Historical-Technology Survey and Possibilities of Sealing Cracks in Fibreglass Plastics

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Abstract: *Modern polymeric materials started to penetrate the visual arts to a large extent in the early 1960s. This worldwide trend was very quickly captured also in former Czechoslovakia. The so-called arts and chemistry collaboration gave rise to outstanding works of arts created above all from unsaturated polyester resins. Basic types of resins with lower strength and chemical resistance were used due to the polyester resin development policy and the lack of suitable raw materials. Only some of the artworks made of polyester resins have survived to this day, most of them showing cracks in the pre-gel layer. Water penetrates into the work through the cracks, damaging inner layers of the laminate and reducing its strength. For long-term preservation of the work, it is absolutely necessary to seal the cracks. This work therefore examines the properties of polyester sealants made of modern polyester resins recommended by the supplier Havel composites. These resins were suitable for processing by both casting and lamination. The most suitable of the tested resins has been chosen based on an assessment of selected properties including workability, adhesion to the substrate or resistance to ageing.*

Keywords: *polymers in art, fibreglass laminates, unsaturated polyester resins, cracks, sealing*

1. Introduction

1.1. Historical context

The boom of polymeric materials after the Second World War was accompanied by growing application of plastics in all branches of production. New polymeric substances were developed, easily workable and showing properties unseen before, and artists were among those who started to experiment with these materials on a greater scale. Globally, polymeric materials began to particularly assert themselves in the arts in the second half of the 1960s. This is evidenced by a contemporary art exhibition in Kassel in 1968, where artworks of modern polymeric materials comprised almost one-half of the presented creations. Somewhat earlier, in 1967, polymeric

materials dominated also the American art scene. Synthetic polymeric materials were already used for most of the works presented at an exhibition of contemporary sculpting of the 1960s that took place in Los Angeles County Museum in that year [1]. In order to ensure correct techniques of work with the new material, the museum founded the Art and Technology Institute where chemists in cooperation with industrial companies producing polymers suitable for these purposes helped artists create works of art.

The development in socialist Czechoslovakia was not behind the world trends in the sphere of application of modern materials. The Art and Craft Central (Ústředí uměleckých řemesel, ACC) was one of those that dealt with experimental tasks in the studied area. A workplace specialising on the introduction of plastics into sculptural practice functioned at the ACC workshops in Prague in Kafka's former atelier in Střešovice. The first attempts concentrated above all on the use and application of new materials and technologies to artwork reproduction and conservation [2]. The studied topics included particularly the use of polyester or epoxy resin, which could serve as a substitute for bronze or stone in the case of a momentary lack of finances.

The use of polymeric materials only as a substitute was abandoned over the course of time, and new materials started to be popularised and their positive characteristics for the visual arts pointed out [3]. Great prospects were ascribed above all to fibreglass, whose wide possibilities of use were repeatedly emphasised. Fibreglass materials asserted themselves particularly in free creation, being used for smaller interior works as well as for monumental realisations both in the exterior and in the interior.

Laminate asserted itself even in the creation of classically oriented sculptors such as František Mrázek (Labutě – Swans, 1965; Malše, 1965), Jiří Hanzálek (Uzdravená – Healed, 1963) or Zdeněk Hošek (Hanačka – Woman from Haná, 1975). More progressively inclined artists managed to use the possibilities of new resins better in their production. Soft organically shaped forms used by Slavoj Nejdl (Racci – Gulls, unknown year) and Zdeněk Němeček's figural composition style were in good harmony with the material. The latter, however, used laminate only as a tool to check the modelled shapes on 1:1 scale. The resulting work was a sculpture, most often rendered in bronze (Basketbalista – Basketball Player, 1977; Gymnasta – Gymnast, 1979). Jiří Novák was perhaps the sculptor who put the specifics and advantages of the use of fibreglass to the best use. It followed already from the substance of Novák's production, which was always strongly focused on the procedure and particularly on the technical aspects of the origin of the work. Novák devoted himself systematically to work with laminate especially in the 1960s, when he created several works intended for the public space in a short time. Regrettably, many of them have not survived. A dynamically built bird for the fountain in Tyl Square in Prague (1958) no longer exists, nor does the mobile sculpture Světlo a stín (Light and Shadow) that was situated at the Exhibition Grounds (Výstaviště) Prague (1961). Important preserved fibreglass works include Rychlost (Speed) from Prague – Strašnice (1959) and Motýlí křídla (Butterfly Wings) in Liberec (1969) (Fig. 1). Both works have been recently restored.

Fig. 1: Jiří Novák – Butterfly Wings (Motýlí křídla), Liberec (1969).

1.2. Technology survey of polyester fibreglass materials

The history of the use of polyester resins dates back to the period before the Second World War. They are esters of dicarboxylic acids with polybasic alcohols supplied as a solution in a suitable reactive monomer. Thanks to the presence of double bonds in the basic chain of the macromolecule, the addition of a suitable catalyst or accelerator leads to the formation of a three-dimensional network of chemical bonds that transforms the original solution into a solid material. Polyester resins that penetrated the visual arts were the latest ones introduced into production [1, 4]. Only basic, so-called phthalic types of polyester resins were produced in former Czechoslovakia in the early 1960s, and even they only on a limited scale [5, 6]. Chemically more resistant types were imported from abroad. It was a consequence of the limited raw material base and of a central planning decision to restrict the development of chemically resistant types [5]. The main producer of polyester resins in Czechoslovakia was Spolek pro chemickou a hutní výrobu (Group for Chemical and Metallurgical Production, Spolchemie). Polyester resins produced in Czechoslovakia are listed in Tab. 1.

Tab. 1: Polyester resins produced in Czechoslovakia (1965) [7].

name and characteristics	type denomination	note
universal resin	Ch-S 104	viscosity of c. 1000 mPa.s^{-1}
resin with higher thermal endurance	Ch-S 108	more viscous, difficult to work
light-stable resin	Ch-S 111	for roofing, very low viscosity
resin for hot-working	no designation yet	
powdered resin	no designation yet	for interconnection of matting and staple
self-extinguishing resin	Ch-S 150	viscous
flexible, softening resin	Ch-S 200	additive, cannot be used separately

It follows from Tab. 1 that the only polyester resin suitable for the creation of laminate statues was universal resin Ch-S 104. It was a resin based on phthalic anhydride, maleic anhydride and ethylene glycol, terminated by methylcyclohexanol, which was neither thixotropic nor pre-accelerated [8]. The addition of a catalyst and a suitable accelerator was necessary for application under normal temperatures; the best accessible ones were organic compounds based on cobalt [9].

Negative forms were used almost exclusively for the creation of laminate works of art, as they made it easy to achieve a quality, smooth external surface [10]. The first layer of the laminate is mostly formed by so-called pre-gel, a polyester resin thickened by Aerosil into a thixotropic paste that did not flow down when applied into a form. Pre-gel can be also filled with pigments in order to achieve a required appearance without the necessity to apply a paint. Other fillings were not used much during lamination (apart from pre-gel), because they impair the fluidity and the mechanical properties of the resin [1]. The inner layers already contain reinforcement, mostly in the form of glass fibres, saturated with the resin. Mattings or fabrics with various weaves are used above all when laminating [10]. Fabrics with plain, satin and twill weave were denoted YPLAST, YTLAS and YPRA, respectively [11]. Low-alkali borosilicate glass, so-called E-glass with high hydrolytic resistance, was exclusively used for the production of glass mattings and fabrics [4].

In terms of endurance, polyester resins are considered very resistant to the effects of the weather conditions. UV radiation, however, leads to rather fast yellowing of the surface in the case of the absence of a UV stabilizer [12]. The quality of the upper (gel-coat) layer is critical for the endurance of fibreglass works of art; it is based on the abidance by the prescribed technology of processing and the thoroughness of the finishing of the surface above all on the joints of the individual segments of the work. Where the surface is damaged and cracks occur, water leaks inside the laminate and gets in contact with the glass reinforcement. Although the glass reinforcement is

made of hydrolytically resistant glass, metal ions migrate to the surface of the glass over the course of time, get into contact with water and create a hydroxide film that disrupts glass [13]. When water gets into contact with the glass reinforcement, its quickly spreads through the material due to capillary forces and considerably reduces the strength of the work. The critical moment comes when water leaks as far as the steel reinforcement inside the laminate work. The steel reinforcement starts to corrode due to the presence of water, which may endanger the stability of the work over the course of time. It follows from the above-mentioned that repair of cracks by sealing is crucial for increasing the lifetime of laminate exterior works. This work therefore deals with the possibilities of preparation and application of sealants from three modern polyester resins into simulated fissures in naturally aged fibreglass.

2. Experiment

Samples of naturally aged polyester fibreglass cut from a white pigmented lid that had been situated in the exterior for about 25 years were used to prepare the testing elements. The size of the elements was c. 3 x 3 x 0.5 cm; their edges were ground off using a disc grinder under water with abrasive paper with the granularity P400. The type of pigment used was ascertained by phase analysis using PHILIPS X'PERT PRO diffractometer (Cu anode).

The sealants were prepared from three different polyester resins supplied by Havelpol, s. r. o. The characterisation of the resins is given in Tab. 2. Resins 1 and 2 were recommended for the given use by the supplier. Resin 3 was added to the testing due to its declared resistance to UV radiation. The sealants were prepared by the application of 5 wt.% of a white pigment paste for polyester resins (supplier: Havelpol) and 10 wt.% of thixotropic filling Aerosil in accordance with the literature [10]. They were applied between the testing elements, which formed a 0.5 cm wide fissure; in order to maintain a constant distance, the elements were re-laminated by a glass fabric from below. The samples with the applied sealant are labelled S1–S3. The samples with the sealant were subjected to moisture-heat ageing, freezing cycles and laboratory ageing – see the conditions of the individual types of ageing below.

Tab. 2: Characterisation of the polyester resins used to prepare the sealants.

name of resin	label	pre-accelerated	time of curing (min)
HAVELpol 1 – basic (ortho)	1	yes	25
HAVELpol 2 – standard (ortho)	2	yes	26
HAVELpol 4 – UV+clear (MMAortho)	3	no	5

Cylinder-shaped samples of pigmented resins with the diameter of 4 cm and a height of approx. 1 cm were created for the evaluation of the changes after artificial ageing. They are labelled R1–R3 in the text.

The samples were artificially aged in four different environments:

- Moisture-heat ageing (MH): climatic chamber, 70 °C, RH: 75 %, 35 days
- UV ageing (UV): UV chamber, UV intensity: 2.22 mW/cm^2, λ=302 nm, 85 h
- Water-freezing cycles (WF12): the cycles consisted of immersing the samples in water (min. 2 h) followed by placement in an area with the temperature of -20 °C (min. 1 h); 12 cycles were carried out altogether
- Laboratory conditions (LAB): temperature: 20 ±2 °C, RH: 40 ±5 %, 35 days

The spectrophotometer Konica Minolta CM-700d was used to measure the colouring of the prepared samples. The colouring was measured in the colour space CIE L*a*b*. The overall colour difference ΔE* was evaluated.

For the overall evaluation of changes of the surface of the prepared samples R1–R3 after artificial ageing, hardness was measured using digital durometer Shore, type A.

Changes in the chemical structure of the tested sealants after artificial ageing were examined using the infrared spectroscopy method, ATR FTIR technique, spectrometer NICOLET iZ10 with a diamond crystal and MCT-A detector cooled by liquid nitrogen with the resolution of 4 cm^{-1} and 64 scans.

3. Results and discussion

3.1. Characterisation of fibreglass lid

The average thickness of pre-gel of the lid was 200 μm. Glass matting roves were used as reinforcement. X-ray diffraction analysis discovered that the resin is pigmented by TiO_2 of rutile type. The analysis discovered no other filling in the lid. The hardness of the surface layer exceeded the value 100 Shore A.

3.2. Work with sealants

Properties important for the application were subjectively assessed when sealing using the prepared sealants. The properties are summed up in Tab. 3. We worked with a small mason's putty knife and a glass stick.

The table implies that the preparation and work with resin No. 3 was the most difficult due to poor spreadability and a very short time until the beginning of gelation.

Tab. 3: Sealant application properties.

property	sample		
	S1	S2	S3
resin colour	yellowish	white	pink
spreadability	good	good	poor
bubble formation	no	no	yes
time for working	sufficient	sufficient	short

3.3. Colour change results

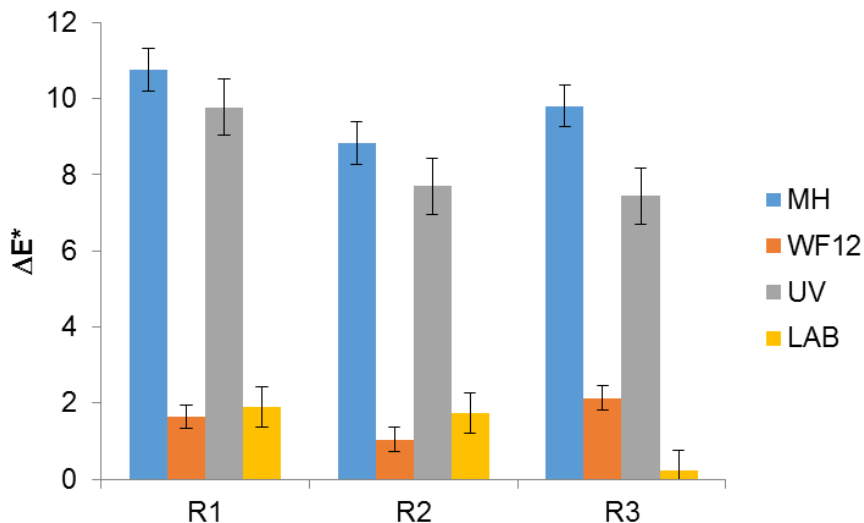The results of total colour difference for the prepared samples R1–R3 are depicted in Fig. 2.

Fig. 2: Overall colour change for samples R1–R3 after artificial ageing.

It follows from the overall colour difference results that a considerable colour change occurred for all resins after MH and UV artificial ageing. When comparing the changes of component b* with the overall colour difference, it has been found out that component b* comprises virtually the whole value of the overall colour difference. This means that the resins have a considerable tendency towards yellowing. Unsurprisingly, the UV colour change was the lowest for sample R3, as the resin was supposed to be resistant to UV radiation. Nevertheless, the difference compared to resin R2 was minimal. Resin 1 showed the greatest changes of colour in all artificial ageing environments except for the freezing cycles, where the greatest change of colour was observed for sample R3. In this case, however, the resin darkened rather than yellowed.

A rather strange phenomenon is the greatest change of colour after moisture-heat ageing for all tested samples. The explanation may lie in the application of a relatively high temperature, as the hardened resin softens and water vapour more easily penetrates the material. Accelerated hydrolysis and oxidation may occur under these conditions, manifesting themselves by the emergence of chromophores and a change of colour. In this case, the changes once again concerned above all component b*.

The overall comparison of colour changes for the individual resins shows that samples R2 were the least prone to changes of colour after artificial ageing showing elements of exterior conditions.

3.4. Cohesion of sealed elements

Three sealed elements for each sealant were subjected to artificial ageing. After the end of artificial ageing, the observation was done, whether some damage in the cohesion of the joint had occurred. The samples were not mechanically burdened after the ageing.

The samples showed no defects after laboratory ageing. After moisture-heat ageing, two S1 samples showed a separation of the sealant from the substrate, which means a reduced adhesion to the substrate. The other samples were all right.

Freezing cycles showed once again adhesion damage to two S1 samples, whereas two samples sealed by S3 suffered from a failure of sealant cohesion and the occurrence of a crack in the sealant. The samples sealed by S2 remained undamaged after all artificial ageing tests. Both the adhesion and the cohesion of the sealant is sufficient for mechanically non-burdened samples.

3.5. Hardness of artificially aged samples

The measured hardness of the tested samples R1–R3 after artificial ageing in different environments is summed up in Tab. 4.

After moisture-heat ageing, the hardness of all samples slightly decreased compared to samples aged in a laboratory. The increased temperature therefore did not lead to an additional hardening of the resins, which means that full and sufficient hardening had taken place already after the preparation of the samples, or possibly a slight hydrolysis of the polymeric network occurred on the surface, resulting in a reduction of the hardness.

Sample R1 showed the greatest hardness decline in the UV radiation environment, which may correspond to the highest tendency towards photo-oxidation and subsequent bond dissociation. A slight decrease in hardness was registered also for sample R3. On the contrary, sample R2 showed a slight increase in hardness as a result of UV radiation, possibly caused by prevailing networking reactions as a consequence of UV radiation.

Tab. 4: Hardness values for artificially aged samples R1, R2 and R3.

sample	hardness (Shore A)			
	LAB	MH	UV	WF12
R1	96.0	94.8	93.8	95.7
R2	96.8	95.0	97.8	96.4
R3	94.3	93.2	93.0	94.1

The exposition of the samples to the freezing cycles had no considerable influence on their hardness.

3.6. FTIR analysis results

Fig. 3 shows the infrared spectra of polished sections of the lid and sealants prepared from the tested polyester resins. When comparing these spectra, we can notice a close similarity of the spectra of the polished sections and sealants S2 and S3, whereas the spectrum of sealant S1 differs from the previous ones in the 1293, 1235 and 1097 cm^{-1} regions. As these are predominantly the so-called "fingerprint regions", we can presume that resin R1 was made of other initial compounds. A very distinct absorbance in the carbonyl group valence vibration region (1722 cm^{-1}) is also visible for sealant S1. This may mean a higher ratio of ester bonds compared to the other resins.

The infrared spectra of the sealants aged in a laboratory were taken as the default ones when examining chemical changes in the structure of the sealants after ageing under different conditions. Fig. 4 compares the spectra of sealant S1 aged in a laboratory, in the moist-heat environment and exposed to UV radiation. No new peaks are evident in the spectrum after ageing by moist heat. There is only a hint of increased absorbance in the 3500 cm^{-1} region (-OH) and a considerable reduction of the intensity of the peak for the wave number 774 cm^{-1}. More considerable changes in the spectrum of sealant S1 are visible after exposure to UV radiation. The individual peaks are no longer as distinct and the individual parts of the spectrum seemingly "melt together". The exposition to UV radiation led to an increase in absorbance for the OH vibration region and to the extension of the peak corresponding to the carbonyl stretching bands (C=O, 1720 cm^{-1}). This may correspond to the dissociation of ester bonds and the formation of new carbonyl and hydroxyl groups.
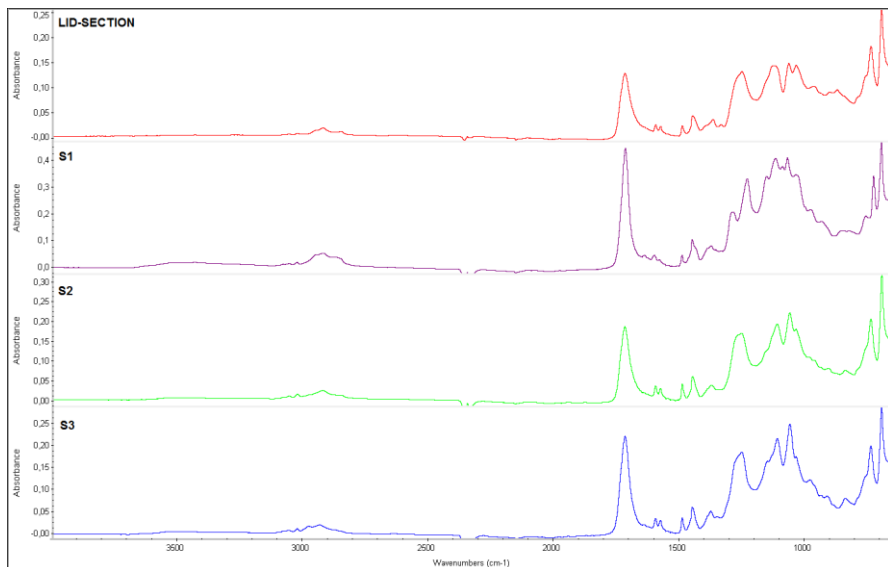

Fig. 3: FTIR spectra of polished sections of the lid and the tested sealants.
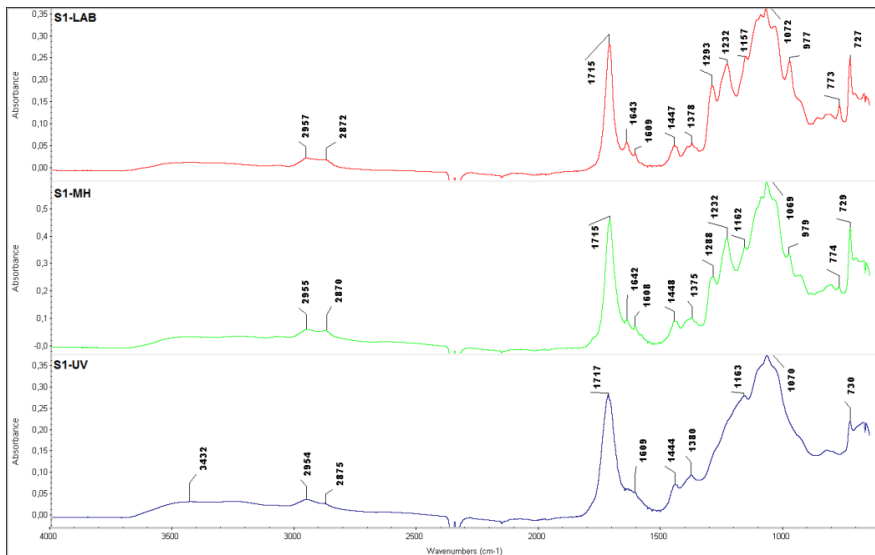
Fig. 4: FTIR spectra of sealant S1 after artificial ageing.

Moist-heat ageing led to no considerable changes in the infrared spectrum for sealant S2 compared to laboratory ageing (Fig. 5).
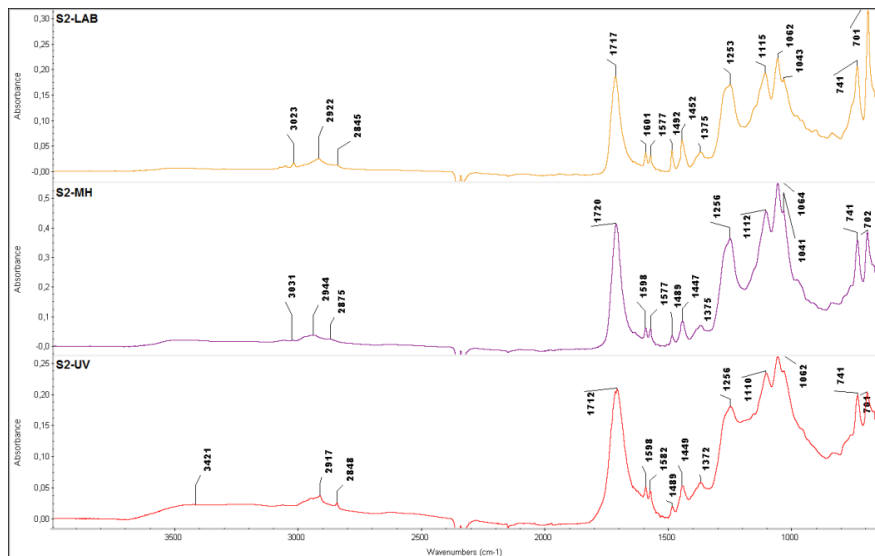

Fig. 5: FTIR spectra of sealant S2 after artificial ageing.

On the contrary, the spectrum after the exposition to UV radiation showed increased absorbance in the hydroxyl group vibration region (3420 cm^{-1}) as well as a shift of the maximum and an extension of the peak corresponding to the carbonyl group (1712 cm^{-1}). These changes were most probably caused by the dissociation of a part of ester groups with the formation of free hydroxyl and carbonyl groups.

The infrared spectra of sealant S3 after artificial ageing are shown in Fig. 6. Sealant S3 showed no considerable changes in the spectrum of the sample after moist heat ageing compared to the sample aged in a laboratory. We can mention a minute increase in absorbance in the hydroxyl group vibration region and in the zone around 1640 cm^{-1}, which might suggest the hydrolytic dissociation of the ester bond. Considerable changes can be observed in the spectrum after the exposition to UV radiation. Although the supplier describes resin R3 as UV-stable, the spectrum after the exposition to UV radiation shows two peaks of the ranges corresponding to the – OH group vibration (3469, 3235 cm^{-1}), an extended and split range corresponding to the carbonyl stretching bands (1723, 1715 cm^{-1}) and new peaks for the wave numbers 1189 and 1160 cm^{-1}. These observations indicate rather substantial changes in the structure of the resin caused most probably by the dissociation of ester bonds. The presence of two peaks in the hydroxyl group vibration region and of the split carbonyl peak means the presence of two kinds of hydroxyl and carbonyl groups.
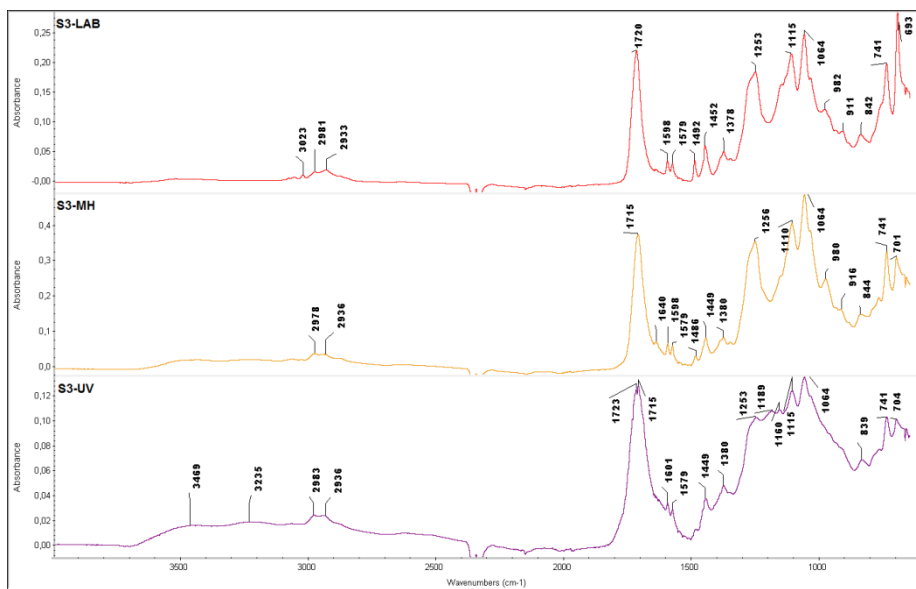

Fig. 6: FTIR spectra of sealant S3 after artificial ageing.

4. Conclusion

A historical survey of the art production in former Czechoslovakia in the early 1960s has shown a great interest in new polymeric materials that were being introduced into the production. A typical example is represented by polyester resins, which after reinforcement with glass fibres enabled the creation of works that could not be rendered from classical materials. The most eminent artist working with polyester resins was Jiří Novák.

From the technology viewpoint, resins available in this country showed worse utility properties such as strength and corrosion resistance compared to foreign materials. An intact continuous pre-gel layer is crucial for the long lifetime of a fibreglass work. In many cases, however, it contains cracks through which water penetrates and disrupts the inner layers.

Out of the tested modern polyester resins, Havelpol 2 resin appears to be the most suitable for the preparation of a sealant usable for the sealing of the cracks. In view of its easy workability, good adhesion to aged laminate and sufficient resistance to ageing, it has excelled among the other tested resins.

5. References

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