Materials and Design 32 (2011) 2456–2461

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Technical Report

Effect of alkaline and acidic solutions on the tensile properties of glass–polyester pipes

M. Stamenović [a], S. Putić [b,*], M. Rakin [b], B. Medjo [b], D. Čikara [c]

[a] Belgrade Polytechnic, Brankova 17, Belgrade, Serbia
[b] Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[c] Faculty of Technical Sciences, Kneza Miloša 7, Kosovska Mitrovica, Serbia

ARTICLE INFO

Article history:
Received 23 July 2010
Accepted 11 November 2010
Available online 16 November 2010

ABSTRACT

The influence of liquids on the state of stresses and tensile strengths in the longitudinal and circumferential direction of glass–polyester pipes is the subject of this paper. The pipes were manufactured in Corporation "Poliester" Priboj, and had a definite structure and known fabrication process. These analyses are of great importance for the use of glass–polyester pipes in the chemical industry.

The tensile properties were tested and determined for specimens cut out of the pipes; flat specimens for the tensile properties in the longitudinal direction and ring specimens for the tensile properties in the circumferential direction. First, the tension test was performed on virgin samples (without the influence of any liquid), to obtain knowledge about the original tensile properties of the studied composite material. Subsequently, the samples were treated by water, as well as alkaline and acidic solutions: sodium hydroxide (strong alkali), ammonium hydroxide (weak alkali), phosphoric acid (weak acid) and nitric acid (strong acid). The solutions were selected because of considerable differences in their pH values. The pipe segments were exposed to each liquid for 3, 10, 30 and 60 days, at room temperature. Then the specimens cut from these segments were subjected to tension testing by the standard procedure. A comparison of the results was made based on the pH values of the aggressive media in which the examined material had been soaked, as well as based on the original tensile properties and the number of days of treatment. Micromechanical analyses of specimen breakage helped in the elucidation of the influence of the liquids on the structure of the composite pipe and enabled models and mechanisms that produced the change of strength to be proposed.

1. Introduction

The intensive development of polymer engineering, as well as the capabilities of polymers in combination with other materials to form new, synthetic structures of improved mechanical properties, has led to a real expansion in the employment of composite materials, which was followed by a continuous improvement of the technology of their manufacture and usage. Composite materials have a wide range of applications thanks to their good properties under loading conditions, specific mechanisms of crack initiation and growth and capabilities for the accumulation of energy, and represent the greatest competitors to classical construction materials. Their advantages lie in their relatively small mass, good strength/mass and stiffness/mass balances, good static and dynamic properties, good resistance to corrosion, simplified fabrication and short mounting time.

All the stated advantages led to composite pipes being very much used today in the chemical industry, building, infrastructure and war techniques. An important application of pipes made of composites glass fibres – polyester resin is in chemical industry. Pipes made for this use are in exploitation under the influence of static and dynamic loads. Considering the conditions of possible exploitation in the chemical industry, the subjects of this study were prediction of the useful life of glass–polyester composite pipes and determination of the influence of fluids transported through such pipes on their tensile properties in the longitudinal and circumferential directions.

The different structures of composite pipes result in differences in stress and strain fields, which can cause different development of failure after the initiation of the first cracks. In the last few decades, many researchers have considered these points. Special attention was always given to the determination of the stress conditions in the longitudinal and circumferential directions. The best results for pipes have been obtained by the radial-cut method and the ring test. The radial-cut method is a simple, inexpensive and approximate method for determining the residual stress state in a cylindrical part. In this method, the ring is cut in the radial direction to release the residual stress. Measurements of the subsequent deformation of the ring in the circumferential and radial directions

* Corresponding author. Tel.: +381 11 3370 391; fax: +381 11 3370 387.
E-mail address: slavisa@tmf.bg.ac.rs (S. Putić).

0261-3069/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.matdes.2010.11.023

give an indication of the magnitude of the stresses present prior to the cut. Aleong and Munro [1] used this method to determine the residual stresses in radially-thick, filament-wound composite rings. In their experiments, the rings were cut along the radius, and the radial and circumferential strains were measured using resistive gauges. Aleong and Munro performed the radial-cut method on eight E/XA-S Grafil carbon–epoxy and three S2-glass–epoxy composite rings with outside to inside diameter ratios of approximately 1.22–1.30. The aim of another study [2] was to characterise the influence of structure on the mechanical performance of cylindrical geometries under various loadings. The specimens studied were glass–epoxy tubes with a $[\pm 55^\circ]_6$ lay-up. All manufacturing parameters were kept constant, except for the winding pattern. The quality of the fabrication was assessed by strict monitoring of the geometry and microstructure of the tubes. The tests performed on the specimens consisted in progressive repeated loadings, aimed at characterising the damage behaviour under various loading conditions. Micro-structural properties, mechanical behaviour and damage mechanisms of composite tubes under pure tensile loading were presented by Bai et al. [3]. The test materials were ±55° filament-wound glass–epoxy tubes.

In another study [4], the effects of hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4) on the physical and mechanical properties of glass–polyester composite pipes internally lined with C-glass were analysed. Specimens cut from the pipes were immersed for various periods, i.e., 30, 60, and 90 days, in 20% acid solutions at room temperature and 100 °C. Material properties determined using these specimens decrease more severely with the increase of temperature. Examining of hardness revealed that the inner surface (lined with glass) has higher hardness values in comparison with the outer surface. The effects of conc. sulphuric acid and the sequential lay-up of glass fibre reinforcements on the diffusion behaviour of glass–epoxy composite laminates were studied in [5]. Material degradation is more pronounced with the increase of sulphuric acid concentration, which can be explained by hydrolytic dissolving of the matrix in contact with this acid. Experimental results for the effect of different HCl concentrations on the stress intensity factor of woven E-glass fibre-reinforced bisphenol–vinylester resin, woven E-glass fibre-reinforced bisphenol–epoxy resin and woven C-glass fibre-reinforced bisphenol–vinylester resin composites were presented in [6]. It is determined that increase of solution concentration led to more pronounced damage of all tested materials, and that E-glass composites exhibited higher damage levels in comparison with C-glass composites. The influence of different conditions on the mechanical properties of glass fibre-reinforced polymer composites, as well as coir fibre-reinforced polymer composites, was analysed and compared in [7]. Degradation studies were performed in different solutions, such as 10% NaOH, 1 N HCl and 10% NaCl, and also in water. The effects of these liquids, as well as environmental weathering, on the mechanical properties of the composites were studied in detail. It is determined that tensile strength of glass fibre-reinforced composites increases in acidic environment, and decreases in all other conditions. Similar trend is obtained for modulus of elasticity E, except for the specimens soaked in water, which exhibited a slight increase of E.

2. Experimental procedures

Composite pipes were fabricated under laboratory conditions. The properties of the components of the analysed glass–polyester pipes were given in official certificates from the producers. The producers of the glass fibres, "OHIS" Skopje and "Vidoe Smilevski-Bato" Gostivar, certified "E"-glass with 1% of alkali (Tables 1 and 2). As the matrix, a thermo-reactive polyester resin was used from the producer "Color" Medvode. A certificate was given for "COLPOLY 7510" for the type: UP/SOM, a highly reactive, low in viscose polyester based on orthophthalic acid in standard glycol (Table 3).

The pipes were made by the "filament winding" method, with the angle of the glass fibres reinforcement being $[90^\circ]_2$-$[\pm 55^\circ]_4[90^\circ]_4$. Specimens for the tests (flat specimens and rings) were cut from the samples of pipes according to the standard dimensions; the flat specimens 250×25 (20 mm gage area) $\times$ 3.5 mm and the rings ϕ 70 $\times$ 35 $\times$ 3.5 mm (average values of all the tested specimens). The cut was realised on a machine type NC-2010 (Nr 95110, Ar 001), with diamond-tip tools and a moving speed chosen to reduce the heat in the specimen.

Testing of the flat test specimens was performed on a servo-hydraulic testing machine SCHENCK TREBEL RM 100, and the ring test specimens on a servo-hydraulic testing machine INSTRON 1332, using an INSTRON FAST TRACK 80800 controller and hydraulic jaws. The testing was defined by the standard ASTM D 3039 [8] for flat specimens and ASTM D 2290 [9] for ring specimens. Loading was registered with a measuring cell of capacity 100 kN. Displacements were measured using a double extensometer HOTTINGER DD1.

The tensile properties (ultimate tensile strength and modulus of elasticity) were first determined for specimens cut out of the pipes that were not placed in any liquid (six flat specimens and six rings), and subsequently for specimens that were exposed to an

Table 1
Structural components of "E"-glass.

Structural component	Percentage (%)
Silicon(IV) oxide	52–56
Aluminium(III) oxide	12–16
Boron(III) oxide	5–10
Sodium(I) oxide, potassium(I) oxide	0–2
Magnesium(II) oxide	0–5
Calcium(II) oxide	16–25
Titanium(IV) oxide	0–1.5
Iron(III) oxide	0–0.8
Iron	0–1

Table 2
Physical properties of "E"-glass fibres.

Properties	
Specific weight (g/cm^3)	2.54
Ultimate tensile strength (MPa)	2400
Modulus of elasticity (GPa)	73
Extension (%)	3.3
Thermal expansion 10^{-6} (K^{-1})	5
Thermal conductivity (W/mK)	1
Dielectrical constant (ξ)	6.7
Specific electrical resistance (Ω cm)	10^{14}
Moisture absorption at 20 °C (%)	0.1

Table 3
Catalogue properties of the polyester resin.

Properties	Specification
Appearance	Viscous yellow liquid
Density (g/cm^3)	1.11–1.12
Viscosity at 25 °C (mPa s)	220–320
Specific weight (g/cm^3)	1.19–1.21
Ultimate tensile strength (MPa)	75–85
Modulus of elasticity (GPa)	3.6
Extension (%)	2–3
Impact toughness/Charpy (kJ/m^2)	10–15

aggressive medium or water for the required number of days (three flat specimens and three rings for each test). The pipe segments were exposed to the liquids on the inner surface (pipe segments were filled with liquids). The solutions were selected because of considerable differences in their pH values; hence, the results obtained for the tensile properties can be compared with respect to the pH value of the medium in which the examined specimens were previously placed. The selected solutions were 25% alkaline and acidic solutions of sodium hydroxide (strong alkaline), ammonium hydroxide (weak alkaline), phosphoric acid (weak acid), and nitric acid (strong acid). The pH values of the applied solutions were measured using a pH-meter, type TESTO 206-pH1 (TESTO, USA), and the results are presented in Table 4.

The pipe segments were exposed to each liquid for 3, 10, 30 and 60 days, at room temperature. Afterwards, they were washed with clean water, dried at room temperature for 2 h, flat specimens and rings were cut from these segments and their tensile properties measured.

The obtained tension test results were compared based on the pH value of the aggressive medium that the examined materials were soaked in and on the number of days they were kept in the specified liquids.

3. Test results and discussion

Stress–strain (σ–ε) diagrams were plotted for all tests. For example, the stress–strain diagrams for virgin samples (without soaking), obtained from tension tests in the longitudinal direction (flat specimens F-WS) and in the circumferential direction (ring specimens R-WS), are presented in Fig. 1.

Table 4
The pH values of the applied liquids.

Liquid	pH value
Sodium hydroxide (NaOH) solution	14
Ammonium hydroxide (NH_4OH) solution	12
Water (H_2O)	7
Phosphoric acid (H_3PO_4) solution	2
Nitric acid (HNO_3) solution	1

The ultimate tensile strength was calculated for the flat test specimens (longitudinal direction) and the rings (circumferential direction) according to Eqs. (1) and (2), respectively:

$$R_{m,l} = \frac{P_{\max}}{b_l \cdot d} \tag{1}$$

$$R_{m,c} = \frac{P_{\max}}{2 \cdot b_c \cdot d} \tag{2}$$

where $R_{m,l}$, MPa, is the ultimate tensile strength in the longitudinal direction; $R_{m,c}$, MPa, the ultimate tensile strength in the circumferential direction, MPa; $P_{\max}$, kN, the maximum applied load force; b_l, mm, the width of the flat test specimen; b_c, mm, the width of the ring test specimen and d, mm, is the thickness of test specimen (flat specimens or rings) – subscripts l and c stand for longitudinal and circumferential direction in the remainder of the text.

The modulus of elasticity, $E_{l,c}$ (GPa), was calculated by linear regression of the rectilinear parts of the force–elongation ($\Delta P/\Delta l$) curves, obtained directly from the testing machine.

All the tension test results for the flat and ring specimens are given respectively in Tables 5 and 6 (for virgin specimens and those exposed to liquids for a certain number of days), and the changes of the ultimate tensile strength and the modulus of elasticity after soaking from the values for the virgin specimens are shown in Figs. 2 and 3, respectively.

Treatment of samples with alkaline solutions led to a decrease in the parameters of their tensile properties (ultimate tensile strength and modulus of elasticity), which in both cases were higher in the longitudinal direction. It can be seen that with increasing pH value of the alkaline solution, their influence on the ultimate tensile strength increased, hence, the differences in comparison with the average values measured for the untreated samples were higher.

Similar trends were exhibited by the results of samples treated with pure water; more pronounced changes were observed in the longitudinal direction. In addition, the decrease of the strength parameters in both directions increased with treatment duration.

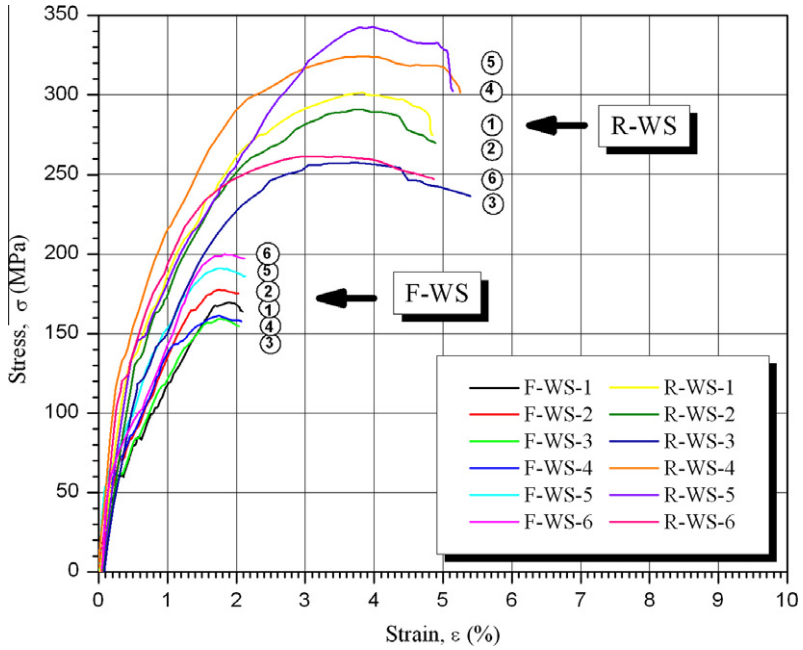

Fig. 1. Comparison of the stress–strain (σ–ε) diagrams from the two tests for the virgin specimens.

Table 5
Average values of the tension test results for the flat specimens (longitudinal direction).

Specimens	pH	Number of days	Ultimate tensile strength $R_{m,l,av}$ (MPa)	Change (%)	Modulus of elasticity $E_{l,av}$ (GPa)	Change (%)
Without liquid	–	–	176.4	–	20.73	–
F-NaOH	14	3	167.9	−4.82	20.33	−1.93
		10	156.3	−11.40	19.64	−5.26
		30	132.4	−24.94	19.03	−8.20
		60	128.8	−26.98	18.94	−8.63
F-NH_4OH	12	3	170.4	−3.40	20.48	−1.21
		10	157.3	−10.83	19.93	−3.86
		30	135.5	−23.18	19.58	−5.55
		60	130.7	−25.91	19.54	−5.74
F-H_2O	7	3	168.3	−4.59	20.66	−0.34
		10	157.8	−10.54	20.28	−2.17
		30	147.4	−16.43	19.92	−3.91
		60	146.9	−16.72	19.89	−4.05
F-H_3PO_4	2	3	176.6	+0.11	20.84	+0.53
		10	179.5	+1.76	21.17	+2.12
		30	187.3	+6.18	21.58	+4.10
		60	187.9	+6.84	21.61	+4.25
F-HNO_3	1	3	178.5	+1.19	20.88	+0.72
		10	188.4	+6.80	21.42	+3.33
		30	194.8	+10.43	22.07	+6.46
		60	198.3	+12.41	22.11	+6.66

Table 6
Average values of the tension test results for the ring specimens (circumferential direction).

Specimens	pH	Number of days	Ultimate tensile strength $R_{m,c,av}$ (MPa)	Change (%)	Modulus of elasticity $E_{c,av}$ (GPa)	Change (%)
Without liquid		–	296.4		31.20	
R-NaOH	14	3	289.8	−2.22	30.94	−0.58
		10	278.4	−6.07	30.31	−2.60
		30	266.7	−10.02	29.16	−6.30
		60	265.4	−10.45	28.98	−6.87
R-NH_4OH	12	3	290.9	−1.85	31.02	−0.32
		10	281.4	−5.06	30.63	−1.57
		30	273.5	−7.72	29.57	−4.98
		60	267.2	−9.85	29.52	−5.14
R-H_2O	7	3	296.0	−0.13	31.07	−0.16
		10	287.8	−2.90	30.82	−0.96
		30	284.5	−4.01	31.37	−2.41
		60	283.8	−4.25	30.31	−2.60
R-H_3PO_4	2	3	297.6	+0.40	31.19	+0.22
		10	304.4	+2.70	31.54	+1.35
		30	310.7	+4.82	32.38	+4.05
		60	310.8	+4.86	32.46	+4.31
R-HNO_3	1	3	299.8	+1.15	31.22	+0.32
		10	307.5	+3.74	31.77	+2.08
		30	315.0	+6.27	32.98	+5.97
		60	316.1	+6.65	33.03	+6.14

Concerning the acidic solutions, the tensile properties also changed, but unlike with the alkaline solutions and water, an increase of these parameters with number of days of treatment was observed. In addition, the increase was more prominent with decreasing pH value. Such behaviour was approximately the same in both directions. Similar results, i.e. increase of strength and stiffness after exposing the glass fibre-reinforced polymer composites to an acidic environment, were obtained in [7].

At the end of this analysis, it can be concluded that the changes of the tensile parameters in alkaline and acids solutions, as well as in water, are proportional to the treatment duration (number of days in liquid). In addition, from the presented results, it is obvious that the values of the ultimate tensile strength and modulus of elasticity during the period of 30–60 days did not change much. Hence, it can be concluded that after 60 days no further significant changes in the values of these properties are to be expected.

It should be emphasised that the changes of the modulus of elasticity are much smaller than those of the ultimate tensile strength of the specimens.

The conclusions can be related to the fact that matrix is ageing due to the action of the liquids on it. In this way, i.e., with a decrease in the quantity of the resin, there was an increase in the

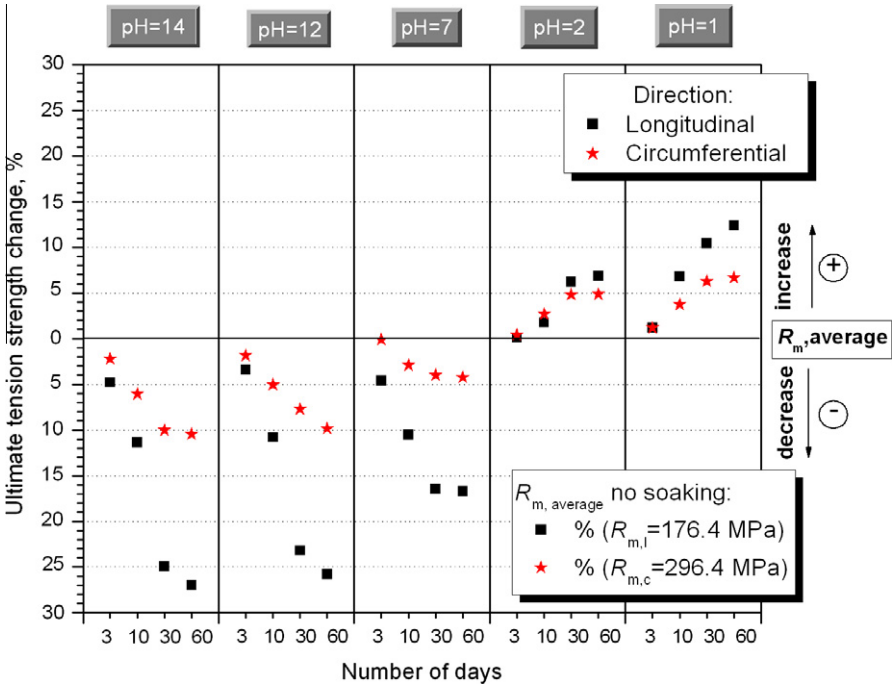

Fig. 2. Ultimate tensile strength change for the specimens exposed to the liquids for a certain numbers of days.

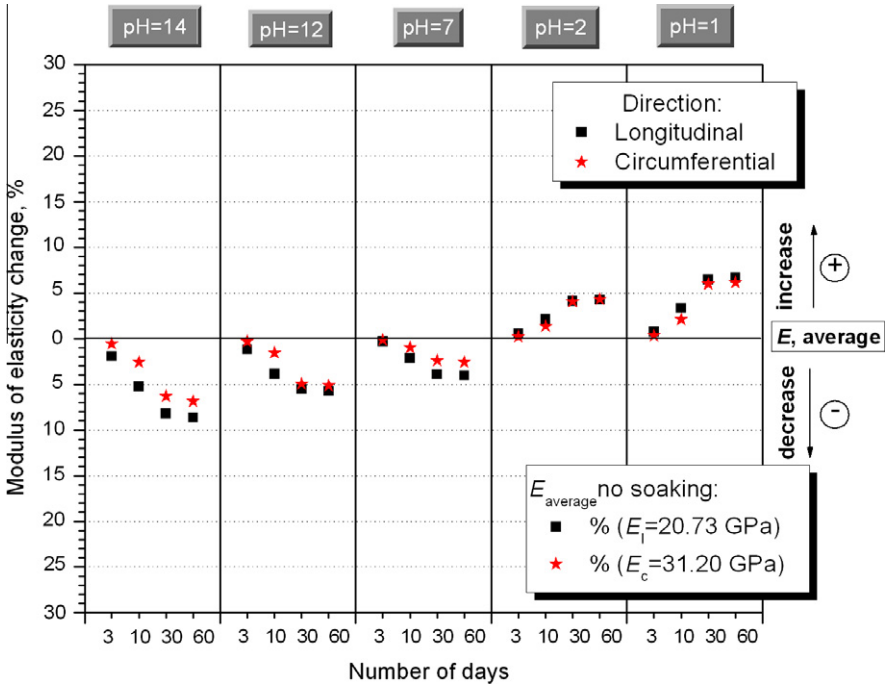

Fig. 3. Modulus of elasticity change for the specimens exposed to the liquids for a certain numbers of days.

number of micro-cracks in the pipes and weakening of the fibre–matrix bond where micro-cracks were initiated and large strain concentration occurred. The loss of resin went from the inner surface of the pipe, considering that this surface was exposed to liquids. Degradation of the fibre–matrix interface is caused by matrix dehydration, as well as penetration of the solutions through micro-cracks into the pipe structure. It is observed that the fibres were not drastically damaged due to the exposure to solutions. Their specific properties lead to different models of initiation and propagation of the crack. This is very important because of the pipe structure, $[90°]_2[\pm 55°]_4[90°]_4$, which produced a different distribution of strains in the layers and hence the fibres were not loaded to the same extent.

Fibres that broke earlier (Fig. 4) caused a disturbance in the crack zone, that is, local shear stresses appeared causing the fibre pullout mechanism.

Information concerning the important contribution of the shear components of strain could be obtained from the stress–strain (σ–ε) curves, which, unlike those of most composites, were not linear. With increasing load level, cracking by fibre–matrix debonding occurred and the crack, which was initiated by breaking of the fibres, grew along neighbouring fibres and caused a macro-crack. This resulted in local cracking of fibres and entire layers, as well as delamination (Fig. 5), but the composite still carried the external loading. With the increase of load, the local failures spread and the final crack appeared with a strong acoustic effect, because of simultaneous cracking of a large number of fibres. The fibres were cracked chaotically in all directions, as shown in Fig. 4.

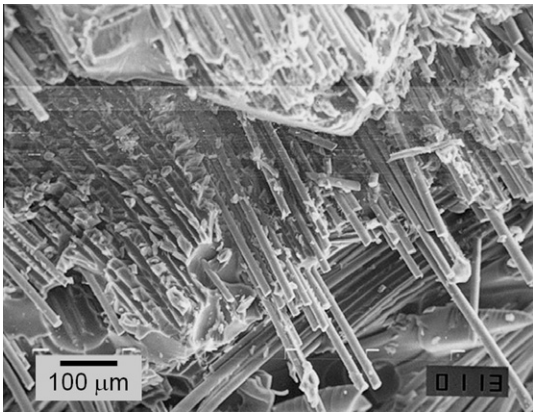

Fig. 4. SEM micrograph of the initially broken fibres.

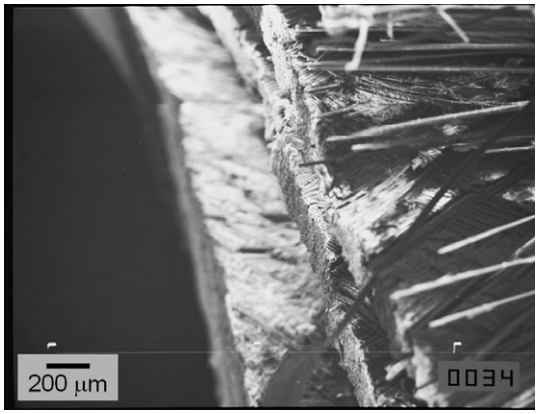

Fig. 5. SEM micrograph of a macro-crack in a flat specimen.

4. Conclusions

The aim of this study was the determination of the strength and stiffness of glass–polyester pipes and, because of their possible application in the chemical industry, the influence of liquids on the changes of these values. Tensile properties were determined on flat test specimens and rings cut out from the pipes. The tests were first conducted on specimens cut out from the pipes that were not placed in any liquid, and also after subjecting the pipes

to the influence of 25% solutions of sodium hydroxide (strong alkaline), ammonium hydroxide (weak alkaline), phosphoric acid (weak acid), nitric acid (strong acid) and pure water. Tensile properties of untreated and treated specimens after 3, 10, 30 and 60 days of exposure were determined.

Considering the alkaline solutions, the obtained results lead to the conclusion that they caused a decrease of the tensile properties. In addition, their influence was higher with increasing alkalinity. This is completely in accordance with the known fact that alkaline solutions (sodium hydroxide and ammonium hydroxide) are highly corrosive. During the treatment of the samples, they coated the inner surfaces and went deeper into the samples through micro-cracks and other surface damages which existed after fabrication and shrinkage of the material. The most significant influence was on the fibre–matrix connection, and this influence spread and directly weakened the load carrying capacity of material. On the other hand, the composite material was strengthened during treatment of samples with acids, i.e. an increase in the tensile properties (both modulus of elasticity and tensile strength) is observed.

The influence of water was not small; a decrease in the values of the tensile properties was registered. Polymers absorb water and the amount of water absorbed depends on their structure, degree of crystallinity and polarity of the molecules. The greatest influence of water is on a matrix that swells. In that way, the fibre–matrix connectivity is weakened and an inhomogeneous stress distribution is the result.

Previously mentioned conclusions are very important considering the possible time of transport of these fluids and life time prediction of composite pipes. However, since the strength and stiffness were almost constant after 60 days and there were no cracks on the outer surface, it is assumed that these values can be taken as relevant for the calculation and in that case, pipelines can be exploited for longer periods.

Acknowledgements

The authors would like to thank to the Corporation "Poliester" Priboj for the glass–polyester pipes. S.P., M.R. and B.M. acknowledge the support from the Serbian Ministry of Science under the current Project OI 144027 and submitted Project OI 174004.

References

[1] Aleong C, Munro M. Evaluation of radial-cut method for determining residual strains in fiber composite rings. Exp Tech 1991;15:55–8.
[2] Rousseau J, Perreux D, Verdiere N. The influence of winding patterns on the damage behaviour of filament-wound pipes. Compos Sci Technol 1999;59:1439–49.
[3] Bai L, Seeleuthner P, Bompard P. Mechanical behaviour of ±55° filament-wound glass-fibre/epoxy-resin tubes: I. Micro-structural analyses, mechanical behaviour and damage mechanisms of composite tubes under pure tensile loading, pure internal pressure, and combined loading. Compos Sci Technol 1997;57:141–53.
[4] Mahmoud MK, Tantawi SH. Effect of strong acids on mechanical properties of glass/polyester GRP pipe at normal and high temperatures. Polym Plast Technol 2003;42:677–88.
[5] Pai R, Kamath MS, Rao RMVGK. Acid resistance of glass fiber composites with different layup sequencing. Part I – diffusion studies. J Reinf Plast Compos 1997;16:1002–12.
[6] Kawada H, Srivastava VK. The effect of an acidic stress environment on the stress-intensity factor for GRP laminates. Compos Sci Technol 2001;61:1109–14.
[7] Sindhu K, Joseph K, Joseph JM, Mathew TV. Degradation studies of coir fiber/polyester and glass fiber/polyester composites under different conditions. J Reinf Plast Compos 2007;26:1571–85.
[8] ASTM D 3039-00: standard test method for tensile properties of polymer matrix composite materials. In: Annual book of ASTM standards; 2000.
[9] ASTM D 2290-00: standard test method for apparent hoop tensile strength of plastic or reinforced plastic pipe by split disk method. In: Annual book of ASTM standards; 2000.