

Influence of High Temperature and Humidity on Polymer Composites Used in Relining of Sewage

Parastou Kharazmi, Folke Björk

Abstract—Some of the main causes for degradation of polymeric materials are thermal aging, hydrolysis, oxidation or chemical degradation by acids, alkalis or water. The first part of this paper provides a brief summary of advances in technology, methods and specification of composite materials for relining as a rehabilitation technique for sewage systems. The second part summarizes an investigation on frequently used composite materials for relining in Sweden, the rubber filled epoxy composite and reinforced polyester composite when they were immersed in deionized water or in dry conditions, and elevated temperatures up to 80°C in the laboratory. The tests were conducted by visual inspection, microscopy, Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) as well as mechanical testing, three point bending and tensile testing.

Keywords—Composite, epoxy, polyester, relining, sewage.

I. INTRODUCTION

IN 1976, Eric Wood and his company Insituform completed a cured-in-place pipe (CIPP method) in U.S., which granted them a U.S. patent for CIPP in 1977 [1], [2]. Nowadays, a number of different materials and techniques are in use for rehabilitation of pipelines. One common example of rehabilitation by lining is the cured-in-place pipe (CIPP) liners which are used mainly in industry and public pipe systems. In CIPP technique, a resin saturated lining tube is installed in a pipeline; the resin is then heated to be cured. The curing process can be by heat curing methods using hot water or steam or by UV-light while for smaller diameter pipes, more commonly are cured at ambient temperature. "It is accepted by the majority in the field that if less than about 25% of the total sewer length contains defects, it is better to use full relining for the sewer system" [3]. It is estimated [4] that about 65,000 km of CIPP liners have been installed worldwide which makes it the leading rehabilitation technique. It is by far the leading method for rehabilitating gravity sewers. Relining methods are typically categorized into four classes based on the American Water Works Association [5]: Lining systems which act as corrosion barriers are considered Class I non-structural.

- Close-fit lining systems that span holes in the host pipe, but require support from the host pipe to prevent collapse are considered Class II semi-structural.

- Class III semi-structural linings also span holes, but have sufficient thickness to resist against external hydrostatic load or vacuum load.
- Class IV fully-structural lining, the existing pipe acts as a right-of-way for the installation of the structural liner.

Relining with composite polymers or coatings, are used in two common Spray-on and Brush-applied techniques in Sweden, the country that this study has been conducted in. They are classified as non-structural (AWWA Class I) lining systems [5], while the other common technique, the flexible sleeve using epoxy composite is usually categorized as a semi-structural lining [5]. The flexible sleeve lining method which is the most common technique of applying relining in domestic pipelines in Sweden is similar to the CIPP method. In a majority of installations, there is no source of heat used for curing after applying the relining material and the material is cured in ambient temperature. However since 2015, a relining company, Aarsleff, has started using UV light to reach adequate curing after installation. The most common matrix resins for the relining applications in Sweden are unsaturated polyester resin [6] and epoxy resins. The unsaturated polyester used in the spray method is reinforced by glass flake and the epoxy resin for brush-applied technique is modified with nitrile rubber. The main resin in the flexible sleeve method is usually a composite based on epoxy which is penetrated to a textile fabric which can be fibrous polyurethane or polyester based textile.

A. Spray-on Method

Polyester resin is widely used in Sweden for the small-diameter water pipe rehabilitation. The material is unsaturated polyester resin which is reinforced with glassflake for providing high values of stiffness and strength, the solvent is vinyl toluene. The second component in a majority of the installations is the curing agent which often is peroxide. The proposed thickness by the resin manufacturer for this type of relining is three layers of 900-1100 µm dry thickness each [6]. It is possible to apply the composite and the hardener after mixing with an ordinary airless spray application in which works by pumping resin at a high pressure, through a tiny hole in the spray gun tip. The tip is designed to break up the composite evenly into a fan-shaped spray of tiny droplets or a 2-comp airless spray in which the resin and hardener are mixed right before application. Relining companies which use this technique allow the customer the possibility of using the water pipe after one day. The following pictures show how the glassflake particles are mixed in random directions in a multilayered cured film of composite that was investigated

Parastou Kharazmi is PhD student in Department of Building Technology, School of Architecture and the Built Environment, KTH Royal Institute of Technology, Stockholm, Sweden (e-mail: kharazmi@kth.se).

Folke Björk is Professor at Department of Building Technology, School of Architecture and the Built Environment, KTH Royal Institute of Technology, Stockholm, Sweden (e-mail: folke.bjork@byv.kth.se).

under light microscopy, scanning electron microscopy and energy dispersive spectroscopy.

As can be seen in Figs. 1 and 2, the main direction of glassflake particles differs at different depths. This is an indication of application of different layers on top of each other after surface curing.

B. Brush-Applied Method

The brush-on rehabilitation method for small-diameter pipes with epoxy uses a type of epoxy composite which is modified with nitrile butadiene rubber. This modification gives an elastic property to the material. In the brush-on technique, a two components epoxy material is applied, the epoxy resin is often a Bisphenol A (BPA) with urethane amine hardener. Epoxy resin is usually formed from reacting epichlorhydrin with bisphenol to form diglycidyl ethers of Bisphenol A (DGBA). This is commonly referred to epoxy functionality. Liquid epoxy resins are converted through these reactive epoxy sites into insoluble and infusible solids. Properties of the final resin also depend on the curing agent. This type of material and method is categorized as corrosion protection and nonstructural.

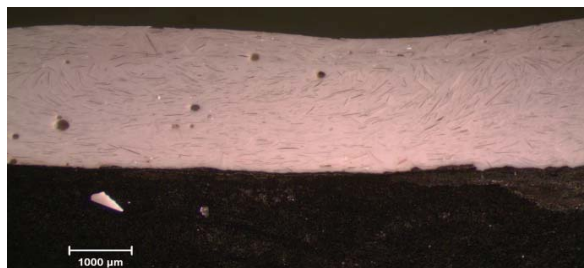


Fig. 1 Cured multi-layered polyester composite under light microscopy

C. Flexible Sleeve

Flexible sleeve with impregnated fiber is the other major technique which uses a prefabricated polyester or polyurethane textile to be impregnated by a two components epoxy resin. The thickness of the flexible sleeve liner inside the old pipe depends on the thickness and diameter of the old piping system. The prefabricated textile is coated with a polymeric layer, mainly polyurethane, for wear protection. The epoxy resin is impregnated to the textile by roller-impregnation process.

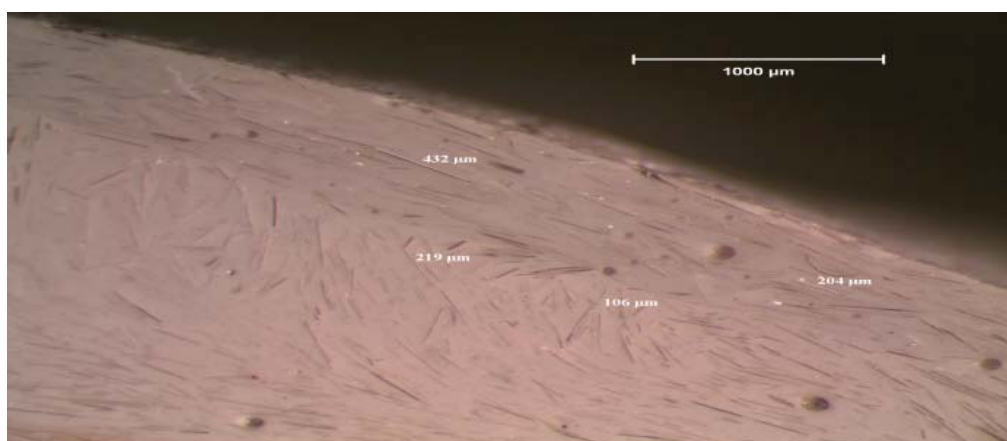


Fig. 2 Cured multi-layered polyester composite under light microscopy

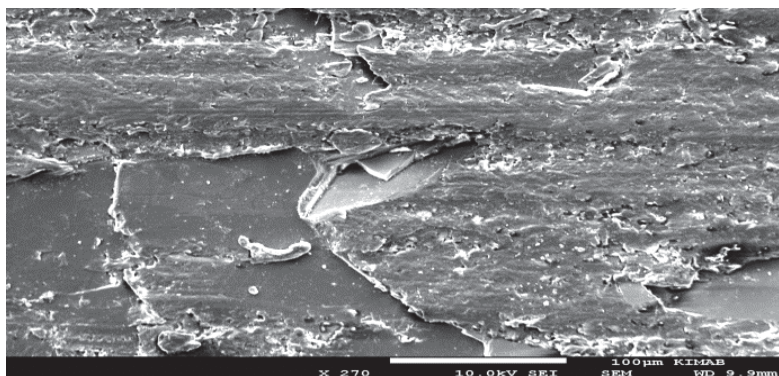


Fig. 3 A Scanning electron microscopy (SEM) photo of polyester composite showing how glassflake is blended in the composite

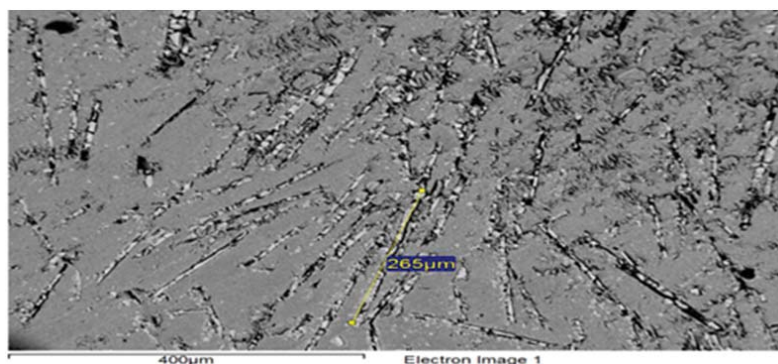


Fig. 4 An Energy-dispersive X-ray Spectroscopy (EDS) shows how glassflake particles are spread in the dried film of polyester composite

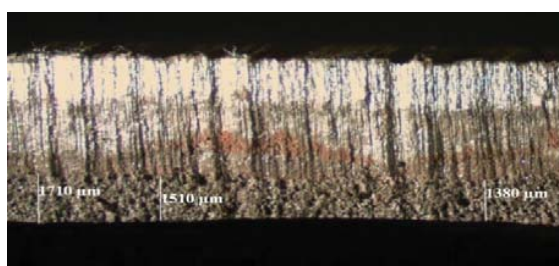


Fig. 5 A 10 year-old pipe relined with epoxy composite under microscope

II. INVESTIGATION OF THE COMPOSITE MATERIALS AFTER EXPOSURE TO ELEVATED TEMPERATURE AND WATER

A. Samples Preparation

For preparing the polyester based samples, a commercially available relining material, based on a polyester resin dissolved in vinyl toluene and filled with glass flakes and filler was used (Jotun's Baltoflake Proline system). The material was mixed with 1.5 vol% of peroxide (Norpol peroxide 13) at room temperature (22°C) and a 1 mm thick layer was obtained by spreading the material on a glass plate covered with a film using an applicator and two distance pieces to control the thickness. The film was cured at room temperature. After one and two hours the second and third layer were applied in a similar way, respectively. The material was then stored at room temperature 22°C for two weeks before starting with the exposure experiments. Half of the sheets with dimension of 10 X 10 cm were placed in plastic jars, then filled with deionized water and placed in ventilated ovens at 40°C, 60°C and 80°C, (the container for sheets exposed to water at 22°C was stored at room temperature). After different periods of time, samples were taken out for evaluation for example, after two, four, six, eight, ten, twelve and fourteen months. Before some of the tests, the samples were dried in a ventilated oven at 40°C and the weight was measured constantly until the measurements reach the equilibrium and the samples were taken out. The rest of the samples were exposed only to the elevated temperatures as well as at room temperature and not water for the comparison studies of the effect of the water.

For preparing samples of epoxy modified with rubber, a commercially available relining material (Zel-Aaren

Innovation Sweden) based on a two component thixotropic epoxy resin modified with rubber was used. The main component (Elasto-Liner component A) was mixed with the hardener (Elasto-Liner component B) at room temperature (22°C) and a 2 mm thick layer was obtained by spreading the material on a Teflon based glass plate using an applicator. The film was cured in room temperature. The material was then stored at room temperature 22°C for two weeks before starting with the exposure experiments. Sheets of the material with dimension of 10 X 10 cm were placed in plastic jars, then filled with deionized water and placed in ventilated ovens at 40°C, 60°C and 80°C, (the container for sheets exposed to water at 22°C was left at the room temperature). Samples were taken out for evaluation after different time period as polyester samples. To dry the sheets, they were placed in the ventilated oven at 40°C and the weight was measured constantly until the weight decrease ended. The same as polyester samples, epoxy samples were also exposed to different temperatures in both wet and dry condition.

Some of the tests such as mechanical testing were done on samples that were not dried thoroughly but only wiped off.

B. Dynamical Mechanical Analysis (DMA)

DMA measurements for the samples were carried out in a Perkin Elmer instrument with single cantilever beam. The temperature was scanned at a constant heating rate of 2°C/min and a constant frequency of 1 Hz from -20°C to 180°C in a nitrogen atmosphere. The measurements were conducted on the material after complete drying as described before. Glass transition temperatures (T_g) were determined- if possible- from the peaks in the curves of loss modulus and tan delta as well as the onset of the drop in loss modulus. Glass transition temperature is an indicator of the degree of curing as well as changes in polymer materials properties.

As can be seen from Fig. 6, there is a constant tendency for T_g to increase by increase in exposure temperature from 22°C until 60°C but it has stopped after 60°C and T_g has decreased for the sample exposed to water at 80°C. It can be noted that samples exposed to water at 80°C has a lower T_g in comparison with material exposed to water at 60°C.

T_g for the epoxy material exposed to different temperatures does not follow the same trend as polyester composite. This can be due to the rubber phase in the material and the

degrading effect of combined high temperature and water. This will be dealt with further in the discussion section.

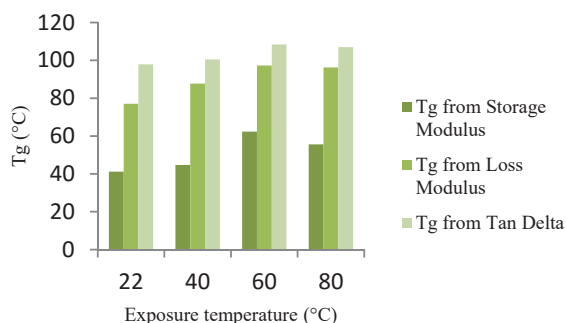


Fig. 6 Tg from DMA measurements for polyester composite exposed to deionized water at different temperatures for two months and after complete drying in the oven at 40°C

Big cracks and delamination after exposure to water was noted in the samples of the polyester composite. This is exemplified with Fig. 7 showing the cross section of specimens for the DMA test exposed 8 weeks at 40°C and Fig. 8 with the same kind of material exposed 8 weeks at 80°C. This behavior was more pronounced at the higher temperature.



Fig. 7 DMA specimens from polyester composite after eight months exposure to water at 40°C for eight months

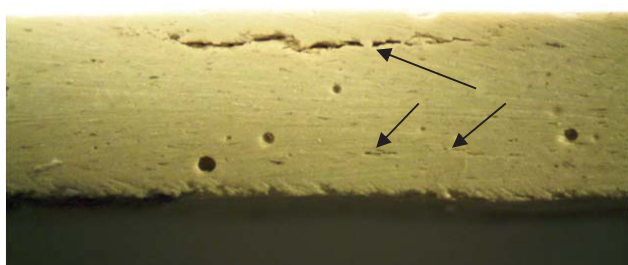


Fig. 8 DMA specimen from polyester composite exposed to water for two months at 80°C under light microscopy

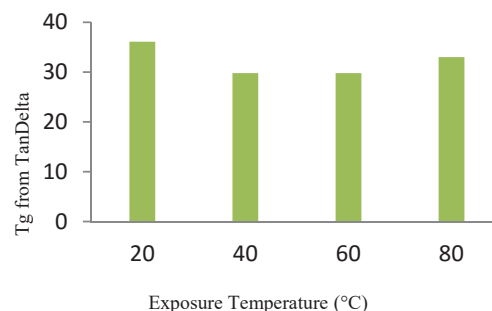


Fig. 9 Tg measurements (Tan Delta) with DMA for epoxy composite for materials exposed to deionized water at different temperatures, for two months and after complete drying in the oven at 40°C

C. Differential Scanning Calorimetry (DSC)

DSC tests were performed to study the glass transition temperature. Three samples of each material with approximately 10 mg mass in aluminum pans of 40 μ l were first heated up from -20°C to 180°C. In the second step, they were cooled down from 180°C to -20°C at the same rate and in the last scan; samples were heated up again to 180°C. The heating and cooling rate was 10°C/min and test was carried out in a nitrogen gas environment. In all scans, temperature was first held for 5 min at -20 and 180°C. Glass transition temperatures T_{g1} and T_{g2} were determined at respectively first and second heating phase.

In DSC measurements (Fig. 10), the polyester composite showed the same result as DMA measurement which was a lower Tg after exposure at the highest temperature of 80 ° in comparison with samples exposed at 60°C. The composite also showed the same trend with increasing Tg which Tg increased up to 60°C and then dropped at the highest temperature of 80°C.

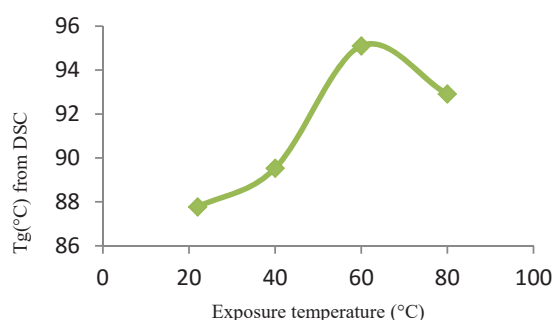


Fig. 10 Tg measurements by DSC for polyester composite exposed to deionized water at different temperatures, room temperature, 40°C, 60°C and 80°C for 8 months and after complete drying in the oven at 40°C

Similar to DMA measurement, epoxy composite samples did not show a special trend related to the exposure temperature in DSC either, (Fig. 11).

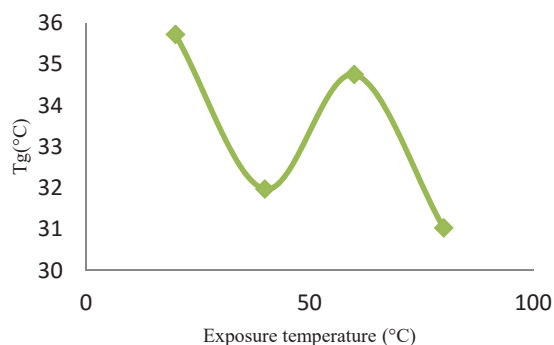


Fig. 11 Tg measurements with DSC for epoxy composite exposed to deionized water at different temperature, room temperature, 40°C, 60°C and 80°C for two months and after complete drying in the oven at 40°C

D. Mechanical Testing

An Instron tensile testing machine was used for measuring the modulus, stress and strain at break. The load cell was 0.5 kN and the specimens were tested at the room temperature (22°C).

E. Three Point Bending for Polyester Composite, Comparison between Dry and Wet Samples

Bending testing was performed according ISO 178. The cross head speed was 2 mm/min and the support length 64 mm. The specimens had a width of 10 mm and a length of 80 mm. Testing was performed at room temperature using an Instron 5566 machine equipped with 3-point bending fixture.

The results that are given in Tables I and II show how samples exposed to water at elevated temperature for 2 months have decreased in E-modulus and stress at break in all temperatures compared to dry samples left in the elevated temperature and not exposed to the water.

TABLE I
THREE POINT BENDING FOR SURFACE DRIED POLYESTER COMPOSITE SAMPLES EXPOSED TO ELEVATED TEMPERATURES AND WATER

Temperature	22°C	40°C	60°C	80°C
E-modulus (MPa)	2236	2593	2458	3006
Stress at maximum load (MPa)	37,8	29,1	26,4	24,6
Elongation at break (%)	2,06	1,48	1,42	1,12

TABLE II
THREE POINT BENDING FOR POLYESTER COMPOSITE SAMPLES EXPOSED TO ELEVATED TEMPERATURES IN DRY CONDITIONS

Temperature	22°C	40°C	60°C	80°C
E-modulus (MPa)	5400	5230	5792	6016
Stress at maximum load (MPa)	65,5	58,9	62,4	57,3
Elongation at break (%)	1,34	1,18	1,08	0,94

Tables I and II show how polyester composite has changed in mechanical properties after exposure to elevated temperatures in wet conditions compared to the same material exposed to elevated temperatures in dry conditions.

F. Tensile Testing for the Epoxy Material, Comparison Between dry and Wet Samples

The testing was conducted using an extensometer. Specimens for tensile testing were prepared based on Type V

(dimension for specimens with the thickness under 4 mm) specimens specified in ASTM D 638 and the cross head speed was 1mm/min. The cross head speed was 2 mm/min, the support length 64 mm and samples had a length of 100 mm, with a width of approximately 10 mm and a thickness of approximately 3mm.

Tables III and IV show the differences when samples prepared from epoxy composite were tested in tensile machine after 2 months exposure and in two conditions of surface dried and complete dried.

TABLE III
TENSILE TESTING MEASUREMENT FOR SURFACE DRIED EPOXY COMPOSITE SAMPLES EXPOSED TO ELEVATED TEMPERATURES AND WATER

Temperature	40°C	60°C	80°C
E-modulus (kPa)	1295	1094	313
Stress at maximum load (MPa)	1,5	1,6	0,69
Elongation at break (%)	156,81	187,94	248,17

TABLE IV
TENSILE TESTING MEASUREMENT FOR COMPLETELY DRIED EPOXY COMPOSITE SAMPLES AFTER EXPOSURE TO ELEVATED TEMPERATURE AND WATER

Temperature	40°C	60°C	80°C
E-modulus (kPa)	7927	4123	1924
Stress at maximum load (MPa)	3,3	3,1	2,3
Elongation at break (%)	137,50	204,77	254,71

Tables III and IV show how the epoxy composite samples have changed in mechanical properties after complete drying compared to the wet condition. However the elongation at break has not changed significantly.

III. DISCUSSION

Both DSC and DMA analysis on polyester composite samples show the same trend regarding a decrease in glass transition temperature (Tg) at 80°C which can be an indication of change in composite and the start of degradation since Tg shows until which temperature the material is stable [7]. This assumption is also proved in inspection of prepared specimens for DMA analyses under microscopy which can be seen in Fig. 7 and Fig. 8 as well as in previous publication [8].

Fig. 7 shows that delamination and cracks happened after exposure not only at 80°C but also at 40°C when exposed for a longer period of time, in this case, 8 months.

Despite polyester composite, Tg for epoxy samples exposed to different temperatures did not follow a special trend based on the exposure temperature. Fig. 9 shows Tg measurements with DMA for epoxy composite is changing unexpectedly to a higher degree at 80°C than 60°C while the changes in material are expected to be greater at 80°C. This can be because of non-suitability of this method for measuring Tg of this type of epoxy composite which is filled with rubber and exposed to elevated temperature and water. The other reason for the differences between polyester composite and epoxy composite in Tg measurements can be due to a different water absorption mechanism in these two types of the composites. The amount of rubber in the epoxy composite causes much higher water absorption [9], as it has been shown in detail in [8]. This

consequently causes a different behavior for the composite during thermal analyses, DSC and DMA. Epoxy composite samples which were exposed to 22°C to 60°C in dry conditions did not show significant change which is expected, as it can be due to the cross-linked and stability of the epoxy in lower temperatures. One of the changing mechanisms of the rubber modified epoxy can be decomposition in the rubber part which can be a phase-separation; this is a more complicated change and can be a reason for different behaviors of epoxy composite in thermal analysis [10].

The comparison between mechanical testing on dry and wet samples in both composites as can be seen in Tables I-IV showed that both materials have changed in wet conditions. One reason for reduction in mechanical properties can be the moisture content in polymer leading to weakening bonds by hydrolysis. Another reason is the water acting as a plasticizer. However materials showed considerably higher stiffness when repeating the same tests after thorough drying. As can be seen in Table IV, elongation for the epoxy composite in dry and wet conditions are quite similar which is an indication of elasticity of the material in both conditions, this quality is important in cases where flexibility of relining material after installation is needed.

IV. CONCLUSION

These experiments indicate that relining material based on epoxy composite filled with rubber which was exposed to different conditions of high temperatures and water did not show significant trends regarding T_g in thermal analyses; however, different tests and visual observation showed that it has changed significantly after exposure in water at the highest exposure temperature, 80°C, as previously shown. Polyester composite show the same tendency of decreasing in T_g at the

highest temperature in this study, 80°C, compared to at 60°C. It also showed obvious cracks and delamination between layers at high temperature as well as after long exposure time.

It was observed that materials have changed in properties significantly when high temperature is combined with water exposure in both visual inspection and water absorption based on the previous study as well as in thermal and mechanical analysis as has been discussed in this study. However, samples did not show significant changes during visual inspection after being exposed to room temperature or 40°C and 60°C in the first four months of the exposure test. This is a positive finding regarding the performance of the relining material after application since the average temperature inside sewage is assumed to be 40°C. Results from mechanical testing showed that despite significant diminish in the stiffness of the materials while tested under the wet conditions, it regains the stiffness greatly after complete drying. The elongation for epoxy composite has not changed significantly in wet and dry conditions which is also a positive result considering the expected performance of the relining material and regarding the need for flexibility to some extent.

ACKNOWLEDGMENT

This research was funded by the Swedish Research Council Formas, the authors also thank the BRiF, Branschföreningen Relining i Fastigheter, and the relining companies for providing valuable information and materials used in this study such as Proline, DaKKI and Aarsleff Co.

APPENDIX

Examples of DMA measurements for polyester balt of lake after exposure in water for two months and complete drying.

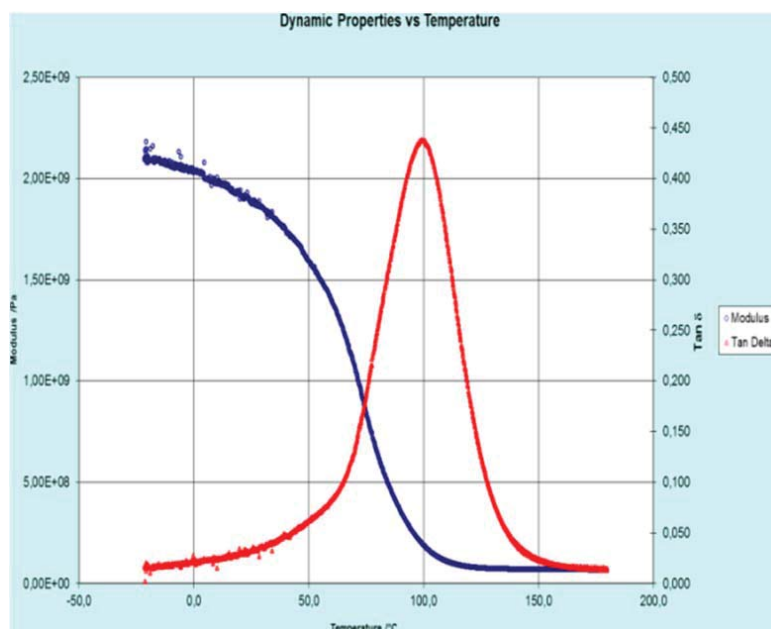


Fig. 12 DMA measurements for the polyester composite after exposure in water at 20 °C and complete drying

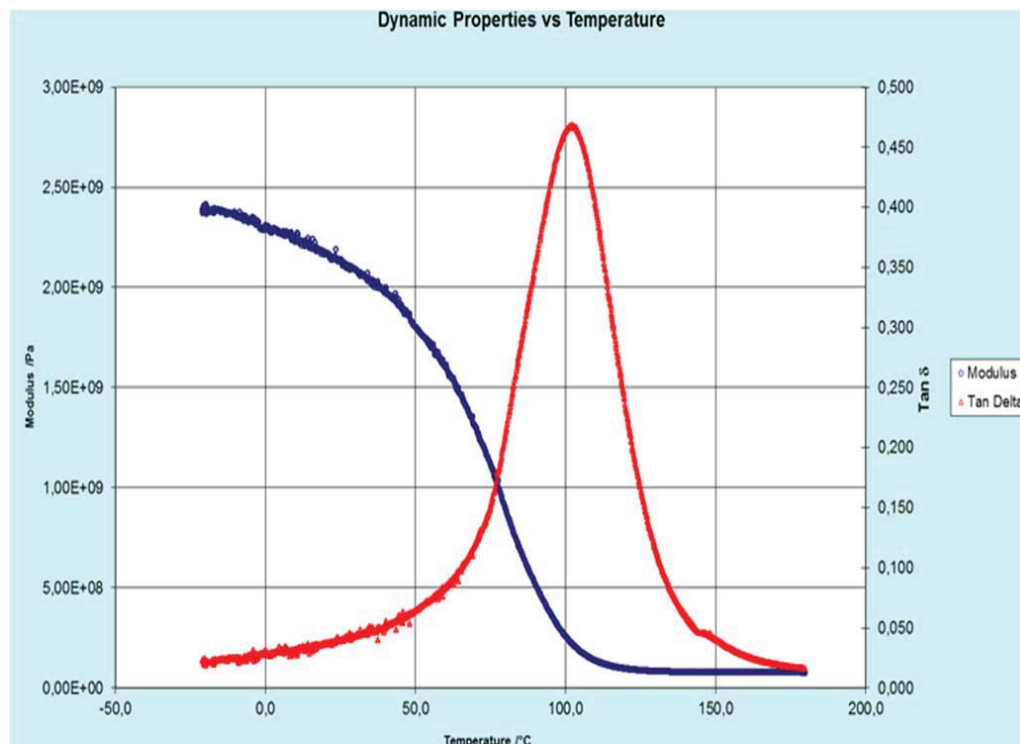


Fig. 13 DMA measurements for the polyester composite after exposure in water at 40 °C and complete drying

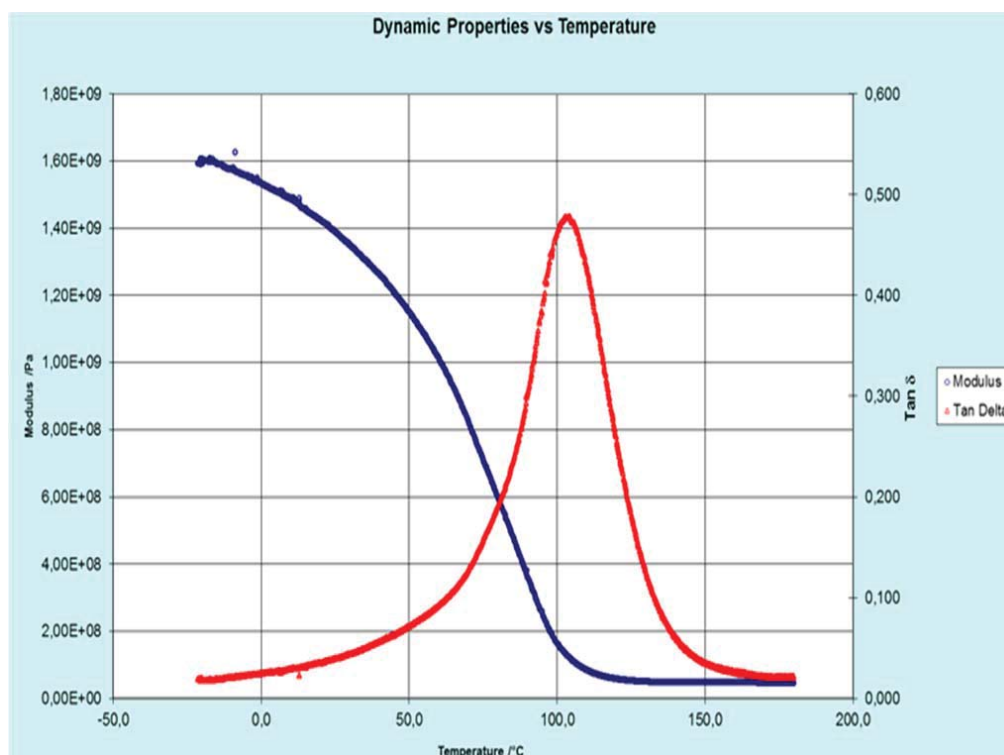


Fig. 14 DMA measurements for the polyester composite after exposure in water at 60 °C and complete drying

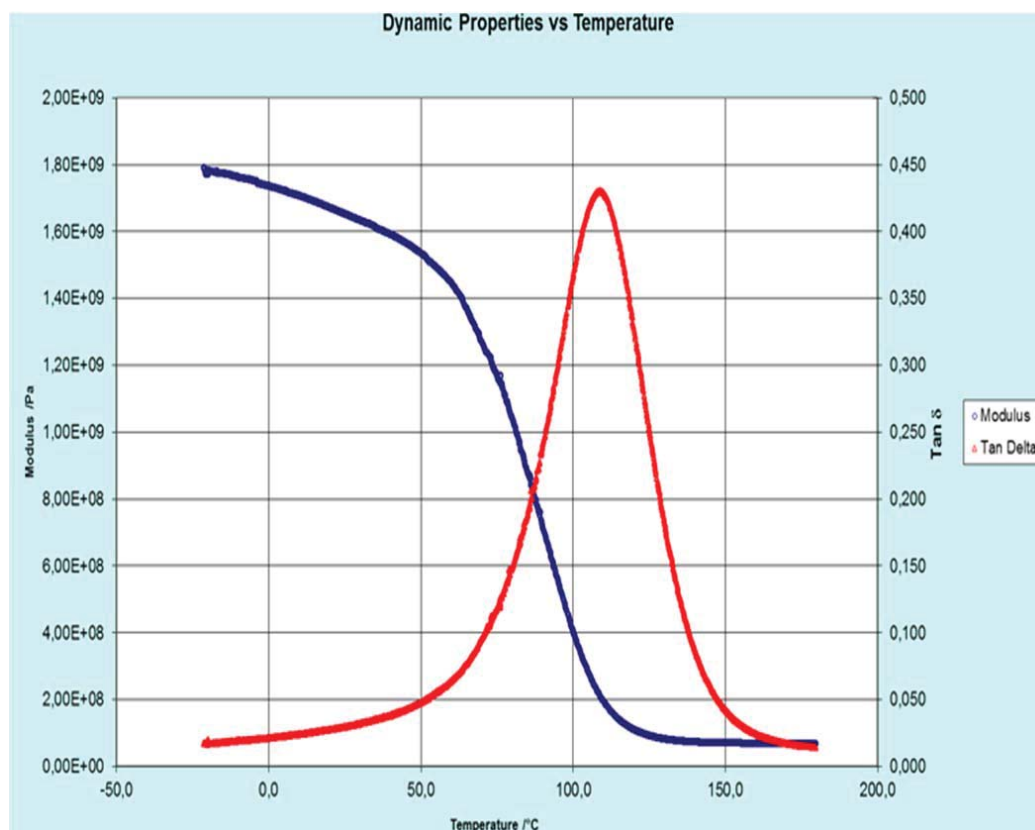


Fig. 15 DMA measurements for the polyester composite after exposure in water at 80 °C and complete drying

REFERENCES

- [1] Jürgen, A., Reinhard L., "Liner Testing in Europe-Methods, Standardization and Experience", ASCE 2013; page 1151-1157.
- [2] E. Wood, "Method of lining a pipe", US 4009063 A, United States Patent, Feb.22, 1977.
- [3] F. Geoffrey, I.G. Vickridge, "Planning Sewerage Rehabilitation and Maintenance-4, Sewers: Repair and Renovation", Chapter 4, 1997, pp.69-83.
- [4] United States Environmental Protection Agency, report, "State of technology for rehabilitation of wastewater collection systems", July 2010.
- [5] Manual M28, Rehabilitation of Water Main, American Water Works Association (AWWA), 2014
- [6] Jotun online website accessed November 10, 2015, <http://www.jotun.com/ww/en/b2b/paintsandcoatings/products/baltoflake.aspx>.
- [7] D.F. Parraa, L.P. Mercuria, J.R. Matosa, H.F. Britoa, R.R. Romanob, "Thermal behavior of the epoxy and polyester powder coatings using thermogravimetry/differential thermal analysis coupled gas chromatography/mass spectrometry (TG/DTA-GC/MS) technique: identification of the degradation products", *Thermochimica Acta* 386 (2002) pp.143–151.
- [8] P. Kharazmi, F. Björk, "Relining of Domestic Piping System with Rubber Filled Epoxy and Reinforced Polyester Composites" *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* Vol:9 No: 2, 2015, pp.284-287.
- [9] I. McEwana, R. A. Pethricka, Stephen J. Shawb "Water absorption in a rubber-modified epoxy resin; carboxy terminatedbutadiene acrylonitrile-amine cured epoxy resin system", August 1998, *Polymer* 40 (1999), pp.4213–4222.
- [10] K. Yamanka, T. Inoue "Phase separation mechanism of Rubber-modified epoxy", *Journal of Materials Science*, 1990 Jan, Vol.25 (1A), pp.241-245.

P.Kharazmi is a researcher and PhD candidate at KTH Royal Institute of Technology, Stockholm, Sweden. She has a master degree from KTH in Chemical Engineering with major in Functionalization of Surfaces and Materials. As her master thesis, she has worked with European Sustain Comp project in École polytechnique fédérale de Lausanne (EPFL) in Switzerland and INNVENTIA Research Institute in Sweden on novel bio-composites. Her extent work and research experiences include research experience in SP Technical Research Institute of Sweden, Institute for Surface Chemistry as well as Swerea /KIMAB Research Institute, Division of Polymer and INNVENTIA AB after her graduate studies. Her expertise includes characterization of novel composite materials, biodegradable polymer sandwiches, fibrous hybrids/composite as well as quality control and inspection regarding corrosion protection systems.