Congresso Brasileiro de Engenharia e Ciência dos Materiais
06 a 10 de Novembro de 2022 | Águas de Lindóia – SP – Brasil

SWELLING EFFECTS OF USING DISINFECTANTS IN THE OUTER POLYMERIC LAYER OF UPPER-DIGESTIVE-TRACT ENDOSCOPE TUBE

Mariel A. F. Aramayo[1], Gabriel A. C. Gonçalves[1], Juan D. S. Martinez[1], Bruno. M. Tavares[2], Ana Rubia Guedes[2] and Idalina V. Aoki[1*]

1 - Chemical Engineering Department of the Polytechnic School of the University of São Paulo (USP), São Paulo, CEP 05508010, SP.
2 - Hospital Infection Control Group of the Hospital das Clínicas (HC) University of São Paulo (USP), São Paulo, CEP 05403-000, SP
**idavaoki@usp.br*

ABSTRACT

The present work studied the structural and morphological changes on the polymeric outer layer of the endoscope tube during its exposure to different peracetic acid-based commercial sanitizing solutions. Six sanitizing solutions were evaluated: S1 (pure sanitizer A), S2 (sanitizer A + inhibitor), S3 (pure sanitizer B), S4 (sanitizer B + inhibitor), S5 (pure sanitizer C) and S6 (pure sanitizer D). The endoscope tubes were cut in samples of 4 cm long. The weight was taken every week the first month and every two weeks for the rest of total immersion for 3 months. The morphology of the outer polymeric layer, before and after immersion period was analyzed by Optical Microscopy (OM) and by Scanning Electron Microscopy (SEM). The chemical characterization was performed by Fourier Transform Infrared Spectroscopy (FTIR). The tests were carried out at room temperature (25 ± 3) °C and the pH of each sanitizing solution was measured employing a digital pHmeter, which values were in the range of (1.9-4.2). In all evaluated conditions, after 3 weeks, there was a tendency to mass increase of the endoscope tube samples indicating different degrees of swelling. There was a weight increase of less than 1 % for S1, S2 and S5, and greater than 1 % for S3, S4 and S6. On the other hand, by imaging techniques, we observed brightness loss and formation of cracks due to contact with the different disinfectant solutions. Two layers were found instead of only one visible, where the both presented significant surface changes. Chemical degradation was observed in the inner black layer by FTIR. Such behavior can be attributed to the phenomenon of polymer swelling and degradation, creating cracks and holes. The outer polymeric layer is mainly constituted of polyurethane (PU) as observed by FTIR analysis and the inner one is made of a mixture of PU and a polyamide (PA) foam.

Keywords: *Polymer swelling, Polymer degradation, Surface characterization, Endoscope tube, Disinfection.*

INTRODUCTION

Cleaning and disinfecting flexible endoscopes are highly challenging, as several components and small diameter cannulations make these processes difficult to perform. Inadequate disinfection is a risk for the transmission of pathogens. Among the chemical disinfectants used in the high-level disinfection, peracetic acid has the advantage of acting on residual organic matter and, for this; it has been chosen by endoscopy services.

For chemical disinfection, the endoscopes are immersed in a disinfectant solution with a corrosion inhibitor, according to the manufacturer's recommendation. In general, manufacturers recommend the use of solutions based on peracetic acid to disinfect the endoscopes(10). On the other hand, Kampf et. al. concluded in their work that some solutions based on peracetic acid have some cleaning capacity, but all of them are not suitable for use in disinfection step due to lose its antimicrobial activity in the presence of various types of organic load – fixed blood and biofilm, which is mainly presented in body fluids, proteins and others(10).

Therefore, the use of peracetic acid must be combined with accurate protocols for cleaning endoscopes to reach the best disinfection. The outer coating of endoscope tubes is made of polymeric materials, such as polyurethane-based structures. The use of polyurethane in biomedical applications has a wide spectrum because of its biocompatibility(7). One of the uses is as external coatings of endoscopes, however, polyurethane has low chemical resistance when exposed to diluted acids and bases, organic solvents and oxidizing agents(8).

In this sense, the present work studied the structural and morphological changes on the polymeric outer layer of the endoscope tube during its exposure to different peracetic acid-based commercial sanitizing solutions.

MATERIALS AND METHODS

Preparation of sanitizing solutions and endoscopes coating samples

Six sanitizing solutions were evaluated and they were prepared following the manufacturer's specifications: S1 (pure sanitizer A), S2 (sanitizer A + inhibitor), S3 (pure sanitizer B), S4 (sanitizer B + inhibitor), S5 (pure sanitizer C) and S6 (pure sanitizer D). The pH measurements were made by 2 methods: the first one by strip-type pH indicator papers (Merck KGaA, Darmstadt, Germany) and the second one by a benchtop pHmeter (PG1800, Gehaka, Brazil) at room temperature (25 ± 3) ºC.

The polymeric layers, which coat the metal, were separated manually employing a sharp blade to slice obliquely through the polymer aiming to visualize the two layers of the coating. These samples before and after exposed in the sanitizer solutions, were analyzed by other techniques.

Gravimetric or mass change tests

The endoscope tubes were cut in samples of 4 mm, measured with a pachymeter (Mitutoyo) and weighed in a semi-micro analytical balance (AX205, Mettler Toledo, d = 0.01 mg) before the immersion in the sanitizing solutions. Mass and diameter measurements of the endoscope tube samples were taken every seven days during the first month and every two weeks, for the last 3 months. The data of weight measurements were used to determine the % mass change by using Eq. (A), where W_o is the weight of sample before immersion, and W_f is the weight of sample after the respective time of immersion in disinfectant solution:

$$Mass\ change\ (\%) = \frac{W_f - W_o}{W_o} * 100 \quad \text{(A)}$$

FTIR-ATR analysis

The endoscope tube pieces were analyzed by Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR) before and after immersion tests. The clear outer film was detached and analyzed, as well as a section of the inner black polymeric layer of the endoscope tube. Analyzes were performed using a FTIR (Bruker, Alpha II) with Platinum/Diamond in Attenuated Total Reflectance (ATR) mode in the range of 4000 cm^{-1} to 600 cm^{-1} with OPUS 8.2.28 software.

SEM analysis

The endoscope pieces were analyzed by Scanning Electron Microscope (SEM, Vega3, TESCAN) employing the secondary electrons detector at 10kV.

RESULTS AND DISCUSSION

Films characterization

The surface of the polymeric layer of endoscope tubes was evaluated by using SEM. Fig. 1a shows the SEM micrograph of the polymer sample of the endoscope, which was not submitted to the disinfection process, in contrast to Fig.1b, where the polymer had disinfection process using sanitizer solution S6.

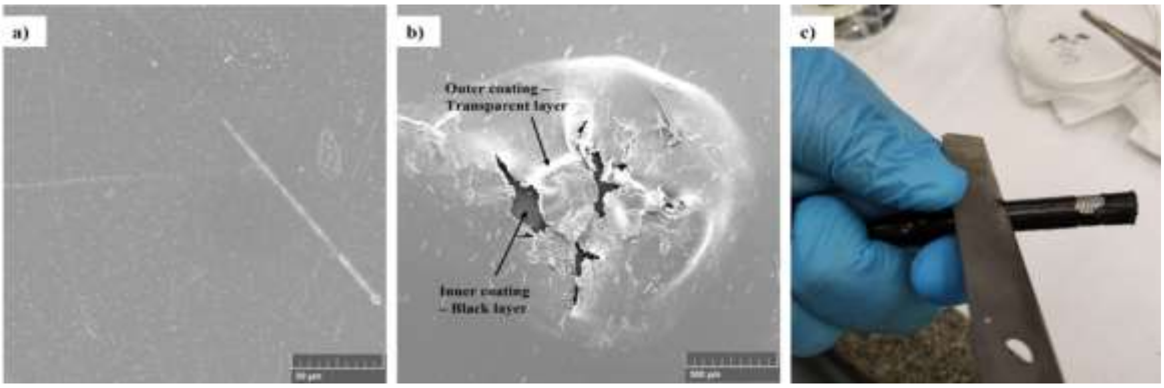

Figure 1: SEM images of endoscope polymer samples a) without contact with sanitizing solution, b) disinfected with sanitizer S6; c) cutting sample layers of polymer to be used in SEM and FTIR analysis.

It was observed the presence of two layers in the polymer, consisting of a clear outer layer and a black thicker inner layer. The outer film before immersion in the sanitizing solution (Fig. 1 a) shows some scribes and after immersion presents some cracks through which the solution enters the inner layer detaching the outer film layer as seen in Fig.1 b and Fig. 1c shows the obtention of slices in the preparation of samples.

The FTIR software library was searched for the spectra presented in Fig. 2 and the clear outer layer was identified as being polyurethane (PU), while the black inner layer was identified as being similar to *"lycra spandex"*, an elastane mostly made of polyurethane (PU) and small parts of polyamide (PA).

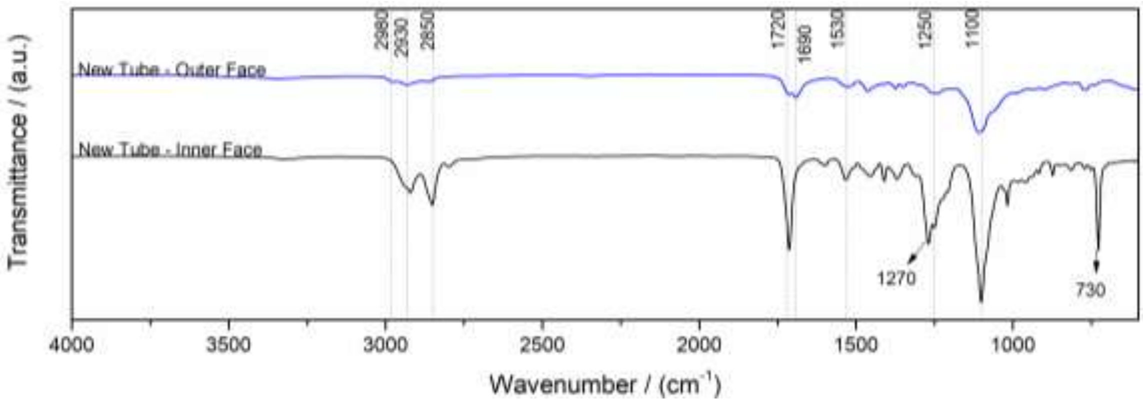

Figure 2: FTIR spectra for the outer and inner face of the new endoscope tube.

Such material suggestions by the library can be supported when analyzing the peaks and bands prominent in each spectrum, as presented in Table 1. The bands presented between 2980 cm^{-1} e 2860 cm^{-1}, as indicated in Tab. 1, may be attributed to symmetric and non-symmetric stretching of the C-H bond of the polymeric long carbon chain[(1)]. While the bands observed between 1720 cm^{-1} e 1530 cm^{-1} may represents the stretching C=O and N-H bonds related to the polymerized urethane with ester bonds (H_2N-CO-OR) as discussed by Mohamed (2014) and Mathur (2012)[1, 2].

Table 1: List of bands and functional groups identified in FTIR spectra.

Wavenumber / (cm^{-1})	**Attribution to a Chemical group**	**Ref.**
2980 – 2860	Symmetric and non-symmetric stretching of the C-H bonds.	(1)
1720	Stretching C=O bonds.	(1, 2, 6)
1530	Stretching N-H bonds.	(1, 2, 6)
1450 – 1350	Stretching C-N bonds.	(3)
1250 – 1100	Asymmetrical and symmetrical stretching vibrations of C-O-C.	(1, 4, 6)
730	N-H out-of-plane wagging.	(3, 5)

Asymmetrical and symmetrical stretching vibrations of C-O-C by ether groups are also observed between the bands 1250 cm^{-1} and 1100 cm^{-1} and are assigned to the polyurethane chemical chain[1, 3, 4]. The presence of polyamide (PA) promoted changes at some characteristic peaks assigned to amides, as higher intensity for the C-H group between 2920 cm^{-1} and 2850 cm^{-1}, due to a longer polymeric C-H chain. There is also a rise of peaks intensity between 1450 cm^{-1} and 1350 cm^{-1}, which are related to C-N stretch, while 730 cm^{-1} assigned N-H out-or-plane wagging[3], which are also present in amides.

pH measurement of the sanitizing solutions

The sanitizing solutions used in this study contain oxidizing agents such as peracetic acid. In Table 2 the results show that S1 followed by S3, S2 are the most acidic conditions and where the worst polymer degradation is expected as mentioned by Sastri (2022)[8].

Table 2: pH measurements of seven sanitizers by two methods.

Product	**Active ingredient**	**pH by pHmeter**	**pH by indicator paper**
S1 (pure sanitizer A)	Peracetic acid	1,88	(1 – 2)
S2 (sanitizer A + inhibitor)	Peracetic acid and anticorrosive agents	2,87	(2 – 3)
S3 (pure sanitizer B)	Peracetic acid 0,2 %	2,40	(2 – 3)
S4 (sanitizer B + inhibitor)	Peracetic acid 0,2 % and phosphate salt mixture	3,63	(3 – 4)
S5 (pure sanitizer C)	Peracetic acid	4,18	(3 – 4)
S6 (pure sanitizer D)	Peracetic acid 0,2 %	3,70	(3 – 4)

Samples mass change

Figure 3 shows that the highest disinfectant solution uptake value to PU material after 13 weeks was 3,08 % (S3) followed by 1,38 % (S2). Besides S3, in S6 was observed disinfectant solution absorption was faster in the first 4 weeks and became slower for longer immersion times. When the material is immersed, the polymeric barrier tends to reduce because of the interaction between the liquid molecules and the polyurethane network, mainly through previous defects as scratches which is usually followed by the solvation of the polymer chains, resulting in swelling[8]. According to IUPAC definition, the swelling process is the increase in volume of a gel or solid associated with the uptake of a liquid or gas[9]. It is worth to say that all the samples released black particles from the inner layer and we have not made adequate correction for the mass changes due to this issue. We intend to do that in the future, because all the solutions are preserved.

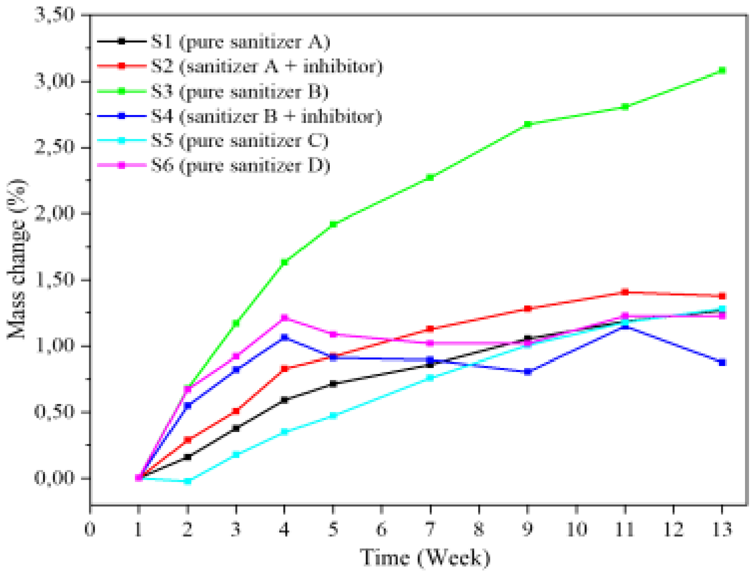

Figure 3: Samples mass change of polymeric coatings immersed in seven different sanitizers for 13 weeks at atmospheric conditions.

<u>Films degradation</u>

The samples exposed in solutions S2, S3 and S6 were the ones that showed the greatest mass change, being the most attacked by their respective sanitizer solutions. In this sense, these samples showed the greatest degradation in the black inner polymeric layer, as indicated in the FTIR spectra shown in Fig. 4.

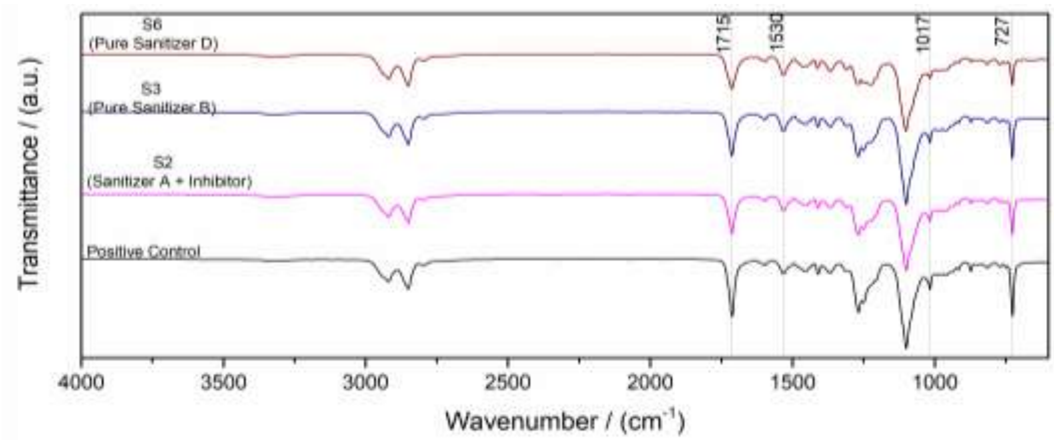

Figure 4: FTIR spectra for Positive Control (black inner polymeric layer not immersed), S2 (immersed Sanitizer A + Inhibitor), S3 (immersed Pure Sanitizer B), and S6 (immersed Pure Sanitizer D).

When compared with the positive control (sample of the black inner polymeric layer), samples S2, S3 and S6 showed a decrease in peak intensity at 1715 cm^{-1}, which may be associated to the hydrolyzed carbonyl group of ester bonds in in the urethane group, as also observed by Mathur and Prasad (2012), [(2)] and Kay, McCabe, and Morton (1993)[(4)].

Shifts of N-H bands to higher (at 1530 cm^{-1}) and lower (at 727 cm^{-1}) intensity may be associated with dissociation and an increase in the number of hydrogen bonds, respectively. Such behavior can be attributed to the structural modifications during the immersion time due oxidation process, as also presented in the studies of Brzeska et al. (2021)[(5)]. On the other hand, the intensity peak reduction observed in 1017 cm^{-1} may be attributed to the oxidation process of the ether bonds, resulting in chain scission, as observed by Stachelek et al. (2010)[(6)].

CONCLUSIONS

The SEM micrographs show the presence of two layers in the polymer which coats the endoscope tubes. The outer polymeric layer is mainly constituted of polyurethane (PU) as observed by FTIR analysis, while the inner black layer is constituted by a mixture of polyurethane (PU) and polyamide (PA). Disinfectants S3 (pure sanitizer B), and S2 (sanitizer A + inhibitor) presented low pH values and high values of disinfectant solution absorption, which leads to changes in the mechanical properties of the swollen polyurethane. Although S6 is not the more acidic sanitizer, it showed the second faster absorption in the first 4 weeks of immersion and a visual mechanical degradation by cracks on polymeric outer surface of endoscope, which was confirmed by SEM images. Chemical degradation was characterized by FTIR-ATR analysis on the black inner polymeric layer by hydrolyses of the carbonyl group of ester bonds and oxidation of the ether bonds.

ACKNOWLEDGEMENTS

This work was supported by CAPES scholarship – Brazil [Coordination for the Improvement of Higher Education Personnel (grants numbers: 88887.507764/2020-00 and 88887.680349/2022-00)] and by CNPq – Brazil [National Council of Technological and Scientific Development (grant number: 310504/2020-1)]. Authors are especially grateful to the Service of Clinical Engineering and Endoscopy Service of Hospital das Clínicas of University of São Paulo (HC, USP) for the samples of sanitizing solutions and endoscopes.

REFERENCES

1. MOHAMED, H. A.; BADRAN, B. M.; RABIE, A. M.; MORSI, S. M. M. Synthesis and characterization of aqueous (polyurethane/aromatic polyamide sulfone) copolymer dispersions from castor oil. Progress in Organic Coatings, v. 77, p. 965-974, 2014.
2. MATHUR, G.; PRASAD, R. Degradation of Polyurethane by *Aspergillus flavus* (ITCC 6051) Isolated from Soil. Appl Biochem Biotechnol, v. 167, p. 1595-1602, 2012.
3. SILVERSTEIN, R. M.; WEBSTER, F. X.; KIEMLE, D. J. Spectrometric identification of organic compounds. John Wiley & Sons, 7th Ed., Hoboken, NJ, 502, p., 2005.
4. KAY, M. J.; MCCABE, R. W.; MORTON, L. H. G. Chemical and physical changes occurring in polyester polyurethane during biodegradation. International Biodeterioration & Biodegradation, v. 31, p. 209-225, 1993.
5. BRZESKA, J.; TERCJAK, A.; SIKORSKA, W.; MENDREK, B.; KOWALCZUK, M.; RUTKOWSKA, M. Degradability of polyurethanes and their blends with polylactide, chitosan and starch. Polymers, v. 13, n. 8, 2021.
6. STACHELEK, S. J.; ALFERIEV, I.; UEDA, M.; ECKELS, E. C.; GLEASON, K. T.; LEVY, R. J. Prevention of polyurethane oxidative degradation with phenolic antioxidants covalently attached to the hard segments: Structure–function relationships. Journal of Biomedical Materials Research: Part A, v. 94A, n. 3, p. 751-759, 2010.
7. JOSEPH, J.; PATEL, R.M.; WENHAM, A.; SMITH, J.R. Biomedical applications of polyurethane materials and coatings. Transactions of the IMF., v. 96, n. 3, p. 121-129, 2018.
8. SASTRI, V.R. Engineering Thermoplastics: Acrylics, Polycarbonates, Polyurethanes, Polyacetals, Polyesters, and Polyamides. In: SASTRI, V.R. Plastics in Medical Devices. Properties, Requirements, and Applications. Pennsylvania, FluoroConsultants Group, 3rd. ed, 2021. cap. 6, p. 167-232.
9. IUPAC - International Union of Pure and Applied Chemistry. Compendium of Chemical Terminology. United States, 2019. Available in: http://goldbook.iupac.org/S06202.html. Accessed on 19 August 2022.
10. KAMPF, G.; FLISS, P.M.; MARTINY, H. Is peracetic acid suitable for the cleaning step of reprocessing flexible endoscopes?. World Journal of Gastrointestinal Endoscopy, v. 6, n.9, p. 390-406, 2014.