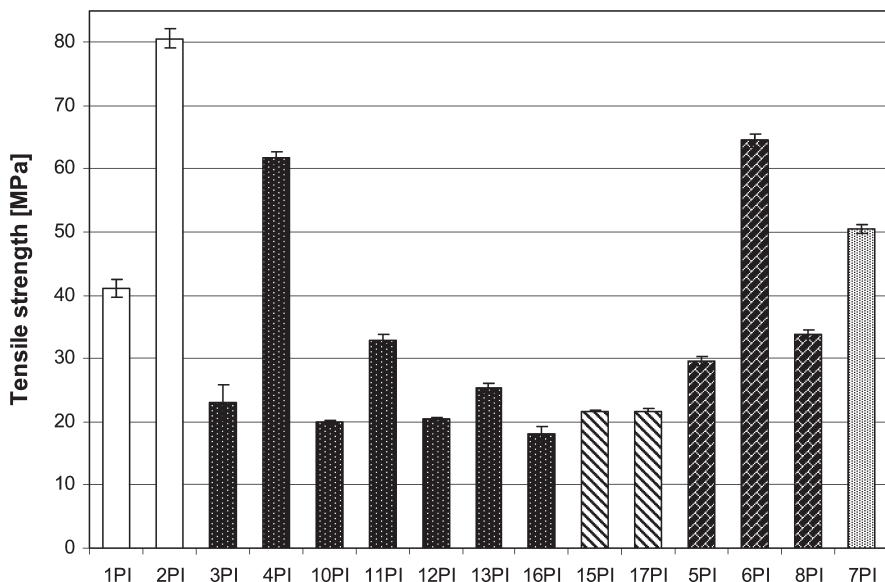


Figure 3.

Tensile strengths of the first series (Columns with the same pattern, show the same material.).

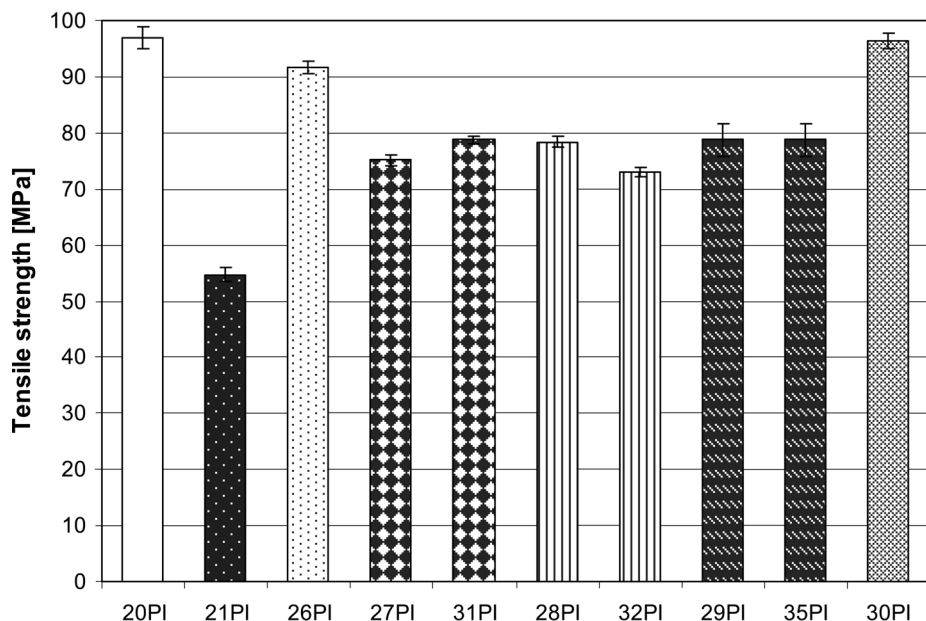


Figure 4.

Tensile strengths of the second series.

rials showed different strengths, the correction was highly effective.

Figs. 7, 8 show the elastic moduli of the examined composite pipe materials. In the case of the first series the trends and the effects were quite similar to those of the strength results.

The compensation with the winding angle was also effective in the case of the elastic moduli results (Fig. 9.).

The best three pipes coincided with three from the four with best strengths. Analyzing the results of the second series, the importance of the differences in the

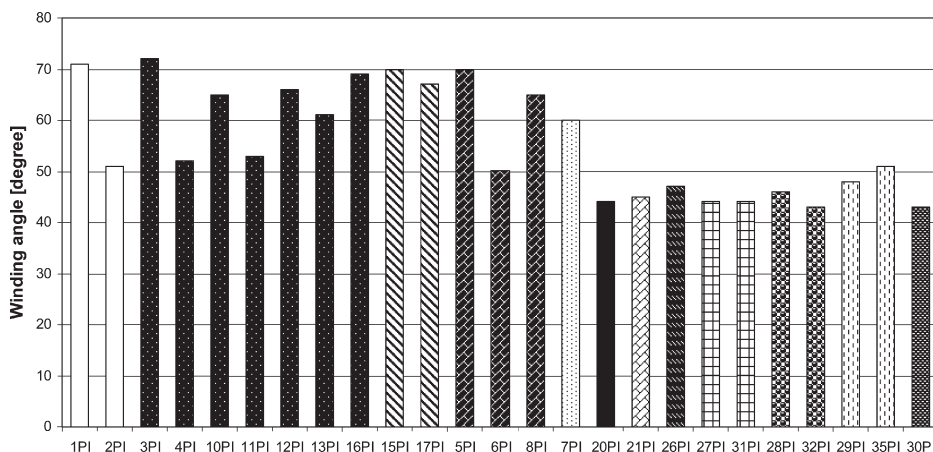


Figure 5.

Winding angles of the examined pipe types.

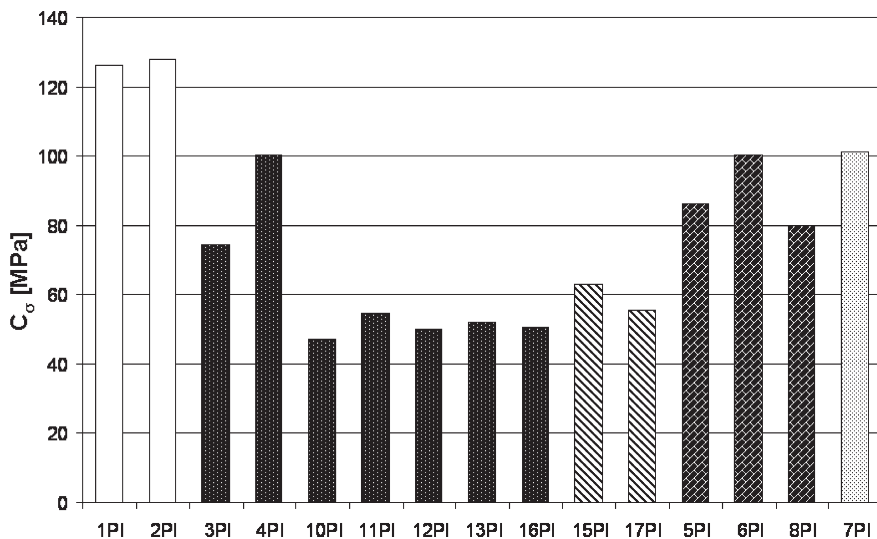


Figure 6.

C_σ values of the first series (corrected of winding angle variations, for explanation see the text).

heat treatments can be demonstrated. The 28PI and the 32PI pipes were manufactured from the same material but with different heat treatment procedures. The elastic modulus of the 32PI pipe was more

than 50% higher than that of 28PI, but the strengths were almost equal. A similar, but even more serious effect can be observed in the case of the 29PI and 35PI pipes.

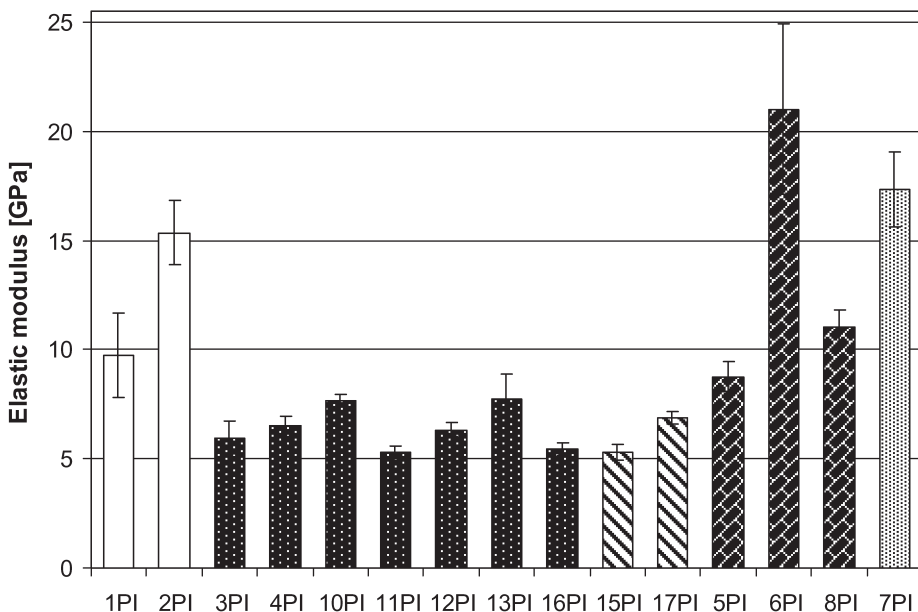


Figure 7.

Elastic moduli of the first series.

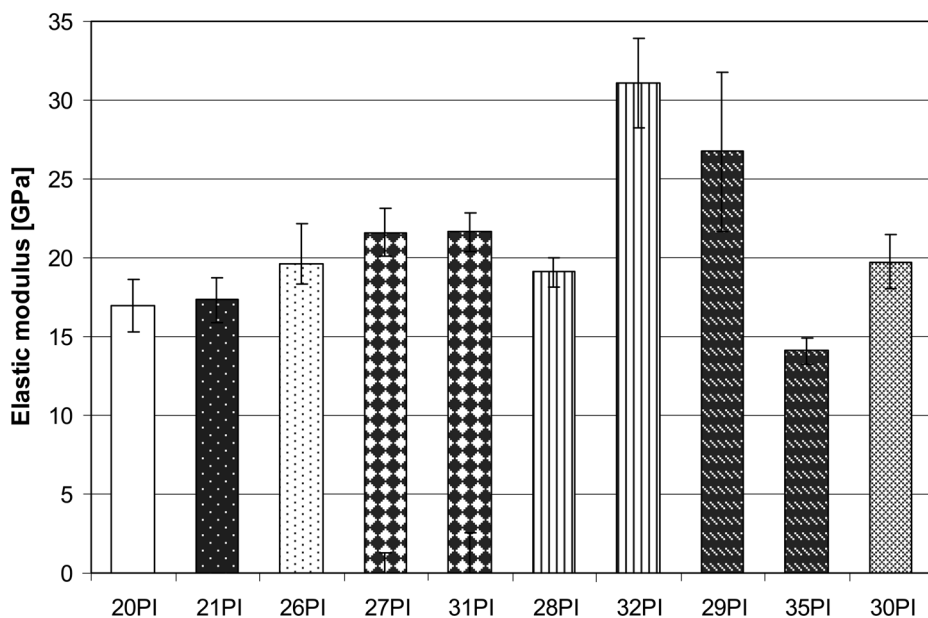


Figure 8.

Elastic moduli of the second series.

Tab. 2 shows the glass and ash contents of the examined pipe materials. Further conclusions cannot be drawn from the results as the ash contents scattered in a

very narrow range, and the determination was not accurate enough, because of the water-glass content of the 3P pipes, as mentioned before.

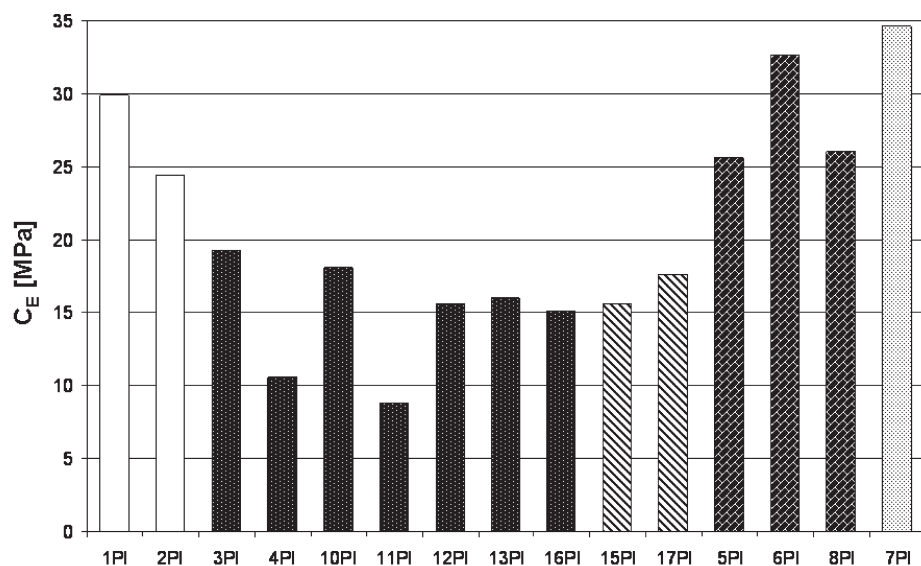


Figure 9.

C_E values of the first series (corrected of winding angle variations, for explanation see the text).

Table 2.
Glass/ash contents of the first series

| First series | | Second series | |
|--------------------|------------------------------|--------------------|------------------------------|
| Code | Glass/ash content [weight %] | Code | Glass/ash content [weight %] |
| 1PI | 69,3 | 20PI | 67,3 |
| 2PI | 66,2 | 21PI | 66,7 |
| 3PI | 69,4 | 26PI | 67,9 |
| 4PI | 69,5 | 27PI | 65,5 |
| 5PI | 66,1 | 28PI | 68,9 |
| 6PI | 68,5 | 29PI | 67,4 |
| 7PI | 67,6 | 30PI | 62,9 |
| 8PI | 68,3 | 31PI | 68,3 |
| 10PI | 67,2 | 32PI | 68,3 |
| 11PI | 65,1 | 35PI | 66,1 |
| 12PI | 69,9 | Standard deviation | 1,76 |
| 13PI | 69,6 | | |
| 15PI | 69,8 | | |
| 16PI | 67,0 | | |
| 17PI | 72,0 | | |
| Standard deviation | 1,83 | | |

Figs. 10, 11 show the effective elastic moduli (E_{eff}) of the pipe materials obtained from the ring compression tests.

During the ring compression tests the directions of the stresses were perpendicular to the ones applied in the tensile tests, the boundary conditions were different and the main load was bending instead of tension. Because of the anisotropy caused by the different winding angles, the tested

composite materials exhibited different properties in the two different loading directions. In general the first series performed better and the second series exhibited lower effective moduli values compared to their tensile moduli values. The opposite trends due to the different winding angles could also be observed in the cases (1PI-2PI, 5PI-6PI-8PI, 28PI-32PI) where the same materials exhibited differ-

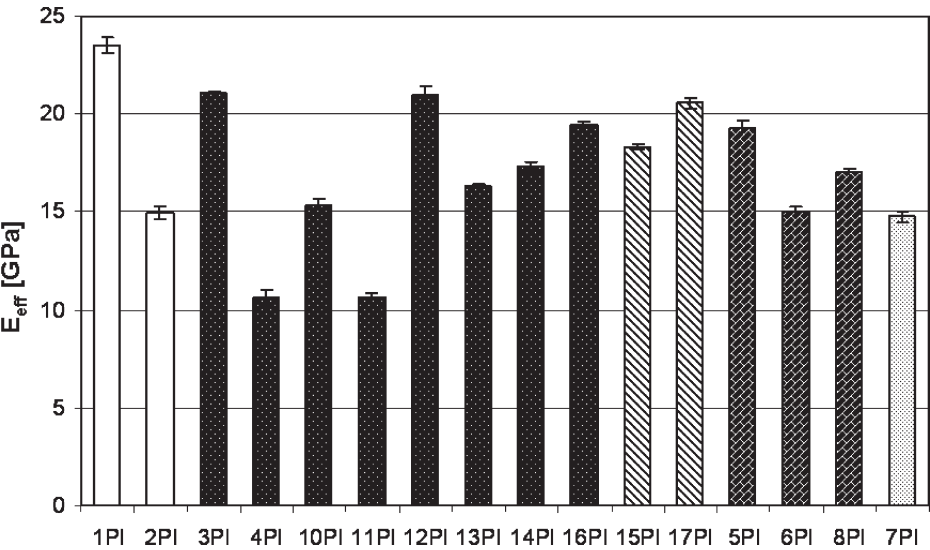


Figure 10.
Effective elastic moduli of the first series obtained from ring compression tests.

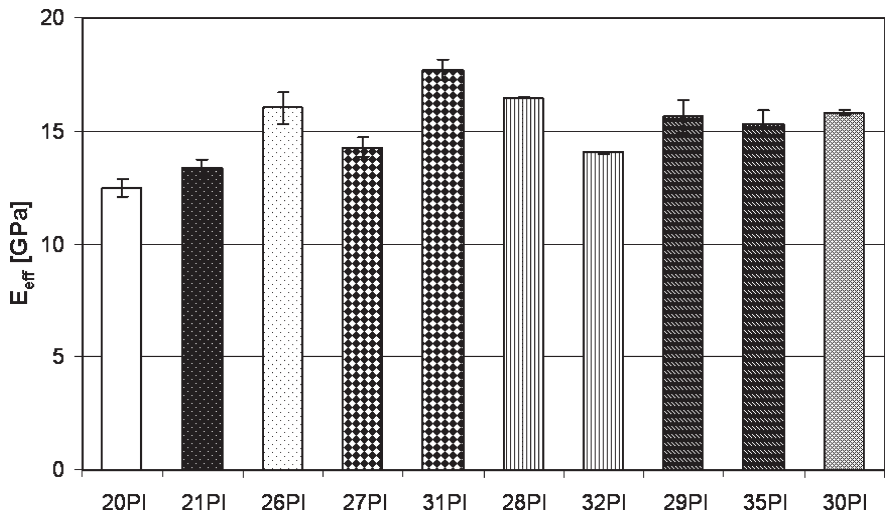


Figure 11.

Effective elastic moduli of the second series obtained from ring compression tests.

ent moduli. In the case of the 28PI–32PI pipes the effect of the different heat treatments was combined with the effect of the slightly different winding angles and the result was a much weaker opposite trend than in the other two cases. The showed opposite trends are the main evidences of the effect of the winding angles. In the case of the 29PI–35PI pipes, there were no opposite trends in the tensile and effective moduli, because the effect of the different heat treatments was much stronger than the effect of the winding angles. The differences between the pipe types in the effective moduli were lower than the ones between the tensile moduli.

During the ring deformation tests most of the failures occurred in pipes with smaller diameters and thicker walls because they were much stiffer than the others and the stresses were much higher in these pipe walls. The 9% deformation tests were passed by each pipe except for 4PI and 6PI and the 15% deformation tests were failed by each pipe except for 1PI, 3PI, 5PI, 10PI, 11PI, 15PI and 16PI. The failure type of the composite ring specimens was typically delamination^[15,16] (Fig. 12).

In order to handle the large number of data, a complex evaluation method developed by Vas^[17] was applied to compare the

mechanical performances of the examined pipes. By creating dimensionless performance factors, the results of the two different tests can be discussed together and the pipe types can be classified.

The definition of the combined performance factor is the following:

$$0 < Y_k = \sqrt{w_1 Y_{1k}^2 + \dots + w_m Y_{mk}^2} \leq 1 \quad (10)$$

The performance factor of the k-th pipe material type for the i-th parameter is the following:

$$0 < Y_{ik} = \frac{X_{ik}}{X_{i \max}} \leq 1 \quad (11)$$

where: X_{ik} – the value of the i-th parameter for the k-th pipe material, $X_{i \max}$ – the best measured value of the i-th parameter, w_i –

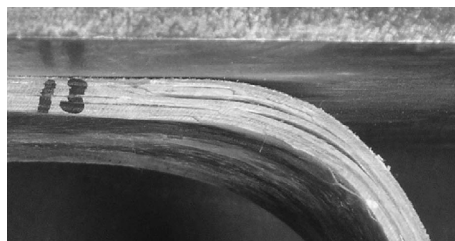


Figure 12.

Delamination of a ring specimen.

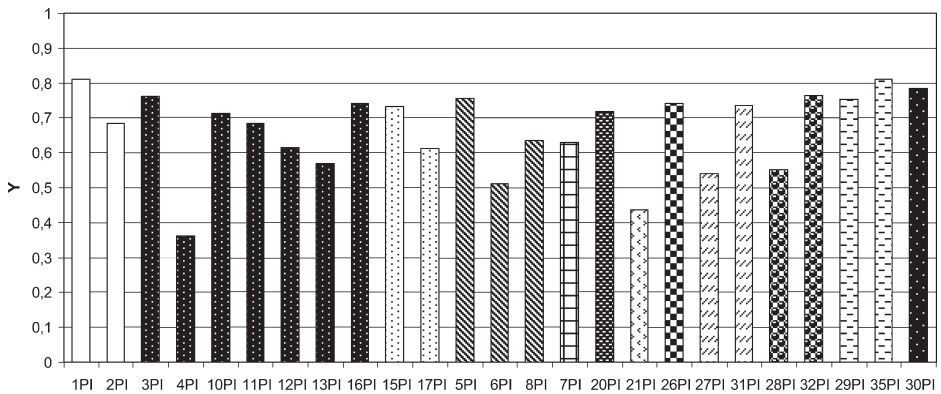


Figure 13.

Performance factors calculated with 5 parameters.

weight factor ($w_1 + \dots + w_m = 1$, in the simplest case $w_i = \frac{1}{m}$), m - the number of the pipe types.

The applied parameters were the following: $X_{ik} \in \{\lambda_{Ak}, \lambda_{Bk}, E_{effk}, \sigma_k, E_k\}$ where: λ_A - parameter for the 9% relative deformation test (1-passed, 0-failed), λ_B - parameter for the 15% relative deformation test (1-passed, 0-failed), σ - tensile strength, E -tensile elastic modulus

Results of the complex evaluation method can be seen in Fig. 13. Analyzing the diagram, it can be stated, that 3P based pipe materials perform in the same range as the pipes based on reference materials.

Eliminating the parameters of the deformation tests (λ_B, λ_A), which are radius and wall thickness dependent, a more

objective comparison can be performed based on material properties (Fig. 14). In this interpretation 3P based pipes exhibit lower mechanical performance than the reference resins, but if the other advantageous properties (e.g. flame resistance) are taken into account the 3P resins seem to be competitive. Present research has proved that development of 3P is advantageous, but further examinations are needed to prove their suitability for high performance pressure pipe applications.

Conclusions

Mechanical properties of filament wound composite pipes made of 3P, 3P hybrid, and other newly developed resins reinforced with glass fiber filaments were compared to

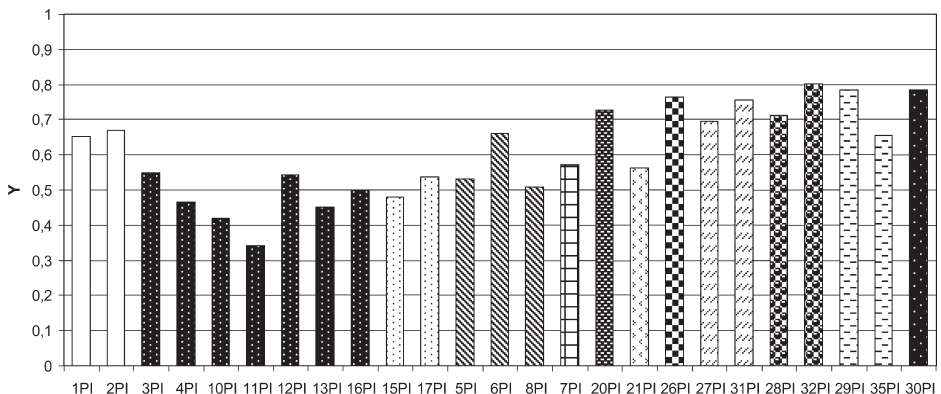


Figure 14.

Performance factors calculated with 3 parameters.

that of the reference pipe types. According to the tensile and ring test results of 26 different composite pipes with 11 different matrix materials the following conclusions were drawn:

- A special cross sectional area calculating method was developed, and applied successfully on tensile specimens cut from the axial direction of the test pipes.
- Tested new matrix materials performed in the same range with reference materials during the tensile and ring tests. Although new materials showed slightly lower mechanical properties, they have lower prizes, and special advantageous properties like fire resistance. Executed investigations showed that 3P resins, 3P hybrid resins, and other tested new type resins can be applied for high performance pressure pipes.
- The effect of different winding angles was found to be serious. An attempt was made to avoid this effect with the application of a correction on strength and moduli values.
- The effects of different geometrical parameters (diameter, wall thickness) and different heat treatments of the test pipes were also observed in special cases, but further examinations are needed to get accurate information about the influence of these factors.
- A new complex evaluation method was applied on test results, and 16905 type vinylester-3P, and 16907 type vinylester-urethane hybrid resins were found to be the best of the newly developed matrix materials.

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- [1] J. Lukács, *Materials Science Forum*, 2005, 473–474, 361.
- [2] D. Stein, “*Rehabilitation and Maintenance of Drains and Sewers*”, Ernst & Sohn, Berlin 2001.
- [3] PO401557 *Hybrid resins and compositions from polyisocyanate and soluble silicate, and production thereof*. Hungarian Patent.
- [4] PO401799 *Process for producing polyaddition and hybrid artificial resins polyisocyanate/polysilicate using blocked polyisocyanates and the blocked polyisocyanates usable in the process*. Hungarian Patent.
- [5] P. D. Soden, R. Kitching, P. C. Tse, Y. Tsavalas, M. J. Hinton, *Composites Science and Technology*, 1993, 46, 363.
- [6] D. Hull, B. Spencer, *Composites*, 1978, 9, 263.
- [7] M. Martens, F. Ellyin, *Composites Part A: Applied Science and Manufacturing*, 2000, 31, 1001.
- [8] P. D. Soden, D. Leadbetter, P. R. Griggs, G. C. Eckold, *Composites*, 1978, 9, 247.
- [9] P. D. Soden, J. Highton, A. B. Adeoye, *Journal of Strain Analysis*, 1985, 20, 139.
- [10] P. D. Soden, R. Kitching, P. C. Tse, *Composites*, 1989, 20, 125.
- [11] Y. Weitsman, *Fatigue of Composite Materials*, 1991, 385.
- [12] D. Perreux, C. Suri, *Composites Science and Technology*, 1997, 57, 1403.
- [13] M. Farshad, A. Necola, *Polymer Testing*, 2004, 23, 163.
- [14] A. N. Montestruc, M. A. Stubblefield, S. S. Pang, V. A. Cundy, R. H. Lea, *Composites Part B: Engineering*, 1997, 28, 295.
- [15] L. M. Vas, Zs. Rácz, *Journal of Composite Materials*, 2004, 38, 1757.
- [16] L. M. Vas, Zs. Rácz, P. Nagy, *Journal of Composite Materials*, 2004, 38, 1787.
- [17] T. Czvikovszky, L. M. Vas, J. Gaál, P. Nagy, Zs. Rácz, Z. Simon, B. Zsigmond, V. Nagy, K. Kis-Kapin, S. Erdélyi, B. Gábor, *Development of new environmentally friendly, anthropocentric resins, composites and technologies*. (In Hungarian) Report of research, Part 3. Grant No.: NKFP-3A/0055/2002. 2005. Budapest