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THE INFLUENCE OF ARTIFICIAL AGING ON RECYCLABILITY AND MECHANICAL STABILITY OF PHARMACEUTICAL PACKAGING

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Abstract: *Recycling of wastepaper and packaging is one of the most desirable options for the purpose of preservation the environment and increasing the sustainability of production. Changes in customer behaviour have increased a demand for packaging materials, such as the growth of online shopping and/or demand for optimal sized packaging foods and medicines. During storage and transport, products can be exposed to different weather conditions, which ultimately affects their quality and disposal. Therefore, in this paper, the influence of moisture and temperature on the mechanical properties of pharmaceutical packaging as well as on the possibility of their recycling was investigated. The printed and formed pharmaceutical packaging was subjected to a process of accelerated aging in a chamber under the action of temperature and humidity, according to standard methods and defined conditions. Thereafter, the samples were subjected to mechanical testing to determine the effect of moisture on the mechanical properties. In addition, the impact of moisture on pharmaceutical packaging recycling performance was examined. Recycling was carried out in laboratory conditions by chemical deinking flotation according to the INGEDE 11 method, while the obtained recycled laboratory sheets were characterized by the determination of optical properties and the image analysis. It was found that the mechanical properties of the tested pharmaceutical packaging were deteriorated. From the results obtained by determination of the optical properties, in recycled samples the brightness decreases with aging. As the sample ages, the printing ink binds to the recycled fibres, so the ERIC is lower in recycled fibres obtained from non-aged samples compared to the old ones. The CIE coefficient b* is higher for samples obtained from recycling of aged pharmaceutical packaging than for samples obtained from recycling of non-aged samples, and aged recycled samples will be yellower than non-aged ones. Therefore, the whiteness is lower in recycled fibres obtained from aged samples. When measuring the image analysis, the obtained results show that the number of ink particles and their surface area are significantly reduced with the duration of aging time.*

Key words: pharmaceutical packaging, artificial aging, recycling, mechanical properties

1. INTRODUCTION

The changes in costumers' behaviour have increased the demand for packaging materials (Holik, 2013). The global increase of production and consumption of different packaging materials resulted in higher environmental loads and waste generation. In order to reduce the overall environmental impact of packaging, in the last decade, the trend of developing sustainable packaging has been growing. Sustainable packaging as defined in research by Steenis et al, (2017) is a packaging that has a comparatively low environmental impact as assessed by life-cycle assessment. Sustainable packaging should be composed of non-toxic materials, most preferably made of natural renewable materials. When it comes to its end of life, it should be recyclable, reusable, biodegradable or compostable. From a consumer-perspective, there are different definitions of sustainable packaging. Nguyen et al, (2020) reported that consumers definition of sustainable packaging is more related to packaging materials (biodegradability and recyclability), and market appeal (attractive graphic design and good price), while Steenis et al, (2017) gave a definition of "a packaging design that evokes explicitly or implicitly the eco-friendliness of the packaging". Packaging design involves a combination of structural and graphical and verbal elements. In that case, the materials are being structural elements with and the main contributor to direct (objective) environmental impacts. Graphical and verbal elements are informational and both may be used to signal sustainability. Verbal features can be used to communicate sustainability explicitly, (e.g. through labelling), while green colouring communicate sustainability implicitly (Steenis et al, 2017). When talking about market appeal, consumers expectations about eco-friendly packaging are related to attractive graphic design, functional performance, and price (Nguyen et al, 2020). According to Tamani et al, (2015) when designing a new packaging products, the packaging industry limitations (the scalability of production process, the row material availability, etc.), the end of life waste packaging management regulation and legislation (related to biodegradability, recyclability, incineration, etc.) and consumer

preferences (transparent packaging, environment-friendly packaging, no extra-cost due to packaging, etc.) should be taken into account.
When it comes to pharmaceutical packaging, the type of packaging affects the emission generated during packaging of medicines and their release to the environment. For example, (Raju et al, 2016) investigated the LCA of two packaging systems in accordance to the CML 2001 impact assessment method and reported that the environmental performance of PVC blister packaging is better than the aluminium blister packaging.
Due to a significant share of plastic packaging in the overall volume of municipal solid waste, different concerns have led to an increased demand for use of biodegradable and renewable light-weight materials for sustainable packaging applications.
The higher use of packaging nowadays has resulted in the higher share of paper based packaging products in the waste stream collection system compared to that of graphic products (Runte et al, 2015). According to CEPI (Confederation of European Paper Industries), defined targets for the recycling of paper-based packaging are 75% by 2025 and 85% by 2030. CEPI suggested a list of recommendations for the improvement of the recyclability of paper packaging products in the paper recycling process (CEPI, 2019). The most important parameters for the good recyclability of paper-based packaging products are repulpability, yield of fibrous material, coarse reject, flake content, stickies, and technical quality. According to the guideline, a design phase should consider the intended purpose and end-of-life stage of the packaging to optimise the recycling of paper packaging, i.e. the producers should take into account the quantity of non-paper constituents, the use of recycled alternative fibres, the use of adhesives, chemicals, coatings and varnishes. When it comes to use of printing inks in packaging, the quantity of used ink should be optimised. The used inks should also be free of mineral oils and with the minimal share of metallic components in the ink formulation. When it is possible, deinkable printing technology when producing packaging from bleached paper and board should be considered (CEPI, 2019). With the appropriate collection and sorting, all paper packaging can be recycled. The increased amount of collected paper resulted in a reduction of the quality of the paper for recycling (Runte et al, 2015). Iosip et al, (2012) showed in their research the importance of selective collection of paper and board and their advanced sorting technologies implementation and their influence on the quality of recovered paper grades supplied to paper mills. Additionally, they showed that utilization of recovered paper batches with a low quality, contributes to an increased environmental impact due to increased energy consumption and higher volumes of generated waste, resulting in higher emissions released into the air and water.
Deinking is of major importance in the production of graphic papers due to the high demand of optical properties of the finished products but it is also becoming of interest in packaging grades, due to the growing tendency of printing some packaging products (Blanco et al, 2013). Deinking is the most important step in the paper recycling process. It depends upon the quality of the collected paper for recycling, the type of printing process and the properties of the printing inks, the age of the product and climatic conditions (light, temperature, moisture and storage time) during its life cycle (Faul, 2010; Kemppainen et al, 2013; Kemppainen et al, 2015; Vukoje and Rožić, 2018). In deinking process, the printing ink and other contaminants must be removed from the recycling mixtures (Kemppainen et al, 2015). The most common deinking process is flotation, where air bubbles are used for collection of hydrophobic ink particles and their removal in the sludge rejects as subsequently formed froth.
The studies conducted up to now, have mainly studied the influence of climatic conditions on the recycling efficiency of the offset prints on newsprint and graphic papers. The research by Kemppainen et al, (2015) showed that deinkability of old or thermally aged ink from offset-printed papers is difficult due to chemical and/or physical interactions, fragmentation during the repulping process (higher amounts of free microscopic ink particles, visible dirt specks, and inky fibres) and formation of strong agglomerates with fibres, which results in flaky pulp suspension. According to Kemppainen et al, (2015) ink particles strongly bound to fibres due to oxidative polymerization reactions that occur at accelerated rates and at a magnifying effect with unsaturated offset ink components, such as vegetable oils and/or alkyd resins.
Given that the effect of moisture and temperature on the process of paper recycling was mainly the topic of the previous known research, the aim of this paper is to determine how humidity and temperature in accelerated aging test, affect the process of ink particles separation during recycling of packaging. Since moisture plays an important role in papers dimensional stability and physical strength (Kemppainen et al, 2013), the influence of temperature and humidity on pharmaceutical boxes physical strength was investigated as well.

2. METHODS

2.1. Materials

Previously formed and printed pharmaceutical boxes were used for this study. The boxes were printed by offset printing process.

2.2. Accelerated aging test

The samples were subjected to the accelerated aging test, i.e. they were exposed to elevated humidity and temperature. Samples were exposed to controlled conditions for 3, 6, and 9 days, at relative humidity of 40% and temperatures of 60˚C. The "Kottermann" air chamber Type 2306 was used in the experiment.

2.3. Flat Crush Test

After the aging simulation, the pharmaceutical packaging samples were subjected to the Flat Crush Test method, manufactured by Lorentzen & Wettre.

2.4. Recycling of the pharmaceutical boxes

Pharmaceutical packaging boxes (aged and non-aged) were recycled according to standard laboratory procedure defined in INGEDE method 11 (INGEDE e. V., 2012). Samples were disintegrated in Enrico Toniolo disintegratior while the flotation process was performed in the laboratory flotation cell. According to INGEDE method 1, a certain amount of pulp suspension was separated after disintegration process before flotation (BF) and after flotation process (F) to prepare laboratory sheets of 45 g/m^2, using automatic sheet-forming device Rapid-Köthen Sheet, PTI. The obtained laboratory handsheets from undeinked pulp (BF) and deinked pulp (F) were used for the evaluation of optical parameters.

2.5. Deinkability evaluation

The efficiency of deinking process was evaluated by determination of undeinked (BF) and deinked pulp (F) handsheets optical properties as well as the residual ink area. The residual ink (particle) area on handsheets was determined by image analysis and data processing, using Spec Scan 2000 (Apogee Systems Inc.). Undeinked (BF) and deinked pulp (F) handsheets were tested for their optical properties. All the measurements were carried out on Technydine Colour Touch 2 Spectrophotometer, according to standard methods: ISO Brightness (ISO 2470), CIE whiteness and colour components *L*a*b** (ISO 11475), ISO Opacity (ISO 2471) and ERIC.

3. RESULTS AND DISCUSSION

Figures 1-7 show the results of the optical properties of recycled fibres before and after conducted flotation process, depending on the aging days of the exposed samples in the climate chamber.

In the Figure 1 it can be seen that by increasing the aging time and with longer exposure of the samples to increased humidity and temperature, the ISO brightness of the obtained recycled handsheets is reduced. However, the ISO Brightness of the fibres obtained after flotation process is smaller compared to fibres obtained without flotation process. This can be explained by the loss of optical brighteners and fillers during flotation process. The loss of fillers can be conformed additionally by the reduction of opacity of deinked fibres during flotation process (Figure 2). The aging time in elevated humidity and temperature does not have a significant influence on the opacity of recycled fibres since the results do not differ significantly.

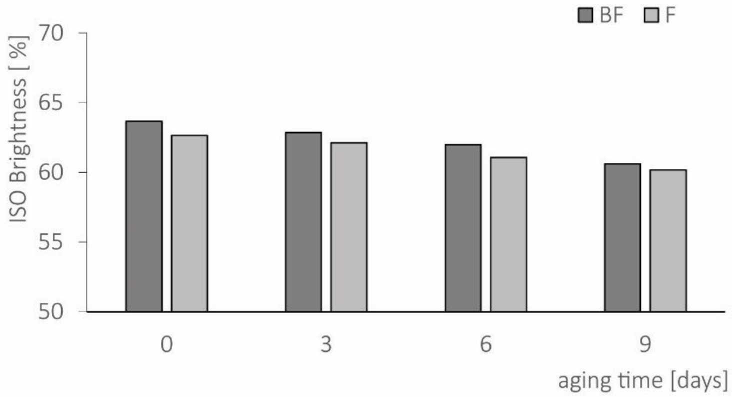

Figure 1: ISO Brightness of recycled fibres depending on aging time

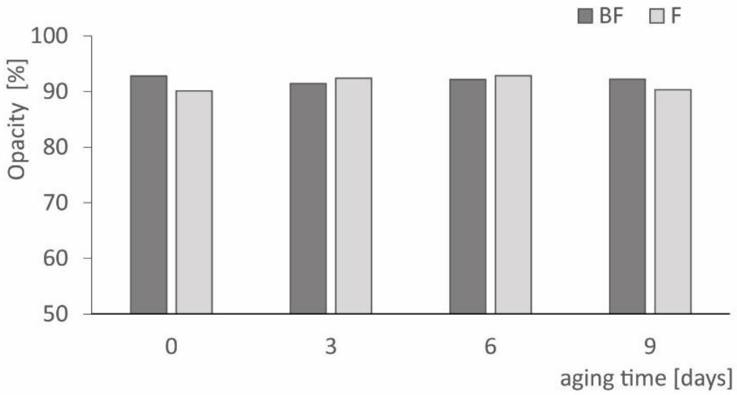

Figure 2: ISO opacity of recycled fibres depending on aging time

The ERIC method evaluates the residual ink by measuring the absorbed light in the infrared range, namely at 950 nm. At this wavelength, the ink absorbs significantly more radiation than paper, and the measurements are quite insensitive to the presence of lignin, dyes or other colorants (Pala et al, 2007). Figure 3 shows that the value of ERIC decreases after flotation process, because in the flotation process the printing ink is removed from the suspension altogether with collected flotation froth (foam). The highest percentage of removed ink particles is visible on the non-aged sample (approx. 38%), while in aged samples the percentage of ink particles removal is significantly lower compared to the non-aged sample (25% in 3 days, 31% in 6 days and 32% for 9 days). Moreover, these results explain the lower ISO brightness of the recycled handsheets obtained from aged samples (Figure 1). As the samples age, the ink film during disintegration breaks into the larger particles (Table 1). Additionally, the printing ink during aging binds to the recycled fibres, so the ERIC values of the aged samples (after the disintegration process) is slightly smaller compared to the ERIC value of the non-aged sample.

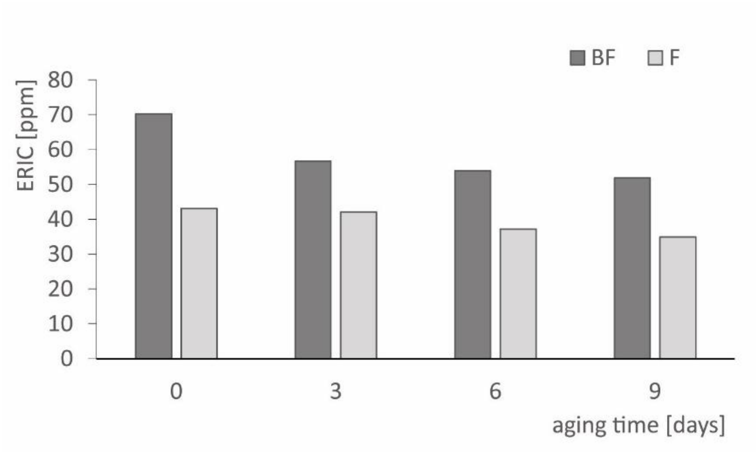

Figure 3: ERIC of recycled fibres depending on aging time

Figure 4a shows that the coefficient *L** is not affected by the influence of elevated humidity and temperature, i.e. the value of the coefficient *L** does not change significantly during aging time. Moreover, the value of the coefficient *L** does not change during deinking process, thus the obtained handsheets have the same values before and after flotation process. Figure 4b shows the values of the difference between the CIE *L** coefficient measured in conditions with and without UV-content of illumination. It can be seen from the results that the largest difference was obtained in all samples after flotation, very likely due to the loss of fillers (probably optical brighteners) during the flotation process.

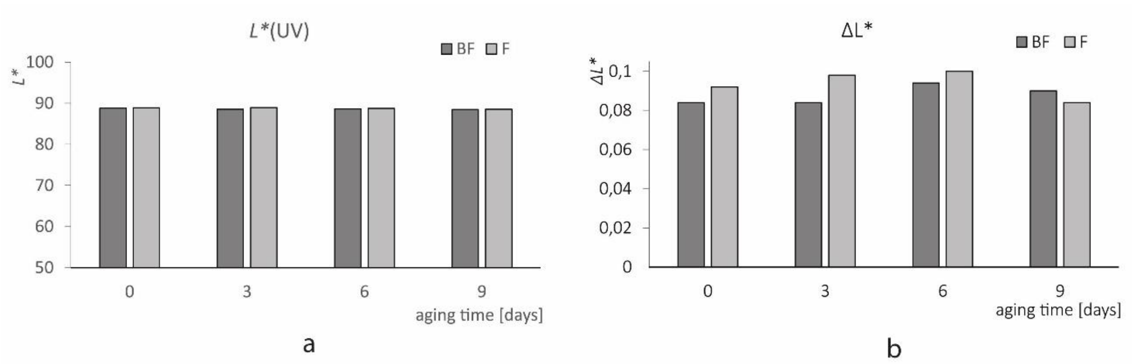

Figure 4: CIE Lightness (L) of recycled fibres depending upon the aging time; a) measured with UV-content of illumination, b) difference measured with and without UV-content of illumination*

The value of the CIE coefficient *a** (Figure 5a) before and after conducted deinking flotation process for samples made from aged boxes, varies considerably and their values differ significantly. In the case of samples made from non-aged boxes, the difference between measurements is also visible, and the result after deinking flotation is twice less than the result obtained before the flotation process. The results show that recycled samples of non-aged boxes and samples of aged boxes after 3 days have a shift to the green area, while recycled samples after aging of 6 and 9 days show a shift to the red area. From the results obtained for the value of *Δa** (the difference between the CIE *a** coefficient measured in conditions with and without UV-content of illumination) (Figure 5b) the largest differences obtained for aged samples, especially after 9 days of aging.

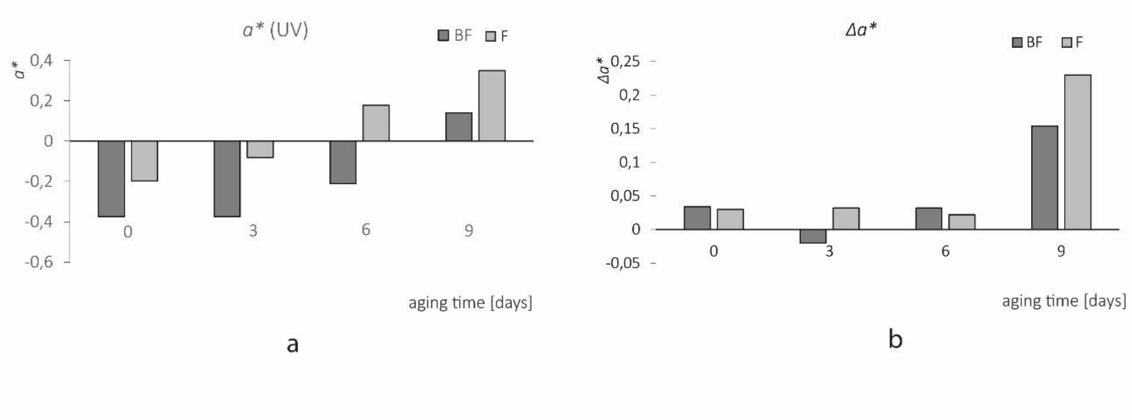

Figure 5: CIE a values of recycled fibres depending upon the aging time; a) measured with UV-content of illumination, b) difference measured with and without UV-content of illumination*

The values of the CIE coefficient *b** for samples made from aged boxes before and after the deinking flotation process have a more positive value than non-aged samples before and after deinking flotation (Figure 6a). This can be explained by the fact that the samples of laboratory sheets are darker after the aging process, i.e. they show a shift to the yellow area. It can also be seen that in all cases, the CIE coefficient *b** has a higher value after deinking flotation process. From the results obtained for the value of *Δb** (the difference between the CIE *b** coefficient measured in conditions with and without UV-content of illumination) (Figure 6b), it can be seen that the largest differences were obtained for aged samples, especially after 3 and 9 days of aging. The smallest difference in the *Δb** value is for samples obtained from non-aged boxes.

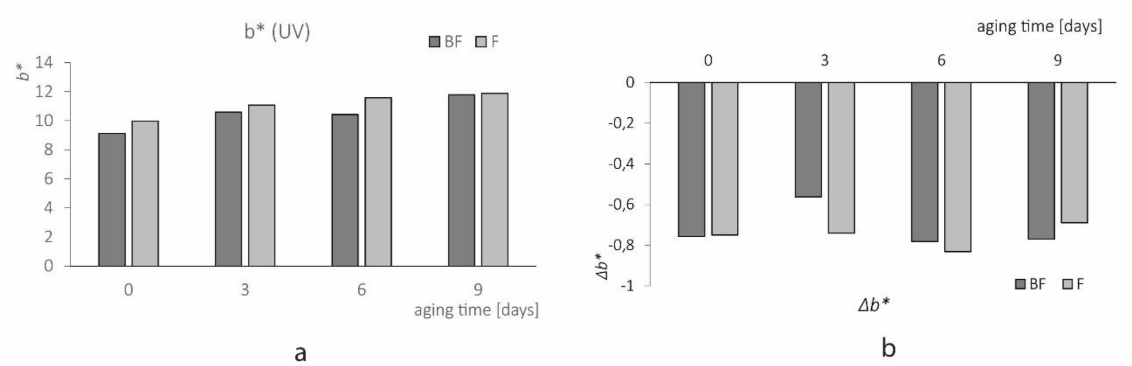

Figure 6: CIE b values of recycled fibres depending upon the aging time; a) measured with UV-content of illumination, b) difference measured with and without UV-content of illumination*

From the results shown in Figure 7a it can be seen that the whiteness value decreases after the deinking flotation process in all measured samples. Sample made from non-aged boxes has the highest whiteness value. The values of whiteness of the mentioned samples are not as high as when graphic paper grades are recycled, probably due to CIE coefficient *b*,* which increases with aging time. However, the obtained results are not so small, and thus it can be said that optical brightener is present in the paper, which loses its effectiveness as the aging process progresses. Figure 7b shows the difference values of whiteness measured with and without UV-content of illumination. Differences in measurement have quite high values, and it can be seen from the results that the differences in whiteness in non-aged boxes before and after the deinking flotation process are very similar. As the aging time (days of aging) increases, the difference of whiteness increases.

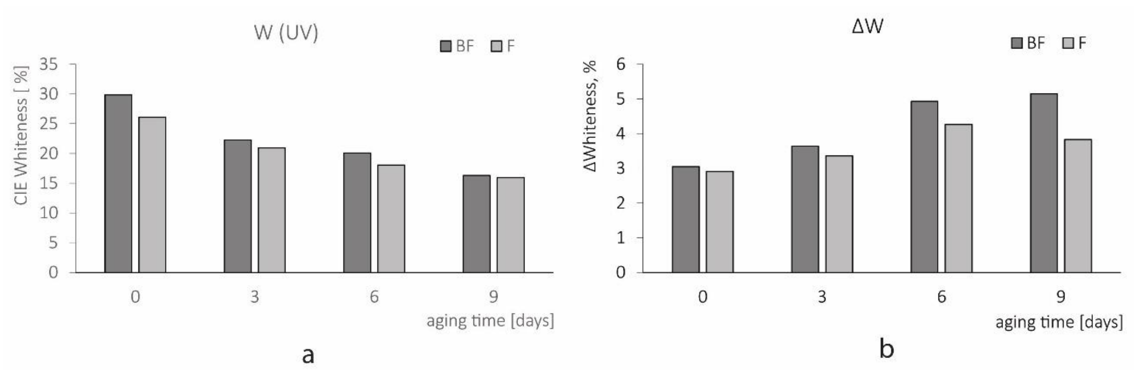

Figure 7: CIE Whiteness values of recycled fibres depending upon the aging time; a) measured with UV-content of illumination, b) difference measured with and without UV-content of illumination

Flat crush test is designed to measure the resistance of paperboard to flute crushing. The results are presented in the values of the force required for their crushing. From the results shown in Figure 8, it can be seen that bending force decreases over aging time, i.e. the bending force of non-aged box was 12.3 kPa, while the bending force of the 9-day-old box required a force of 11.87 kPa. Even though these values do not vary significant, the results may indicate that the mechanical properties of the boxes were slightly deteriorated by the influence of elevated humidity and temperature. The paperboard used for production of pharmaceutical boxes must be stable for a longer period of time, so it is assumed that the length of exposure time to elevated humidity and temperature of the samples should be increased in order to notice more significant changes in the mechanical properties of the boxes.

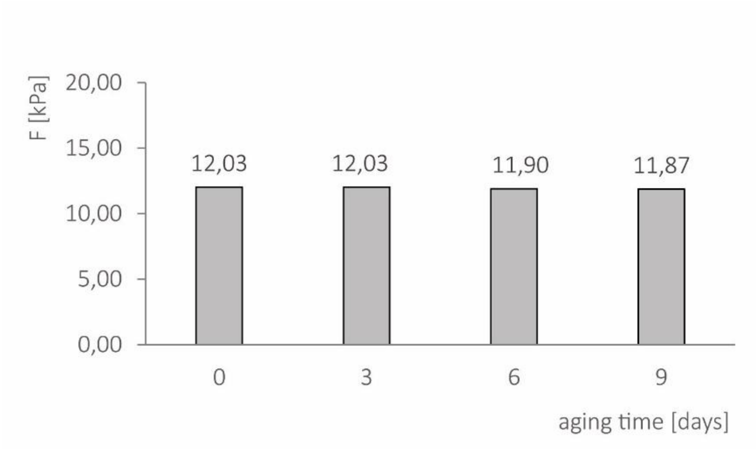

Figure 8: Flat Crush Test results

The results of the image analysis are presented in two size classes, i.e. ink particles smaller and larger than 0.04 mm^2 (Table 1). The results show the number of ink particles and their surface area. According to the obtained results, it can be concluded that the print on the packaging breaks into very small particles during disintegration process, mostly in the class of sizes smaller than 0.04 mm^2. In addition, it is seen that the total number of particles decreases with aging time. The number of particles decreases significantly after the flotation process in all samples, as well as their surface area. The results are in accordance with the ISO Brightness and ERIC values (Figures 1 and 3). Larger particles are clearly visible to the naked eye and manifest themselves as specks in the finished sheet. Particles smaller than 40 μm in size cannot be visible by the naked eye, but they contribute to a general greyness to the appearance of the paper (Thompson, 1998). As the aging process progresses, the number of larger particles and their surface increases.

Table 1: Image analysis results: The ink particle number and their area in size classes smaller and larger than 0.04 mm^2

aging time [days]	Smaller than 0,04 mm^2				Larger than 0,04 mm^2			
	Undeinked pulp (BF)		Deinked pulp (F)		Undeinked pulp (BF)		Deinked pulp (F)	
	No.	P [mm^2]	No.	P [mm^2]	No.	P [mm^2]	No.	P [mm^2]
0	577	4.59	272	2.10	7	0.36	6	0.52
3	676	6.22	362	3.55	18	1.01	16	1.09
6	378	3.05	242	3.41	8	0.47	5	0.60
9	388	3.00	246	2.25	8	0.53	8	0.68

4. CONCLUSIONS

Elevated humidity and temperature in the accelerated aging test affected the process of the printing ink separation from the surface of the printing substrate, i.e. cardboard during recycling, which resulted in production of recycled fibres with different optical properties compared to recycled fibres from the recycling process of boxes that were not exposed to aging test. The results showed that in recycled samples the ISO brightness decreases with aging.

The value of ERIC decreases after flotation process in all samples because the printing ink is separated in the process altogether with collected flotation froth. The largest percentage of removed ink particles is visible on the non-aged sample. As the sample ages, the printing ink binds to the recycled fibres, resulting in lower ERIC value of non-aged samples compared to the old ones. The CIE coefficient $b*$ is higher for samples obtained from recycling of aged boxes than for samples obtained from non-aged boxes, and it is clear that samples obtained by recycling of aged boxes will be yellower than non-aged ones. Therefore, the CIE whiteness is lower in laboratory paper sheets obtained by recycling of aged boxes. When measuring the image analysis, the obtained results show that the number of ink particles and their surface area are significantly reduced over aging time. Therefore, it can be assumed that by the occurrence of the aged paper based packaging material in the recycling plant would reduce the quality of the recycled fibre in terms of its optical characteristics, i.e. such material have lover brightness and whiteness values. Furthermore, it was found that the mechanical properties of the boxes were slightly deteriorated by the influence of elevated humidity and temperature, since there are insignificant differences in the values of the forces required for their bending. The bending force decreases over aging time, i.e. the bending force of non-aged box was 12.3 kPa, while the bending force of the 9-day-old box required a force of 11.87 kPa. Further research related to influence of elevated temperature and humidity in accelerated aging test on the recycling performance of pharmaceutical packaging, should be focused on the stickies potential in recycled fibres due to presence of adhesives in packaging.

5. ACKNOWLEDGMENTS

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