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DETERMINATION OF LIQUID DETERGENT PODS AS A POTENTIAL MICROPLASTIC SOURCE

Karolina Gwizdała[1], ✉, Paweł Szarlej[1], Przemysław Gnatowski[1], Edyta Piłat[1], Maciej Sienkiewicz[1], Justyna Kucińska-Lipka[1]

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Abstract. Washing pods became a popular way to add detergent to washing machines. Despite the claims about the degradability of the pod film, the sludge in pipes can be observed after the usage of such pods. This study focused on a quantitative and qualitative analysis of washing pod films as a source of microplastic.

Keywords: microplastic, polyvinyl alcohol, liquid detergent pods.

1. Introduction

Microplastic represents one of the most significant pollutants on our planet. Over the years, the pollution associated with microplastic has steadily increased. The global production of plastics in 2018 was 359 Mt, while in 2019 it was 368 Mt, and in 2020 it was 367 Mt. It can be noted that in 2020 there was a decrease in the production of plastics; the reason was the fall in demand due to the COVID-19 crisis. On the other hand, in Europe, there was also a decrease in the production of plastics by 9.4 Mt in three years (2017 – 64.4 Mt, 2020 – 55 Mt) due to the restrictions imposed by the European Commission.[1-3]

Due to improper storage/recycling of plastic waste, plastics are prone to fragmentation and degradation when exposed to weather conditions (wind, sunlight, rain, etc.), which contributes to the formation of smaller plastic fragments called microplastics. Microplastics are a threat to our planet and living beings because, compared to plastics, we cannot see them with the naked eye due to their microsize.[4]

The definition of microplastic (MP) is not fully defined. In 2017, the European Union Commission (EU Commission) defined microplastics as: "synthetic water-insoluble polymers of 5 mm or less in any dimension". Subsequently, this definition was further clarified by the European Chemicals Agency (ECHA) at the request of the EU Commission: "microplastic" means a material consisting of solid polymer containing particles, to which additives or the substances may have been added, and where ≥ 1 % w/w of particles have (i) all dimensions $1\text{nm} \leq x \leq \leq 5$ mm, or (ii), for fibers, a length of $3\text{nm} \leq x \leq \leq 15$ mm and length to diameter ratio of > 3". The definition does not apply to: "polymers that are (bio)degradable".[5] This study evaluated microplastics from commonly used household products such as laundry capsules.

The coating material of the laundry pod is made of a water-soluble film. It is generally based on polyvinyl alcohol (PVA), the modified backbone of which may contain additives to improve its properties. The films are formulated to dissolve easily during the washing process, including cold water cycles. The solubility of PVA in water is strongly related to the degree of hydrolysis, which is also known as the degree of saponification of polyvinyl acetate during the reaction. The resulting PVA is completely hydrolyzed when all acetate groups are converted to hydroxyl groups. On the other hand, if a certain proportion of acetate groups is allowed to remain, then partially hydrolyzed PVA is obtained. In addition, partially hydrolyzed PVA has higher water solubility than completely hydrolyzed PVA.[6-9]

PVA used in liquid detergent pods (LDPs) is formed by partially hydrolyzed polyvinyl acetate, and partially by acetylated PVA (Fig. 1) obtained during hydrolysis of polyvinyl acetate. The solubility of PVA in water depends on its degree of hydrolysis (DH) and its degree of polymerization (DP).[6]

This study aims to quantitatively and qualitatively evaluate microplastics from commonly used household products such as laundry capsules. Microplastic samples were collected from laundry capsules of leading brands in the market and discount brands dissolved in water at a washing temperature of 313 K. Quantitative analysis of the collected microplastic samples and qualitative analysis of the laundry capsules will be performed using optical microscopy, Fourier transform infrared spectroscopy techniques, and by determination of mass change.

[1] Department of Polymer Technology, Faculty of Chemistry, Gdansk University of Technology,
11/12 Narutowicza St., Gdansk, 80-233, Poland
✉ *s159821@student.pg.edu.pl*
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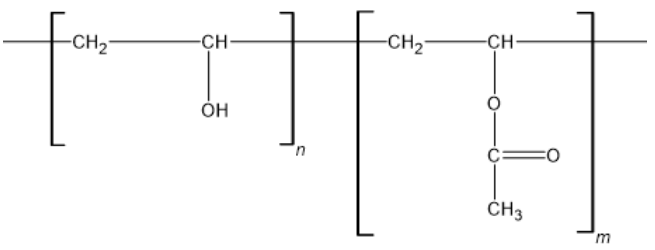

Fig. 1. Structure of PVA formed by partial hydrolysis of polyvinyl acetate

2. Experimental

2.1. Materials

Three types of liquid detergent pods film of different brands, such as Vizir (V), Persil (P), and Formil (F), were studied. The pods were first cut, and the liquid was mechanically removed. To remove the residues of detergents from the inside of the pod, the surface was wiped with acetone.

2.2. Determination of Mass Change

The mass change was determined by the difference between the film mass and dry mas change (Eq. 1). Film mass was measured, and then dissolved in 500 mL of tap or distilled water at 313 K. Dry mass was determined by evaporating 50 mL of the obtained test solutions in a Petri dish at 353 K for 8 h, and then left overnight at room temperature for 12 h to dry completely. The dish was weighed on an analytical balance before and after evaporation during the examination.

$$bridge\Delta m = \frac{(m_1 - m_0)}{m_0} 100\,\%, \qquad (1)$$

where m_0 is the mass of the LDPs film, and m_1 is the dry mass of evaporated test solution.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy method has been used to perform structural analysis of LDPs film and samples of dissolved LDPs film in distilled water. The FTIR analysis was performed using a Bruker Tensor 27 Spectrometer in a spectral range from 4000 to 500 cm^{-1}, averaging 128 scans with a resolution of 4 cm^{-1}.

Hydroxyl group correlation was calculated from the ratio of the area under the curve for the O-H band at ν=3300 cm^{-1} and the C-H bending vibration at δ=1450 cm^{-1}, which remained almost constant. Acetyl bridges correlation was calculated from the ratio of the area under the curve for the C-H band at ν=1710 cm^{-1} and bending vibration related to CH_2 groups at δ=1450 cm^{-1}, which remained almost constant.[10] The correlation plots were made for the LDPs film and the dissolved LDPs film in distilled water.

2.4. Optical Microscopy

Optical microscopy has been used to analyze the morphology of samples obtained after dissolving the LDPs film in distilled water and collecting water samples during the washing machine cycle. The study has been performed using a Delta Optical MET-1000-TRF microscope, a Sony imx183 microscope camera, and dedicated software Toup View.

Images have been taken using the overexposure method in the dark field and the reflection mode.

3. Results and Discussion

3.1. Determination of Mass Change

The mass measurements and results calculated for mass change for the three samples examined are shown in Table 1. Mass change measurements have been performed for the LDPs film samples dissolved in tap water and distilled water.

Table 1. Mass measurement and result of mass change

Sample	Mass of the LDPs film [g]	Dry mass [g]	Mass change [%]
Dissolution of the LDPs film in tap water			
V	0.577	0.748	+ 29.64 ± 4.72
P	0.608	0.747	+ 22.86 ± 5.78
F	1.069	1.077	+ 0.75 ± 1.07
Dissolution of the LDPs film in distilled water			
V	0.682	0.575	- 15.69 ± 5.43
P	0.681	0.605	- 11.16 ± 4.02
F	1.091	0.868	- 20.44 ± 4.92

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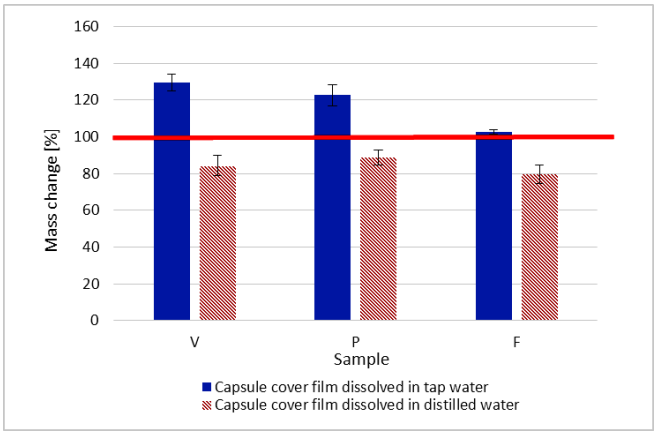

Fig. 2. Comparison of the mass change of LPDs film dissolved in tap and distilled water

The results of the mass change of the LDPs film dissolved in tap water and distilled water, along with the standard deviation, are presented as a bar graph in Fig. 2.

In Fig. 2 the bold vertical line indicates the initial mass of the LDPs film (100 %) before dissolution in tap/distilled water. Analysis of Fig. 2 and Table 1 reveals an increase in the weight of the samples when dissolving them in tap water. The mass change of the capsule film sample after dissolution in tap water is greater by 29 % for material V, by 22 % for material P, and by 2 % for material F than the mass of the capsule film before dissolution. This is due to the presence of mineral salts in the tap water, which crystallized during the evaporation of the sample.

On the other hand, in the case of dissolving the sample in distilled water, it is possible to notice a loss of mass by 15 % for material V, 11 % for material P, and 20 % for material F, then the mass of the film itself. This is due to the absence of mineral salts in the distilled water and the possibility of partial degradation of the capsule film under the influence of water.

It should also be noted that sample F has the highest percentage of capsule film weight to whole capsule weight and is 4.25 %. While the capsule film of sample P is 3.8 %, and the capsule film of sample V is 2.6 % of the whole capsule weight. This means that capsule F has the highest PVA content.

In contrast, capsule V's cover film has better solubility than the cover film of capsules P and F, which may be due to the different chemical compositions of the LDPs film used to make the material.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR analysis examined the V, P, and F material film and solutions of the dissolved film in distilled water (V distill., P distill, and F distill.). Fig. 3 shows the obtained spectra of the tested material for samples V, P, and F, respectively. The FTIR characteristic bands for PVA film were summarized in Table 2.

Table 2. The FTIR characteristic bands for PVA films

Assignment	Vibration type	Wavenumber as per reference[11]
O-H stretching	υO-H	3340
CH_2 stretching	υC-H	2942
C=O carbonyl stretching	υC=O	1690
CH_2 bending	δC-H	1430
C-H deformation	γC-H	1324
C-O stretching	υC-O	1081
C-C stretching	υC-C	839

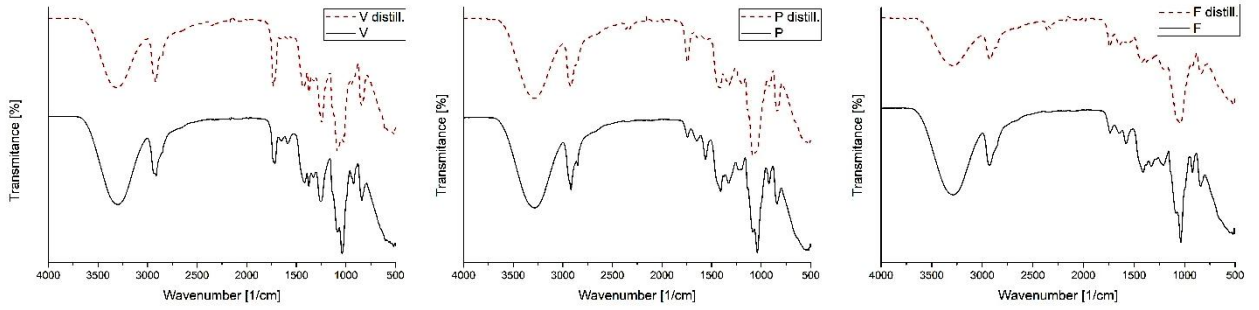

Fig. 3. FTIR spectrum for the studied materials (from left: V, P, and F)

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All LDPs films exhibited (Fig. 3, lines) a broad band in the range of 3600–3000 cm^{-1}, which could be addressed to the stretching vibrations from the hydroxyl group. Another maximum, observed at ~2900 cm^{-1}, originates from stretching vibrations, symmetric and asymmetric of the -CH group. The strong signal at ~1740 cm^{-1} can be attributed to the stretching vibrations of the C-O bond in the ester group. On the other hand, the signal at ~1250 cm^{-1} could be addressed to the deformation vibrations of the hydroxyl group. The doublet seen in the range of 1100–1080 cm^{-1} was probably coming from the stretching vibration of the C-O, characteristic of alcohols.[11]

The FTIR spectrums for the films dissolved in distilled water (Fig. 3, dotted lines) showed a very similar course to the original films. Signals originating from stretching vibrations of hydroxyl, alkyl, and ester groups were present. However, in the case of ester groups (~1740 cm^{-1}), the intensity of the signals was much higher than in the case of the film, while for the hydroxyl vibrations (3600–3000 cm^{-1}), the signals were lower than for the LDPs film itself. Based on FITR spectra analysis, it can be concluded that all of the films of washing pods were probably based on polyvinyl alcohol (PVA). However, based on the differences between the spectra, it can be determined that some other material was used to modify the PVA structure.

The relationship between the studied material type and the hydroxyl group concentration is represented in Fig. 4. The dissolution of the LDPs film resulted in a reduction of the total number of available hydroxyl groups. This can be seen in the case of material V, which decreased its amount of hydroxyl groups by more than 50 % in the sample dissolved in distilled water. In contrast, dissolving the P and V material in distilled water also reduced the number of available hydroxyl groups, but to a greater extent in comparison to the V material. It can be seen that the film of washing capsule V had the most hydroxyl groups in its structure, followed by film F, and film P was characterized by the least number of hydroxyl groups in its structure.

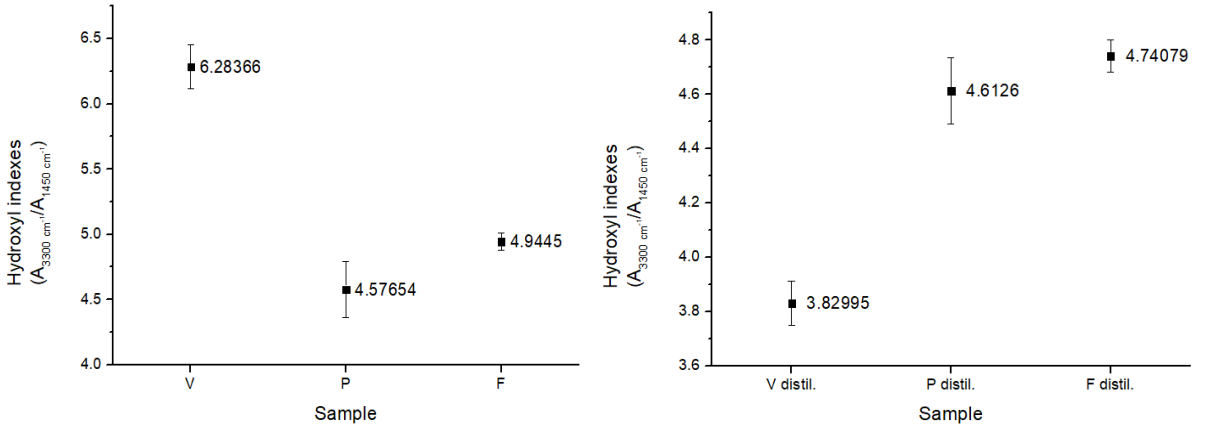

Fig. 4. The correlation between the type of studied material and the hydroxyl index ($A_{3300\ cm^{-1}}$ / $A_{1450\ cm^{-1}}$) for LDPs film and dissolved LDPs film in distilled water, respectively

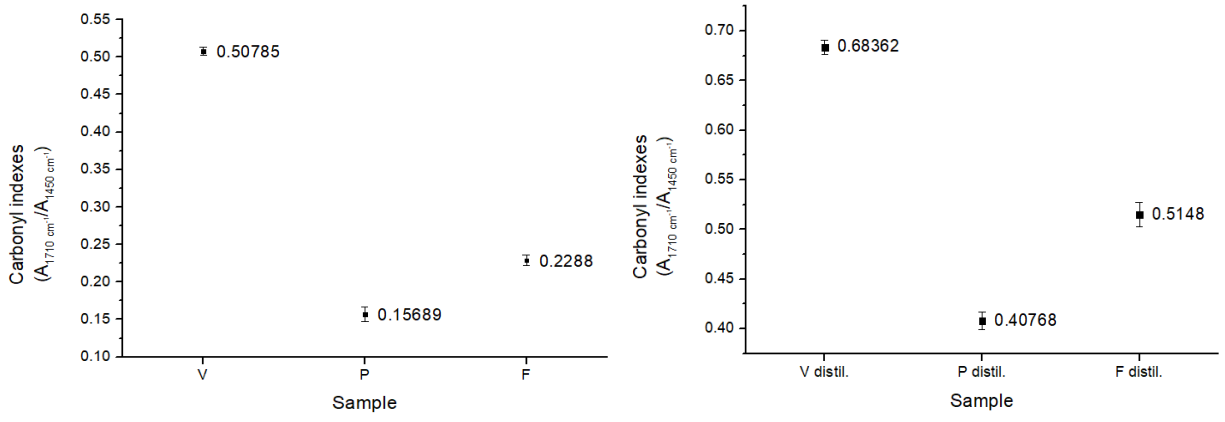

Fig. 5. The correlation between the type of studied material and the carbonyl index ($A_{1710\ cm^{-1}}$ / $A_{1450\ cm^{-1}}$) for LDPs film and dissolved LDPs film in distilled water, respectively

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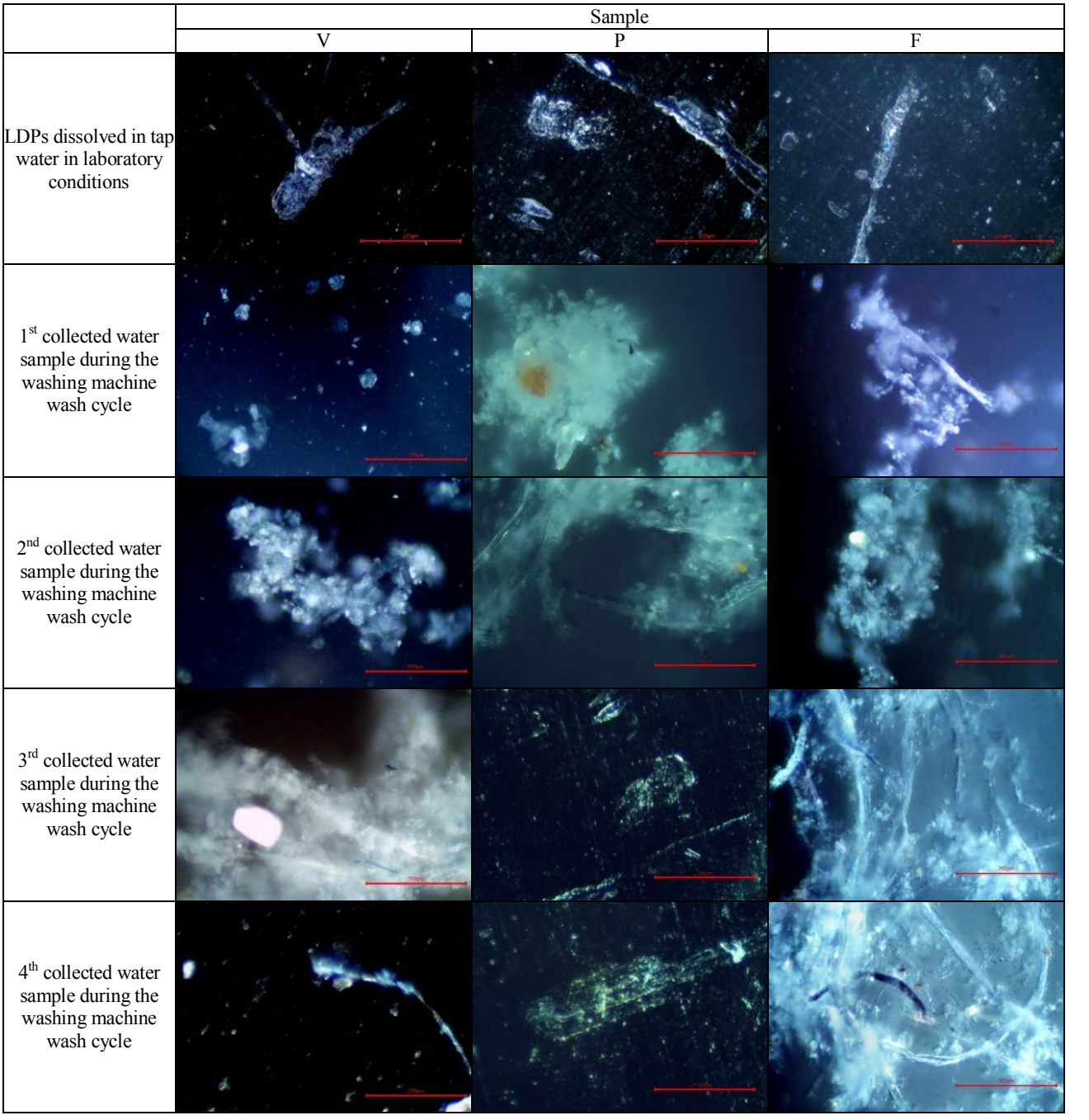

Fig. 6. Optical microscope images of a droplet of material V, P, and F (mag. x20)

The relationship between the type of studied material and the concentration of acetyl bridges is represented in Fig. 5. The film V had the most acetyl bridges but significantly fewer than the hydroxyl groups (0.5 *vs*. 6.2). The film of material P had the least amount of acetyl bridges. The number of acetyl bridges increased in all the examined materials, which were dissolved in distilled water.

3.3. Optical Microscopy

Fig. 6 shows images of droplets of the studied material both for samples obtained during laboratory tests (whole capsule dissolved in tap water) and for four water samples taken during a washing machine cycle.For the droplet images of solutions obtained in the laboratory, individual large and medium agglomerations can be observed,

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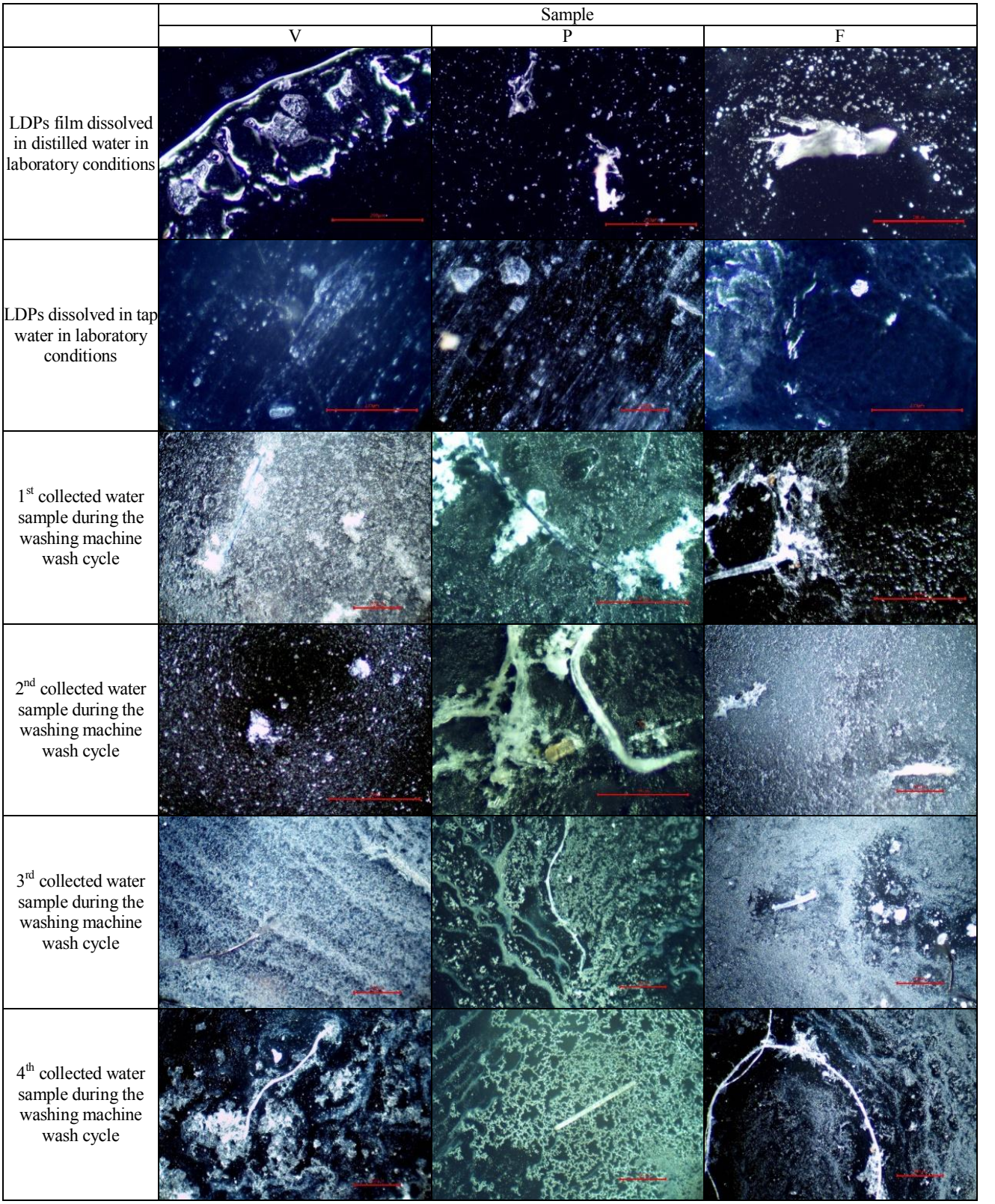

Fig. 7. Optical microscope images for and evaporated droplets of material V, P, and F (mag. x10, x20)

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which may be formed due to the incompletely dissolved film of the test material in combination with detergent residues. The dark field also allows us to see tiny particles that reflect light, which may indicate the presence of mineral salts in the tap water.

For the images of the four samples of water taken during the washing cycle, it is possible to see agglomerations but also fibers and colored dots that may come from the washed clothes. During the washing process, the hydrophobic ion tails of detergents penetrate the dirt particles and then begin to form micelles around them. Stirring and rubbing the fabric helps detach the dirt particles from the fabric and close the resulting micelles. As the dirt particles break away, individual fibers may also break away. Therefore, the agglomerations observed for the samples collected during the washing machine wash cycle may be formed from detergents, dirt, and fibers with micelles.

Fig. 7 shows images of evaporated droplets of the sample of LDPs film dissolved in distilled water, and the sample of LDPs dissolved in tap water in laboratory conditions for 4 water samples collected during a washing machine cycle.

Analysis of the images of LDPs film dissolved in distilled water shows that the most residual material accumulates at the edge of the droplet, as seen in the photo for material V. The images for materials P and F show the formation of agglomerations, which may be a residue from the incomplete dissolution of the LDPs film or contamination from outside.

On the other hand, by analyzing images of evaporated droplets coming from the solution of LDPs dissolved in the tap water we can observe the formation of single larger agglomerations, which may be incompletely dissolved capsules or detergents forming micelles. Also, small agglomerates can be seen, which could represent mineral salts found in tap water.

For the photos of the evaporated droplet from four samples of water collected during the washing machine cycle, larger agglomerations can also be observed, similarly for the evaporated droplet from the solutions obtained during laboratory studies. The main difference between these images is the presence of clothing-derived fibers in the evaporated droplet images from the four samples taken during the wash cycle. Larger agglomerations may be formed due to micelle formation by detergents. The smaller agglomerations probably originate from mineral salts found in tap water.

4. Conclusions

Laundry detergent pods are currently the most popular form of adding detergent to laundry. The LDPs contain a surfactant to help remove dirt and various additives such as perfumes or active optical agents. On the other hand, the capsules cover film is probably made of polyvinyl alcohol. Despite claims of degradability of the films by the manufacturers, sediment can be observed in the pipes after usage of such pods, resulting in the formation of microplastics, which later enter the environment. For this reason, this work focuses on the study of laundry capsule film as a potential source of microplastics.

The research conducted in this study confirmed that the studied laundry capsule films were not entirely soluble in water. By determining the mass change content, it can be concluded that after the dissolution of the capsule film during the wash cycle, the residues of the PVA-based film remain in the water along with mineral salts. It gives a solid base ground for further research on assessing washing pods as the potential microplastic source, as their biodegradability for a prolonged time has to be estimated.

FTIR analysis determined that the laundry capsule films were not identical and may differ in structure. These differences may be due to the modification of the PVA structure and the content of acetyl and hydroxyl groups. Sample P, which had the lowest number of both hydroxyl groups and acetyl bridges, had the lowest mass loss among tested samples. It gives proof that modifications of PVA structure by producers of washing pods have an impact on their degradability in water.

Analyzing the images taken by an optical microscope, agglomeration formation can be observed. Agglomerations can be formed due to contamination from outside and by the incomplete dissolution of the layer covering the laundry capsules. By analyzing samples taken during the wash cycle, agglomerations can also be observed forming around fibers from clothes. In this case, the agglomerations may form as a result of micelle formation by detergents.

Based on the results, it is clear that detergent pods can be a potential source of microplastics, and they are probably one of the worst ways to add detergent to washing machines.

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ВИЗНАЧЕННЯ КАПСУЛ ДЛЯ РІДКИХ ПРАЛЬНИХ ЗАСОБІВ ЯК ПОТЕНЦІЙНОГО ДЖЕРЕЛА МІКРОПЛАСТИКУ

Анотація. *Капсули для прання стали популярним способом додавання детергенту в пральні машини. Незважаючи на твердження про деградабельність плівки капсули, після використання таких капсул у трубах можна спостерігати осад. Метою цього дослідження був кількісний і якісний аналіз плівок капсул для прання як джерела мікропластику.*

Ключові слова: *мікропластик, полівініловий спирт, капсули для рідких пральних засобів.*

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