Ageing of Some Lacquers Due to Microbiological Stress

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This paper shows the ageing study of some coatings and / or impregnation lacquers due to microbiological stress through fungal attack. Dielectric spectroscopy has shown that the dielectric losses of the investigated materials increase as result of microbiological ageing. The mean recorded increases are about 4 times for the alkyl-epoxy-melamine copolymer, 2 times for epoxy polymer and 1.5 times for urethane polymer in agreement with the mould coverage degree of about 20 %, 10 %, and 3 %, respectively. The fungal attack of the investigated polymers led to a decrease in volume resistivity of about 65 % for the alkyl-epoxy-melamine copolymer, 45 % for the epoxy polymer, and 14 % for polyurethane, in agreement with the increase of dielectric losses and degree of mold coverage of the samples. FTIR determinations have shown that fungal attack significantly increased the number of aliphatic -OH and C-H bonds and decreased the number of C–O bonds, respectively of C–O–C oxiran groups and C-C aromatic bonds. DSC thermograms recorded at different temperature ranges and the activation energies calculation for first major oxidation process indicate that after the fungal attack the thermooxidative reactivity of the investigated polymers increases.

Keywords: coatings, lacquers, moulds, dielectric loss, resistivity, microbiological stress

The lacquers based on synthetic polymers have many applications in electrical engineering such as layers of corrosion protection, electro-insulating films and / or impregnation of insulating materials, consolidation of magnetic core and windings of transformers and / or electric motors [1], etc. Under the concerted and synergistic action of the stress factors (electrical, thermal, climatic, mechanical - especially vibration, microbiological [2-5] etc.) specific to the exploitation environment of electrical equipment, the lacquers based on polymer materials suffer ageing processes that degrade their functional physical-chemical properties [6, 7], which lead to the reduction of the equipment life. Lacquers based on polyurethane [8], epoxy resins [9-13], polyesters [14, 15], acrylics [15, 17], alkyl-epoxy-melamine copolymers [18], etc., are usually used in the electrical applications for various purposes. According to the place of use, they are exposed to thermo-oxidative stress [19], the microorganisms action, electrical stress, mechanical stress, etc.

The enzymatic apparatus of the microorganisms and their metabolic products produce the polymeric materials biodegradation [20-22] with implications on the durability of various construction systems such as: corrosion protection with polymeric protective layers [2-4, 23-25], underground plastic pipelines [26, 27], underground power cables [28-30], etc.

Recent studies have shown that extreme low frequency (ELF) electric fields cause changes in moulds metabolism [31-34], and that the frequencies of 50Hz stimulate the growth and multiplication of filamentous fungi [35, 36], which leads to the intensification of the polymers biodegradation processes [3, 37-39] and acceleration of microbiological corrosion [40-45]. It has also been found that after the penetration of mycelial hifes in panting layers, the insulation resistance of the protective layers decreases significantly, which leads to the micro corrosion and macro cells activation [4, 25].

It must be noted that technological progress has significantly increased the share of reactive electrical consumer (such as: LED lighting, commutation power supply, etc.), which has the consequence of increasing the share of harmonic signals generated in electrical networks [46-49]. In these conditions, both electrical stresses that affect insulation systems (especially the polymer ones) and electromagnetic pollution level of the environment increase - with all the consequences on the natural bioelectrochemical processes in the biosphere [36, 50] and on the durability of materials in the built systems [7, 39, 51-58].

The degradation of polymeric materials is a complex process consisting in structural and physical-chemical properties modifications under the action of different stress factors: UV, gamma rays, natural weathering, microbial agents [59-61]. The presence of oxygen accelerates these degradation processes [62, 63]. The modifications of chemical structure and thermal oxidation stability of polymeric materials could be assessed by using different analytical methods, the most common being vibrational spectroscopy (FTIR) and thermal analysis (DSC, TG/DTA) [64-67].

In view of these considerations, the paper aims to study the effect of microbiological stress on electrical and thermochemical properties of some lacquers based on polyurethane, epoxy resin and alkyl-epoxy-melamine copolymer.

Experimental part

For the comparative evaluation of resistance to mould action and influence of microbiological stress on the ageing of some polymeric lacquers, samples of siliceous sheet metal plates for electrical use were prepared as in [1].

These samples were covered by immersion with three types special lacquers from different insulation classes epoxy resin, polyurethane, and alkyl-epoxy-melamine copolymer.

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Sample Cod	Lacquer	Structure	Solvent
L - 528	528 EZ [38]	monocomponent alkyl-epoxy-melamine	Thinner 528 EZ - a mixture of aromatic hydrocarbons and alcohols
L - G	ROPOXID 501 [39]	bicomponent - epoxy	Acetone
L - S	SIGMADUR™ CLEARCOAT [11]	bicomponent - polyurethane	Thinner 21-06 a mixture of aromatic hydrocarbons and alcohols

Table 1
TYPES OF INVESTIGATED LACQUERS

The investigated lacquers polymerization was carried out by heating with 1.5 degrees / min and after 3 h at 155 ± 5°C, natural cooling in a thermostatic oven with air circulation [1]. The samples were exposed to the moulds action both in a buffered mineral solution type Czapek - Dox, prepared from MERCK p.a. reactive, by dissolving in 1000mL of distilled water of: 2g $NaNO_3$; 0.7g KH_2PO_4; 0.3g K_2HPO_4; 0.5g KCl; 0.5g $MgSO_4 \cdot 7H_2O$; 0.01g $FeSO_4$ and gelled by adding 30g of Agar-Agar and sucrose 30g / L (acting as source of food - easily digestible carbon for microorganisms) [3, 69, 70]. The Czapek-Dox Gel was inoculated by spraying with saline solution of about 106 spores / mL of the species *Aspergillus niger*, *Aspergillus ustus*, *Aspergillus flavus, Chaetomium globosum, Paecilomyces varioti, Penicillium citrinum, Stachybotris atra, Trichoderma viride* and *Cladosporium herbarum*. The microbiological samples thus prepared were incubated at 30 ± 2°C with a relative humidity of 90 ± 5 %, in the dark. At 7 days and 28 days of incubation the samples were visually and microscopically analyzed with a Handheld (USB) digital microscope from Dino Lite.

Before to exposure to microbiological attack and after 28 days of incubation on the samples in table 1, by dielectric spectroscopy technique (with an AMTEK - 1296 Dielectric interface (Solartron Analytical) equipment) determined the dielectric loss $tg\delta$ of the lacquers films investigated.

Also, based on the insulation resistance values measured at ambient temperature (22 ± 3°C) with a FLUKE 1550B MegaOhmMeter (in DC at 250V with a circular measuring electrode described in [4, 25] having a contact surface of 20cm^2) the volume resistances [1] of the lakes investigated before and after exposure to microbiological stress were calculated. Fourier transformed infrared spectra were recorded on a Jasco FTIR -4200 (Jasco, JP), coupled with and Attenuated Total Reflectance (ATR) Jasco PRO 470-H module, at resolution of 4 cm^{-1}.

The DSC measurement were performed on a Setaram DSC 131 EVO equipment (Setaram, FR) using different heating rates (5, 10, 15 °C/min) between 30 - 340°C, in oxidant atmosphere (air, 50mL/min), in Al pans (30µL) with pierced lids in the range of 30 - 340°C. The mass of the samples was between 3-6mg. The calibration of the DSC instruments was verified using a pure Indium standard.

Results and discussions

Figures 1-3 show representative images for the changes of investigated samples under the action of microbiological stress. Analyzing figures 1 - 3, it can be noted that, in all samples, mould growths are much more intense on the edge than in the samples center.

The intense growth of mould on the samples edge is explained by the fact that in these areas, the colony molds are supplied with metabolized carbon through their hifes both from the culture medium with sucrose and the lacquer structure, unlike the samples center, from where the mycelial hifes do not reach to the culture medium (Czapek-Dox gel).

It can be also noted that, on the center of ***L-G*** and ***L-528*** samples, mycelium was formed and mould growths are less intense on relatively large areas, unlike the ***L-S*** sample which shows only a few low developed fructifications of the mould.

In the samples areas covered with mycelium and mould colonies, it was found that ***L-528*** lacquer has a lowest resistance to the mould species action, (about 20 -25 % coverage), ***L-G*** lacquer has an intermediate resistance (about 10 % coverage), and ***L-S*** lacquer has the highest resistance (less than 3 % coverage).

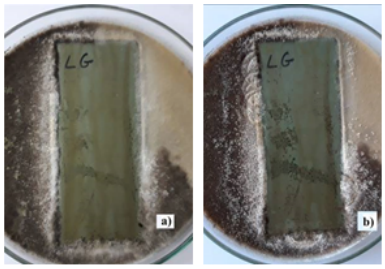


Fig. 1. L-G sample image after incubation with Aspergillus niger: a) - 7 days; b) - 28 days

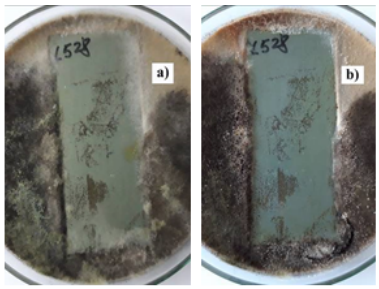


Fig. 2. L-528 sample image after incubation with Aspergillus niger : a) - 7 days; b) - 28 days

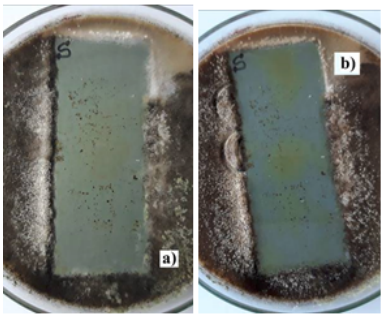


Fig. 3. L-S sample image after incubation with Aspergillus niger: a) - 7 days; b) - 28 days

The fungal species identified from both mixed inoculums were *Aspergillus niger* (black) and *Chaetomium globosum* (white) on ***L-G*** and ***L-S*** samples, while for ***L-528*** sample besides these species (*Aspergillus niger* and *Chaetomium globosum*), was also *Trichoderma viride* as seen in Figures 1 to 3 and from the details recorded with the USB microscope (shown in figs. 4-6).

The results of the insulation resistance ***R*** and of the volume resistivity $\boldsymbol{\rho}$ [1] on the investigated samples, before (initial) and after exposure to the microbiological stress (aged), are shown in table 2.

Analyzing the data shown in table 2 it is noted that, after exposure to microbiological stress the investigated lacquers insulation resistance decreases, the insulation ages, the ageing degree k being given by the following equation (1), where ρ_i, is the resistivity of the initial material, and ρ_a is of the aged material.

$$k = 100 \cdot \frac{\rho_i - \rho_a}{\rho_i} [\%] \quad (1)$$

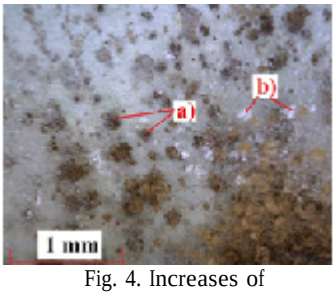


Fig. 4. Increases of
a) - Aspergillus niger and
b) - Chaetomium globosum on L-G sample

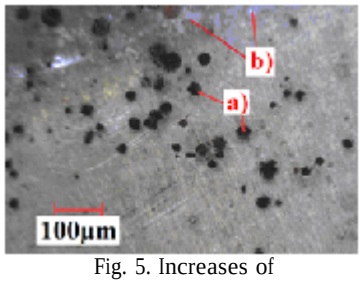


Fig. 5. Increases of
a) - Aspergillus niger and
b) - Chaetomium globosum on L-S sample

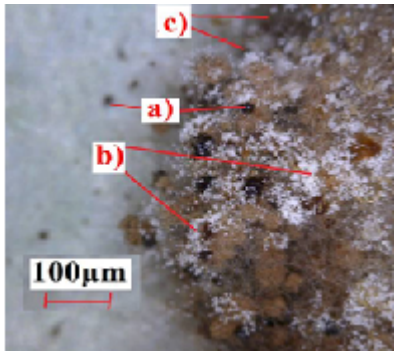


Fig.6. Increases of a) - Aspergillus niger
b) - Chaetomium globosum and
c) - Trichoderma viride on **L-528** sample

Table 2
RESISTANCE AND VOLUME RESISTIVITY (contact area =20 cm²)

Sample code	Layer thickness *d* [mm]	Resistance [GΩ]		Volume resistivity [Ω·cm] x 10^{15}		Aging degree (%) $k = 100 \cdot \frac{\rho_i - \rho_a}{\rho_i}$
		Initial R_i	Aged R_a	Initial ρ_a	Aged ρ_a	
L - 528	0.034	3.56	1.25	20.9	7.3	65
L - G	0.033	11.95	6.52	72.4	39.5	45
L - S	0.033	12.94	11.10	78.4	67.2	14

k values in table 2 are in accordance with the resistance at moulds action of investigated materials, respectively with the coverage degree of samples with moulds.

The results obtained by dielectric spectroscopy and the dielectric losses ***tgδ*** in 1Hz-10KHz range before and after the microbiological ageing of the investigated materials are shown in figure 7.

Analyzing the values in figure 7 it can be seen that, after the microbiological ageing of the investigated lacquers, the dielectric losses increase systematically.

Thus, at 10kHz, the increase recorded for lacquer ***L-528*** is from 0.0116 to 0.0457 (about 4 times), for ***L-G*** lacquer from 0.00859 to 0.0172 (about 2 times) and for lacquer ***L-S*** from 0.0043 to 0.00645 (about 1.5 times). There is a correlation between the volume resistivity evolution in the ageing process (table 2) and the dielectric loss (fig. 7).

In figures 8 are presented the FTIR spectra recorded on both samples (initial and exposed to fungi).

The FTIR spectrum of the ***L-528*** sample (fig. 8a) contains characteristic bands of the alkyl-epoxy-melamine system

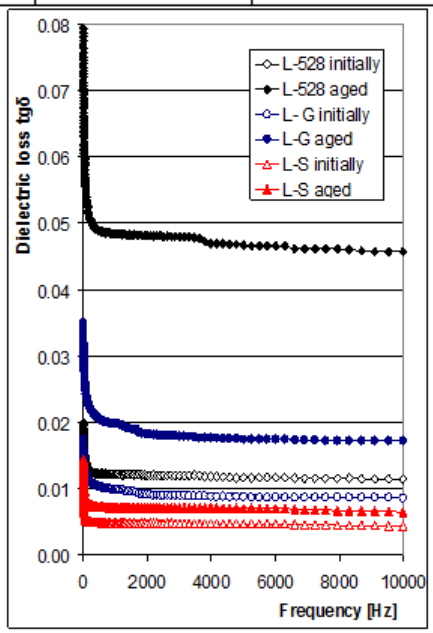
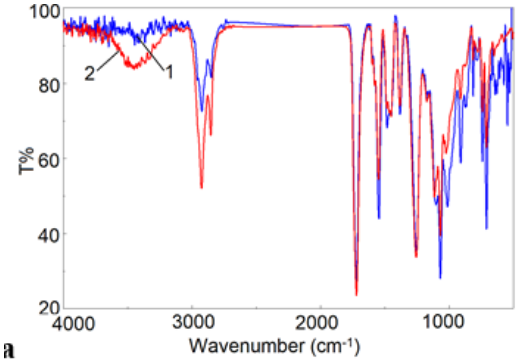
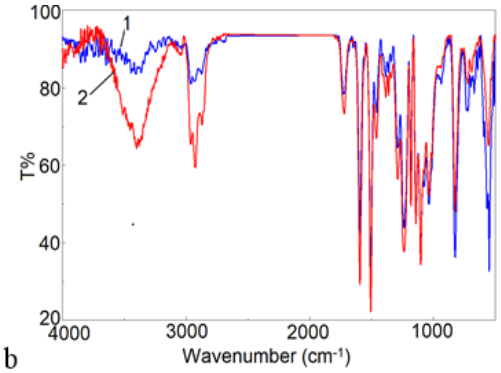


Fig. 7. tgδ evolutions for investigated materials





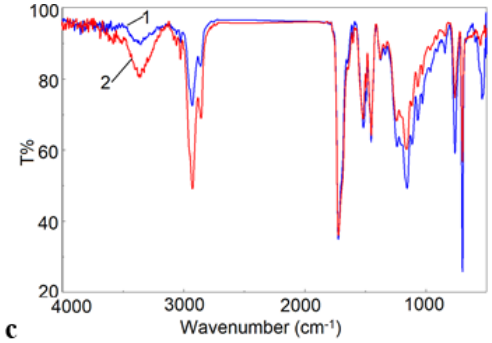


Fig. 8. ATR/FTIR spectra recorded on samples: L - 528 (a), L-G (b), L-S (c); initial (1) and exposed to fungi (2)

[71-73]: a wide band between 3780-3050cm^{-1} (intermolecular hydrogen bonded of -OH group of the alkyl molecules and alkyl-epoxy molecules), 2924 and 2851cm^{-1} (symmetric and asymmetric vibrations of C-H), 1721cm^{-1} (C = O of COOH or ester groups), 1550cm^{-1} (overlap of N-H deformation and C-N stretching of melamine molecules), 1483cm^{-1} (asymmetric and symmetric mode of -CH_2), 1383cm^{-1} (-CH bending), 1320-1020 cm^{-1} (C-O-C stretching of ester group) and 741cm^{-1} (C-H of aromatic ring), an absorption band. The absorption bands at 911cm^{-1} and 814cm^{-1} (stretching of C-O and of C-O-C oxiran group, respectively) suggest that the sample ***L-528*** contains some unreacted amount of epoxy resin.

The fact that, following microbiological treatment, the characteristic vibrations share for C–O bonds and C-O-C oxiran groups are significantly diminished, suggests that these groups have been preferentially converted by enzymatic catalysis into -OH groups (which number has been significantly increased). The exposure to fungi leads to some changes in FTIR spectra as compared to the unexposed ones: an increase in the intensity of the bands corresponding to OH group (3452cm^{-1}), appearance of various types of -CH vibrations (2926m^{-1}, 2854cm^{-1}, 1483cm^{-1}, 1383cm^{-1}) and C = O (1721cm^{-1}). Also, it has been observed a systematically shift to higher wavenumbers of the position of these bands after exposure. These changes are signs of material biodegradation.

The increase in intensity of -CH bonds has been assigned to the formation of new aliphatic C-H bond due to enzymatic additions of water to the double bonds in the polymer chain [20, 74], which is also sustained by the significant increase of -OH groups number.

A similar behavior was observed for the samples ***L-G*** and ***L-S*** (figs. 8b - 8c) after the exposure to fungi: increase in intensity of -OH bands (3404cm^{-1} for ***L-G***, 3360cm^{-1} for ***L-S***, respectively), of aliphatic -CH bonds, and of C=O bond (1722cm^{-1}).

These changes for ***L-G*** are higher, than for ***L-S***. To create a better image of the influence of the fungi exposure on the chemical structure changes, and to avoid the applied ATR (Attenuated Total Reflectance) pressure influence on the spectral band intensities, the area of the main group of peaks relative to a reference A area of a spectral band in which the material doesn't show significant changes following ageing has been calculated (table 3). The chosen reference bands were: 1420-1350cm^{-1} for ***L-528***, 1640-1420cm^{-1} for ***L-G*** and 1480-1410cm^{-1} for ***L-S*** samples.

Analysing the data from table 3 it can be noticed that, after exposure of investigated materials to fungi action, the number of connections specific for different groups and the peak area change significantly. For the quantitative evaluation of structural changes due to fungi action over 28 days of exposure, the change index of peak area ***Ipa*** were calculated for the five domains of wavenumber (types of bonds) with major changes (table 4), using the following equation (2):

$$Ipa[\%] = 100 \bullet \frac{PA_f - PA_i}{PA_i} \quad (2)$$

where:

- PA_f is the peak area of the exposed sample for 28 days of fungi action
- PA_i is the peak area of the initial sample (reference).

Analyzing the data in table 4, it can be noticed that, ***Ipa*** calculated for the -OH groups increased following exposure at fungi action, the most pronounced increase (of 831%) was recorded for the ***L-G*** lacquer. These increases of the -OH polar groups in the investigated materials structure explain the increases in dielectric losses recorded following microbiological ageing (fig. 7). Significant increases in ***Ipa*** were also recorded in the characteristic spectrum for C-H aliphatic groups. These increases of ***Ipa*** for -OH and C-H aliphatic groups can be explained by a water addition process (enzymatic catalysis) at C = C double bonds in the investigated polymer chains during exposure to fungi action.

Higher ***Ipa*** values for the -OH groups (47% - 831%) than for C-H aliphatic groups (97% - 126%) can be explained by reduction of C-O bonds and C-O-C oxilan group (negative

Table 3

INFLUENCE OF THE FUNGI EXPOSURE ON THE MOLECULAR STRUCTURE OF THE ANALYSED SAMPLES

Sample	Peak area/$A_{1420-1350}$				
	3680-3080cm^{-1}	3040-2730cm^{-1}	1780-1640cm^{-1}	1210-820cm^{-1}	760-560cm^{-1}
L-528 initial	1.5	3.6	6.6	17.9	5.4
L-528 exposed to fungi	3.7	7.1	7.6	11.5	1.8
	Peak area/$A_{1640-1420}$				
	3700-3080cm^{-1}	3020-2730cm^{-1}	1790-1660cm^{-1}	1320-860cm^{-1}	860-500cm^{-1}
L-G initial	1.6	3.1	1.5	28.1	9.3
L-G exposed to fungi	14.9	7.0	1.9	22.0	7.6
	Peak area/$A_{1480-1410}$				
	3700-3120cm^{-1}	3050-2730cm^{-1}	1790-1600cm^{-1}	1390-820cm^{-1}	800-500cm^{-1}
L-S initial	1.0	2.5	4.6	10.4	2.7
L-S exposed to fungi	3.5	5.4	5.5	7.3	1.8

Table 4

CHANGE INDICES OF THE PEAK AREA SPECIFIC FOR DIFFERENT TYPES OF BONDS

Sample	Bond				
	–OH	C–H alifatic	C=O	C–O ; C–O–C	C–H aromatic
L-528	Peak area/$A_{1420-1350}$				
	3680-3080cm^{-1}	3040-2730cm^{-1}	1780-1640cm^{-1}	1210-820cm^{-1}	760-560cm^{-1}
	147	**97**	**15**	**–36**	**–67**
L-G	Peak area/$A_{1640-1420}$				
	3700-3080cm^{-1}	3020-2730cm^{-1}	1790-1660cm^{-1}	1320-860cm^{-1}	860-500cm^{-1}
	831	**126**	**21**	**–22**	**–18**
L-S	Peak area/$A_{1480-1410}$				
	3700-3120cm^{-1}	3050-2730cm^{-1}	1790-1600cm^{-1}	1390-820cm^{-1}	800-500cm^{-1}
	250	**116**	**19**	**–30**	**–33**

Ipa values 22% - 36%), groups which, following the enzymatic action of the fungi by reaction with water, were converted to hydroxyl groups (-OH).

It is noted that ***Ipa*** in the characteristic spectrum of C-H aromatic groups has significant negative values (from -18% to -67%), which shows that, a part of the aromatic rings in the investigated polymers structure are broken by enzymatic catalysis (during the microbiological ageing) and they form linear chains with C–H aliphatic groups and -OH hydroxyl groups.

In the C = C carbonyl bonds spectrum, ***Ipa*** values are relatively small (up to 21%), indicating that the oxidation processes due to enzymatic action of the fungi are less pronounced.

In figure 9 are presented the DSC curves recorded at 10°C/min on the initial ***L-528, L-G*** and ***L-S*** samples, respectively the biological aged samples. The DSC technique was used to assess the resistance to thermo-oxidation of the analyzed samples, by the determination of the Onset Oxidation Temperature (OOT) parameters [65], for both initial and exposed to fungi samples at different heating rates (5, 10, 15°C/min). A decrease of the OOT values means that the material is more degraded. The OOT values were used to obtain the oxidation activation energies E_a value (table 3) using the Kissinger method [75]. The way to obtain these values has been detailed previously [76, 77].

Figure 9 shows the structural complexity of the studied systems, namely the overlapping, simultaneous development in different temperature ranges of parallel processes (such as: oxidation in different positions, formation of volatile products, curing processes, etc.).

This fact raises difficulties in defining the characteristic temperatures, including of those of starting temperatures in OOT oxidation process (decisive for material ageing). In this context, the OOT values indicated in figure 9 and used to calculate the E_a values of table 5 are indicative.

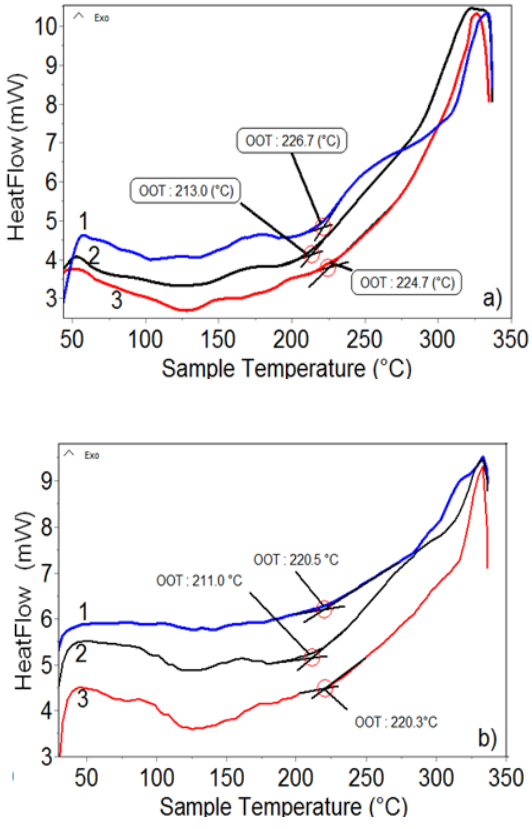


Fig. 9. DSC curves (air & 10 °C/min) recorded on initial (a) and exposed to fungi (b) samples: **L-528** (1), **L - S** (2); **L-G** (3)

Table 5

E_a VALUES OBTAINED FROM OOT DATA USING KISSINGER [75] METHOD

Sample	E_a [kJ/mol]
L-528 initial	239
L-528 exposed to fungi	221
L-G initial	217
L-G exposed to fungi	207
L-S initial	185
L-S exposed to fungi	148

From table 5 it can be observed a general decrease of the E_a values after the exposure to fungi for all samples, which indicates that microbiological ageing decreases the resistance to thermooxidation processes of investigated materials.

Conclusions

Microbiological aging of some lacquers based on polyurethane, epoxy resin and alkyl-epoxy-melamine copolymer under fungi action was studied by dielectric spectroscopy, FTIR, DSC, and volume resistivity. The dielectric loss of investigated materials increases because of the microbiological ageing process. The increases are about 4 times for the alkyl-epoxy-melamine copolymer, 2 times for the epoxy polymer and 1.5 times for the polyurethane polymer. These values match with the mould coverage degree in the analyzed samples, (20, 10, and 3% respectively). The increases in dielectric loss show that microbiological attack in the polymers structure increased by content in polar groups such as -OH, C = O, etc.

The fungal attack of the investigated polymers led to a decrease in volume resistivity by about 65%, 45% and 14% for the alkyl-epoxy-melamine copolymer, epoxy polymer and polyurethane respectively. These values that are according with increases in dielectric loss and coverage degree with mould of the analyzed samples.

FTIR determinations have shown that the fungal attack significantly increases the number of -OH and C-H aliphatic groups and decreases the number of C-O bonds, C-O-C oxilan groups and C-H aromatic groups. The fungal attack does not significantly stimulate the formation of carbonyl type oxidation products.

Thermal analysis allowed the calculation of activation energies of the first major oxidation process and showed that following fungal attack increases the thermooxidative reactivity of the investigated polymers.

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References

1.BORS, A.-M., LINGVAY, D., CARAMITU, A., IORDACHE, I., MARIN, D., LINGVAY, I., Mat., Plast., **56**, no.1, 2019. p. 129

2.RUS, T., CARAMITU, A., MITREA, S., LINGVAY, I., DEMISEE 2016, 20 – 22, 6, p. 60, IEEE Xplore, DOI: 10.1109/DEMISEE.2016.7530466

3.CARAMITU, A., BUTOI, N., RUS, T., LUCHIAN, M.A., MITREA, S., Mat. Plast., **54**, no. 2, 2017, p. 331.

4.LINGVAY, I., FORTUNA, L., VARGA, E., BORS, A.M., NICULA BUTOI, N.O., LINGVAY, D., Electrotehnica, Electronica, Automatica (EEA), vol. **66** (4), 2018, p. 52.

5.RADU, E., MITREA, S., PATROI, D. VOINA, A., MOSCALIUC, H., LINGVAY, I., IEEExplore, DEMISEE 2016, p. 38.

6.BUTOI, N., LUCHIAN, A.-M., CARAMITU, A., MITREA, S., RUS, T., Electrotehnica, Electronica, Automatica (EEA), vol. **65** (1), 2017, p. 72.

7.RADERMACHER, L., BORS, A.-M., LINGVAY, D., NICULA BUTOI, N.O., VOINA, A., MARIN, D., Electrotehnica, Electronica, Automatica (EEA), vol. **66** (4), 2018, pp. 66.
8.*** https://www.ppgpmc.com/Products/7531/SIGMADUR-CLEARCOAT.aspx
9.BRIA, V., MUNTENITA, C., GRAUR, I., Mat. Plast., **55**, no. 3, 2018, p. 295.
10.LADANIUC, M.A., HUBCA, G., GABOR, R., NICOLAE, C.A., SANDU, T., Mat. Plast., **52**, no. 4, 2015, p. 433.
11. YAN, X., CAI, Y., LU, R., MIYAKOSHI, T., International Journal of Polymer Science, vol. 2017, Article ID 5017356, https://doi.org/10.1155/2017/5017356
12. MUNTENITA, C., BRIA, V., ENI, C., CIRCIUMARU, A., GRAUR I., Mat. Plast., **55**, no. 3, 2016, p. 509.
13. LADANIUC, M.A., HUBCA, G., GABOR, R., NICOLAE, C.A., ALEXANDRESCU, E., SANDU, T., Mat. Plast., **54**, no. 1, 2017, p. 125.
14. GAWDZINSKA, K., NABIALEK, M., BRYLL, K., SZYMANSKI, P., SANDU A.V., Mat. Plast., **54**, no. 3, 2017, p. 539.
15. STEIGMANN, R., SAVIN, A., IFTIMIE, N., Mat. Plast., **55**, no.3, 2018, p. 410.
16. ANDREESCU, C.F., GHERGIC, D.L., BANATEANU, A.M., BECHIR, A.M., PATROI, D.N., HANCU V., Mat. Plast., **54**, no. 2, 2017, p. 244.
17. ROMANEC, C., STAN, C.I., HINGANU, M.V., SCUTARIU, M.M., ROSU, S., HINGANU, D., Rev. Chim. (Bucharest), **69**, no.11, 2018, p. 4052.
18 ***http://www.cesivo.ro/Lac-de-impregnare/Lac-de-impregnare-EZ528-4-Litri-372.html
19. RUS, T., BORS, A.M., CARAMITU, A.R., LINGVAY, I., VAIREANU, D.I., Mat. Plast., **55**, no. 2, 2018, p.167.
20. LOREDO-TREVINO, A., GUTIERREZ-SANCHEZ, G., RODRIGUEZ-HERRERA, R., AGUILAR, C.N., J. Polym. Environ., vol. **20**, 2012, pp. 258.
21. ASHWINI, R., ANCHANA DEVI C., International Journal of Biology Research, vol. **3** (1), 2018, p. 180.
22. LEJA, K., LEWANDOWICZ, G., Polish J. of Environ. Stud., vol. **19** (2), 2010, p. 255.
23. RAVIKUMAR, H.R., RAO, S.S., KARIGAR, C.S., Indian Journal of Science and Technology, vol. **5** (1), 2012, p. 1977.
24. RUS, T., RADU, E., LINGVAY, I., LINGVAY, M., CIOBOTEA-BARBU, O.C., CAMPUREANU, C., BENGA, F.M., LAZAR, G.C., VAIREANU, D.I., U.P.B. Sci. Bull., Series B, vol. **79** (4), 2017, p. 167.
25. VARGA, E., FORTUNA, L., LINGVAY, D., BORS, A.M., NICULA, N.O., LINGVAY, I., Mat. Plast, **55**, no. 3, 2018, p. 320.
26. LINGVAY, J., GROZA, C., LINGVAY C., CSUZI, I., Korroz. Figy, vol. **49** (3), 2009, p. 31.
27. BORS, A.M., BUTOI, N., CARAMITU, A.R., MARINESCU, V., LINGVAY, I., Mat. Plast., **54**, no. 3, 2017, p. 447.
28. LINGVAY, J., SZATMARI, I., LINGVAY, M., TUDOSIE, L., Korroz. Figy, vol. **53** (3), 2013, p. 71.
29. LINGVAY, I., ÖLLERER, K., LINGVAY, C., HOMAN, C., CIOGESCU, O., Rev. Chim. (Bucharest), **58**, no. 7, 2007, p. 624.
30. SZATMARI, I., LINGVAY, M., TUDOSIE, L., COJOCARU, A., LINGVAY, I., Rev. Chim. (Bucharest), **66**, no. 3, 2015, p. 304.
31. STANCU, C., LINGVAY, M., SZATMARI, I., LINGVAY, I., International Symposium ATEE, Bucharest, 2013., IEEE Number CFP1314P-CDR
32. LINGVAY, M., STANCU, C., SZATMARI, I., LINGVAY I., Electrotehnica, Electronica, Automatica (EEA), vol. **61** (1), 2013, p. 43.
33. LINGVAY, M., CZUMBIL, L., Electrotehnica, Electronica, Automatica (EEA), vol. **62** (3), 2014, p. 84.
34. LIPCINSKI, D., LINGVAY, D., RADU, E., VOINA, A., Electrotehnica, Electronica, Automatica (EEA), vol. **64** (1), 2016, p. 89.
35. RADU, E., LIPCINSKI, D., TĂNASE, N., LINGVAY, I., Electrotehnica, Electronica, Automatica (EEA), vol. **63** (3), 2015, p. 68.
36. LINGVAY, D., BORS, A.G., BORS, A.M., Electrotehnica, Electronica, Automatica (EEA), **66**, no. 2, 2018, p. 5.
37. VOINA, A., NITA, P., LUCHIAN, A.M., LINGVAY, D., BUTOI, N., BORS, A.M., LINGVAY, I., Electrotehnicã, Electronicã, Automaticã (EEA), vol. **65** (2), 2017, p. 60.
38. NITA, P., LINGVAY, M., SZATMARI, I., LINGVAY, I., Electrotehnica, Electronica, Automatica (EEA), vol**. 61** (3), 2013, p. 40.
39. OPRINA, G., RUS, T., LINGVAY, D., CARAMITU, A.R., MITREA, S., Electrotehnica, Electronica, Automatica (EEA), vol. **65** (1), 2017, p. 81.
40. SZATMARI, I., TUDOSIE, L.-M., COJOCARU, A., LINGVAY, M., PRIOTEASA, P., VISAN, T., UPB Scientific Bulletin, Series B: Chemistry and Materials Science, vol. **77** (3), 2015, p. 91.
41. COJOCARU, A., PRIOTEASA (BARBU), P., SZATMARI, I., RADU, E., UDREA, O., VISAN, T., Rev. Chim. (Bucharest), **67**, no. 7, 2016, p. 1264.
42. LINGVAY, J., SZATMARI, I., PRIOTEASA, P., LINGVAY, M., TUDOSIE, L. M., Korroz. Figy., vol. **54** (1), 2014, p. 15.
43. PRIOTEASA, P., LINGVAY, M., SZATMARI, I., BURUNTEA, N., LINGVAY, I., Electrotehnica, Electronica, Automatica (EEA), vol. **62** (2), 2014, p. 60.
44. LINGVAY, J., RADU, E., MITREA, S., LINGVAY, M., UDREA, O., SZATMARI, I., Korroz. Figy., vol. **54** (2), 2014, p. 40.
45. LINGVAY, I., RUS, G., BURUNTEA, N., UPB Scientific Bulletin, Series B: Chemistry and Materials Science, vol. **63** (3), 2001, p. 29.
46. CHICCO, G., POSTOLACHE, P., TOADER, C., Electric Power Systems Research, 2011, vol. **81** (7), p.1541.
47. SPAFIU, P.C., LINGVAY, D., MATEI, G, Electrotehnica, Electronica, Automatica (EEA), vol. **65** (1), 2017, p. 24.
48. MARIN, D., MITULEÞ, A., LINGVAY, M., Electrotehnica, Electronica, Automatica (EEA), vol. **61** (2), 2013, p. 58.
49. MATEI, G., LINGVAY, D., SPAFIU, P.C., TUDOSIE, L.M., Electrotehnica, Electronica, Automatica (EEA), vol. **64** (4), 2016, p. 52.
50. LINGVAY, I., LINGVAY, C., VOINA, A., Revue Roumaine des Sciences Techniques serie Electrotechnique et Énergetique, vol. **53** (2 bis), 2008, p.85.
51. LINGVAY, I., BORS, A.M., LINGVAY, D., RADERMACHER, L., NEAGU, V., Rev. Chim. (Bucharest), **69**, no. 12, 2018, p. 3593.
52. RADERMACHER, L., LINGVAY, D., BORS, A.M., NICULA (BUTOI), N.O., MARIN, D., Electrotehnica, Electronica, Automatica (EEA), vol. **67** (1), 2019, p. 68.
53. LINGVAY, I., VOINA, A., LINGVAY, C., MATEESCU, C., Revue Roumaine des Sciences Techniques serie Électrotechnique et Energetique, vol. **53** (2bis), 2008, p.95.
54. LINGVAY, I., HOMAN, C., LINGVAY, C., Rev. Chim. (Bucharest), **58**, no. 11, 2007, p. 1051.
55. OPRINA, G., RADERMACHER, L., LINGVAY, D., MARIN, D., VOINA, A., MITREA, S., Rev. Chim. (Bucharest), **68**, no. 3, 2017, p. 581.
56. LINGVAY, I., LINGVAY, C., HOMAN, C., CIOGESCU, O., Rev. Chim. (Bucharest), **57**, no. 12, 2006, p.1279.
57. LINGVAY, I., GABOR, M., VOINITCHI, C.D., LINGVAY, C., Rev. Chim. (Bucharest), **57**, no.4, 2006, p. 378.
58. OLLERER, K., LINGVAY, J., Korroz. Figy., vol. **45** (4), 2005, p. 133.
59. YOUSIF, E., HADDAD, R., Springer plus, vol. **2**, 2013, p. 398.
60. ZAHARESCU, T., MARINESCU, V., HEBDA, E., PIELICHOWSKI, K., Journal of Thermal Analysis and Calorimetry, vol. **133** (1), 2018, p. 49.
61. KOCKOTT, D., Polym. Degrad. Stab., vol. 25, 1989, p. 181.
62. GARDETTE, M., THERIAS, S., GARDETTE, J.L., JANESCKA, T., FOLDES, E., PUKANSKY, B., Polym. Degrad. Stab., **98** (11), 2013, p. 2383.
63. LUNGULESCU, M.E., ZAHARESCU, T., PLESA, I., PODINA, C., J. Optoelectron. Adv. Mat., vol. **16** (5-6), 2014, p. 719.
64. CELINA, M., OTTESEN, D.K., GILLEN, K.T., CLOUGH, R.L., Polym. Degrad. Stab., vol. **58**, (1-2), 1997, p. 15.
65. ILIE, S.D., SETNESCU, R., LUNGULESCU, E.M., MARINESCU V., ILIE, D., SETNESCU, T., MARES, G., Polym. Testing, vol. **30**, 2011, p.173.
66. LINGVAY, I., STANCU, C., BUDRUGEAC, P., CUCOS, A., LINGVAY, C., International Symposium ATEE 2011, Bucharest, p. 437, http://ieeexplore.ieee.org
67. LINGVAY, J., BUDRUGEAC, P., Korroz. Figy., vol. **48** (3), 2008, p. 45.
68. STERE, E., POPA, I., BOTU T.A., Electroinsulating epoxydic varninish for glass threads and production method, patent RO 100096 (B1) 12. 29. 1987

69. *** IEC 68-2-10 (1988) Basic Environmental Testing Procedures. Part 2: Tests-Test J and guidance: Mould growth
70. RADU, E., PATROI, D., OPRINA, G., VOINA, A., LINGVAY, I., Rev. Chim. (Bucharest), **67**, no.10, 2016, p. 1973.
71. CAKIC, M.S., RISTIC, I.S., JASO, V.M, RADICEVIC, R.Z., ILIC, O.Z., Prog. Org. Coat., vol. **73**, 2012, p. 415.
72. ODETOYE, T.E., OGUNNIYI, D.S., OLATUNJI, G.A., Prog. Org. Coat., vol. 73 (4), 2012, p. 374.
73. ONG, H.R., KHAN, M.R., RAMLI, R., YUNUS, R.M., Proc. Chem. vol.16, 2015, p. 623.
74. KHAN, S., NADIR, S., SHAH, Z.U., SHAH, A.A., KARUNARATHNAA, S.C., XU, JIANCHU X., KHAN, A., MUNIR, S., Environmental Pollution, vol. 225, 2017, p. 469.
75. KISSINGER, H.E., Analyt. Chem., vol. **29** (11), 1957, p. 1702.
76. LUNGULESCU, E.M., LINGVAY, I., UNGUREANU, L.C., RUS, T., BORS, A.M., Mat., Plast., **55**, no. 2, 2018, p. 201.
77. LUNGULESCU, E.M., LINGVAY, I., BORS, A.M., FORTUNA, L., NICULA (BUTOI), N.O., Mat. Plast., **56**, no. 1, 2019. p. 87.

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