DEVELOPMENT OF MULTICOMPONENT FIBER BOX WITH IMPROVED FIRE RESISTANCE AND BARRIER PROPERTIES

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One of the main purposes of packaging materials is to protect the packed object from mechanical damage that can happen during transport, storage or handling. Extending the functionality of packaging from just mechanical protection to additional moisture and fire protection would present an added value to packaging materials and would be of high interest in preserving archives and cultural heritage objects.
In the present research work, we developed a pH neutral fibre material that provides a moisture barrier, inhibits burning and can be shaped into different packaging designs. A multilayer composite was developed, with the outer layers made from pH neutral acid-free paper, compatible with ISO 9706:2014 (the requirement for permanence) and ISO 11108:2016 (the requirement for permanence and durability). The produced pH neutral papers were coated (on the inside) with 6 different combinations of moisture barrier agents and fire-retardant coatings (containing styrene acrylic copolymer, hydrostatin, sodium silicate + aluminium hydroxide/carbonate and lignin), combined into a multilayer material. The developed materials were analysed in terms of their water vapour transmission rate, Cobb absorption and fire retardancy to simulate worst-case scenarios for archives or cultural heritage sites. The results showed that the material coated with the combination of styrene acrylic copolymer aqueous dispersion and mixtures of sodium silicate and aluminium hydroxide achieved the best performance in terms of moisture/fire resistance and could be successfully converted into packaging products for protecting museum objects.

Keywords: pH neutral paper, multilayer packaging, water vapour transmission rate, water absorption, fire resistance

INTRODUCTION

Packaging intended for protecting archival or cultural heritage (CH) objects needs to meet two main requirements: it should effectively protect the content against risk factors, such as humidity, moulds and fire, and be inert regarding its interaction with the protected object. Labels "acid-free", "conservation", and "archival" are used to characterize inert packaging materials that are suitable for storing CH products for long periods. For CH goods, there is a range of packaging materials to choose from, according to specific needs, but they have their own limitations. For example, while plastic materials have different advantages regarding humidity and water protection (in case of floods), there are several problems regarding migration and inertness. A study reported by POPART research[1] project showed that thirteen plastic samples emitted more than 200 different volatile organic compounds, and for some plastics, the potential for degradation products, such as acids and leached plasticizers, catalysing further degradation "must be very carefully tested and monitored". Other frequently used solutions are pH neutral papers and boards, which effectively protect the content from some environmental risk factors, but have downsides regarding others. Besides, one must remember that cellulose is by no means inert. Regrettably, the parameters stipulated by international standards may not always guarantee perfect paper durability.[2]

Applied and fundamental research on paper ageing and testing methods to determine paper stability are still in great demand.[3] Even though the subject has been widely researched, the relationship between natural and artificial ageing remains a source of contention, and this point is of critical concern to conservationists.[4] Zervos,[5] Strlič and Kolar[6] present and discuss the various features of natural and accelerated ageing of cellulose and paper in great detail. On the other hand, according to Jablonsky *et al.*,[7] the main problem is that when correlating the concentration of fracturing units and the degree of polymerization results, frequent errors emerge, mainly because of using various measurement units. In addition, some misleading interpretations have been adopted that normally lack the necessary consistency needed to establish a systematic order in the available information. A critical analysis of the available literature shows that the application of chemical kinetics principles to issues of cellulose degradation is still in its infancy.

While these topics affect the overall knowledge about fibre-based papers, some researchers tried to solve some of the materials challenges and enhance packaging solutions with chitosan,[8] while others tried to find additives that are appropriate for prolonged use of archival paper.[9] The protection of fibre-based packaging has been mostly done through some kind of coating, with the main focus on single paper sheets and with no regard for converting the material into a 3D shape. There are a number of researches in the field of paper coatings targeting water vapour and fire-retardant protection. Rovera *et al.*[10] have used wheat gluten/silica hybrid coatings on paperboard for food packaging applications to lower water vapour transmission rate (WVTR); they achieved four times lower WVTR compared to the uncoated paper substrate. A study on the barrier properties, as well as antibacterial properties of cellulose-based multilayer coated paperboard used for fast food packaging was also performed by Wang *et al.*[11]

Currently, commercially available CH packaging made of paperboard does not have all the extra protection functionalities (water and fire in case of accidents), but mainly fulfils the mechanical protection requirements. Some researches on composite materials for archival storage can be found mainly in patents. For example, Hollinger Jr.[12] describes a composite material with three layers: the first and the second layer is from cellulose material, the middle layer is a vapour barrier. Cellulose layers are buffered with calcium carbonate, magnesium bicarbonate, or a mixture thereof. The middle layer is a vapour barrier consisting of metalized polyester. This patented formulation does not include fire protection. Moreover, the metalized polyester layer is not eco-friendly.

Therefore, to solve the problem of currently missing multifunctional composite materials for storage of archival documents and objects, in the present study, we developed a multilayer composite packaging material. Our multifunctional packaging material is composed of two pH neutral papers, coated with a combustion reduction/suppression coating that inhibits combustibility and reduces moisture absorption, thereby protecting archival objects and documents. The multifunctional fibre material is flexible and can be transformed into a variety of packaging structures, as presented in Figure 1.

EXPERIMENTAL

For the presented research, pH neutral paper made of bleached kraft pulp (grammage 240 g/m^2), produced on a pilot paper machine (Pulp and Paper Institute, Slovenia) was used. The paper was produced according to ISO 9706:1994 and ISO 11108:1996 standards for archival paper permanence and durability. As the paper itself is hygroscopic and flammable, different coatings that decrease water vapour diffusion into the paper and reduce flammability were applied to the paper surface. Six different samples (S1 to S6) with different combinations of coatings were prepared (Table 1).

The pH neutral papers were first coated with fire retardant coatings on a Sumet coating machine CU8/250, using the film press coating application. The process parameters (*i.e.* pressure, velocity, IR and hot air drying) were optimized to get 35 g/m^2 coat weight. Later, a moisture barrier was applied on top of the fire-retardant coating, using the screen printing technique (screen mesh: 44 l/cm) and immediately (when wet) pressed with another uncoated pH neutral paper sample to get multi-layered samples (S1-S6).

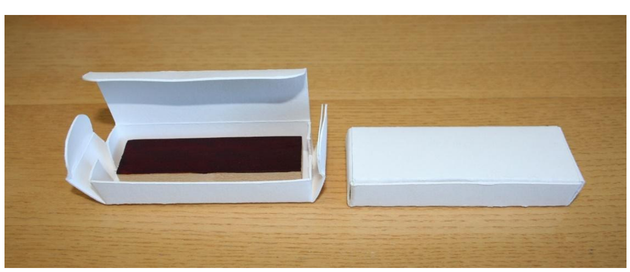

Figure 1: The developed and converted packaging solution with optimum coating properties

Table 1
Samples with different moisture barriers and fire-retardant coatings

Sample	Coatings	
	Moisture barrier	Fire-retardant
S0	None	None
S1	An aqueous dispersion of styrene-acrylic copolymer	Hydrostatin
S2	An aqueous dispersion of styrene-acrylic copolymer	Sodium silicate + aluminium hydroxide
S3	An aqueous dispersion of styrene-acrylic copolymer	Sodium silicate + carbonate
S4	Lignin	Hydrostatin
S5	Lignin	Sodium silicate + aluminium hydroxide
S6	Lignin	Sodium silicate + carbonate

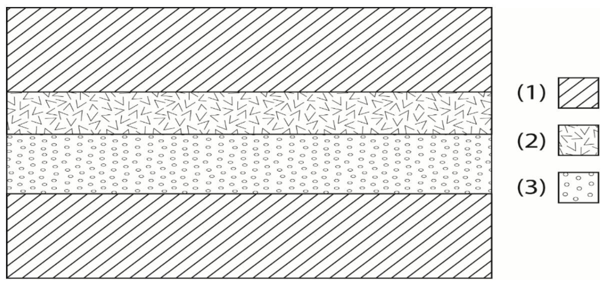

Figure 2: Structure of the developed multilayer material, where (1) is paper, (2) fire-resistant coating and (3) water vapour barrier

With this approach, several goals were achieved. First, the functional coatings are inside the composite material and are not in direct contact with CH objects, which decreases the possibility of unwanted migration. Second, as the coatings are not on the surface, their mechanical damage caused by converting processes (creasing and cutting) is avoided. This decreases the possibility of losing the functionality of the applied coatings. Third, with this approach, natural adhesion forces of the acrylic coatings to glue together the two layers of the paper were used, which also reduces the need for an extra adhesive. The final structural solution that has appropriate grammage (>300 g/m^2) for packaging prototyping is presented in Figure 2.

After preparing the composite material, the samples were analysed to determine the sample with the optimal characteristics that could be used for packaging prototyping. To characterize moisture barrier, WVTR (gravimetric method according to ISO 2528:2017) and water absorption (Cobb 60 according to ISO 535:2014) tests were carried out.

To evaluate the fire-retardant coating, the ignition time and burned area were measured according to internally developed methods. Samples were cut into 10 × 10 cm and held 3 cm above the laboratory burner with a constant flame. To ensure the constancy and temperature of the flame, an IR gun was used. The ignition time was defined as the time in seconds when the sample catches on fire. After the natural extinguishing of the flame (no extra fire extension was used), the samples were analysed using image analysis (ImageJ software) and the unburned area of the samples was determined.

RESULTS AND DISCUSSION

To test the composite material regarding WVTR is essential, if the developed material is intended to be exposed to moist environment that could affect the object packed inside the packaging (material degradation and mould growth). As can be seen in Figure 3, the samples could be divided into two groups regarding water barrier properties. In the first group, there are the reference samples (S0) and samples (S4, S5 and S6) with lignin coating as a water vapour barrier. Their WVTR is above 580 g/m^2/24 h, which is contrary to our preliminary research, where samples with lignin coating (without fire retardant coating) had a decreased WVTR. On the other hand, the samples coated with an aqueous dispersion of styrene-acrylic copolymer (S1, S2 and S3) reached much lower values, below 200 g/m^2/24 h. This indicated that the polymer successfully closed some of the pores and inhibited the water vapour transmission and uptake into the material.

Besides WVTR, the direct water absorption to the composite was also determined to simulate a direct flooding effect on the packaging. In Figure 4, one can observe that all the coated samples absorb less water than reference sample S0. The Cobb 60 value of the coated samples is around 30% lower than that of the reference sample. It is also notable that the water absorption of all the samples is below 25 g/m^2, which is required in ISO 16245:2009 standard regarding materials for archive storage. There is no large difference between the samples coated with lignin and those coated with acrylic polymer coating, which was mainly intended for water vapour protection (where the influence is seen – Fig. 3).

Samples S3 (19.5 g/m^2) and S6 (20.6 g/m^2) had the highest water absorption, besides the uncoated paper (SO), while the sample S1 had the lowest one, with the value of 16.4 g/m.^{2}

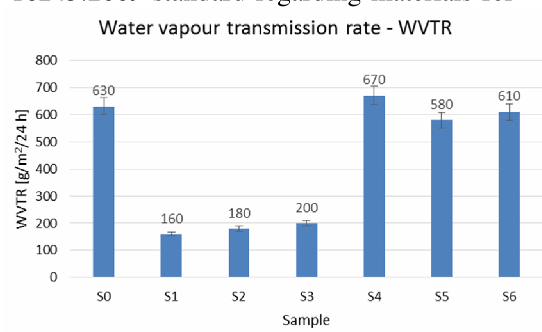

Figure 3: Water vapour transmission rate for all samples

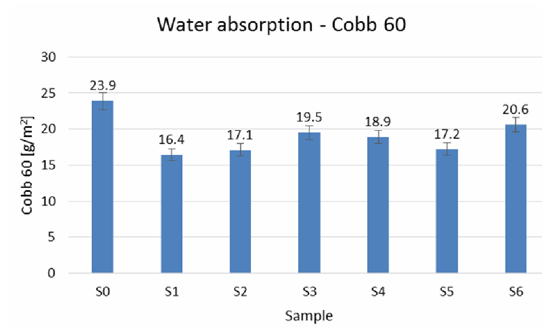

Figure 4: Water absorption values for all samples

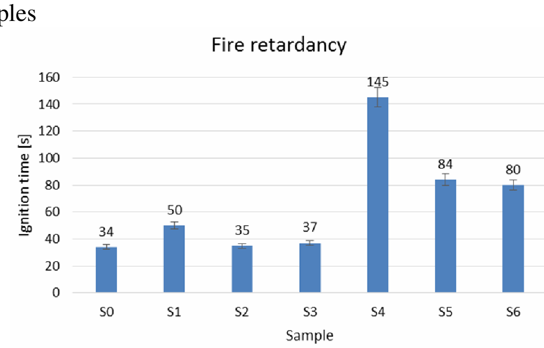

Figure 5: Ignition time of the samples after fire retardancy tests

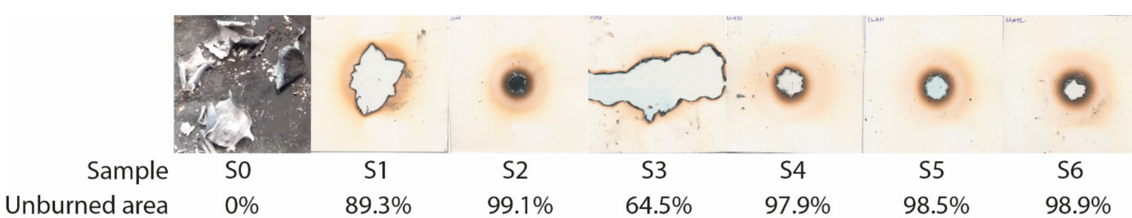

Figure 6: Appearance and unburned area of the samples after fire retardancy tests

To assess the performance of the coated samples in terms of fire protection, the samples were tested following an internally developed method, where the ignition time and the unburned area of the samples were measured. As presented in Figure 5, the ignition time of samples S0–S3 is below 50 seconds, while samples S4–S6 ignite later than in 80 seconds. While samples S1–S3 are coated with three different fire retardants, as well as samples S4–S6, the main reason for the difference in ignition time between these two groups of samples could be the moisture barrier. While fire retardants decelerate burning and hopefully also extinguish it, the remained or unburned area of the samples was calculated to see their effect, and the results are presented in Figure 6. The appearance of all the samples after the fire retardancy test can be seen in Figure 6 as well.

From Figure 5 and even better from Figure 6, it can be seen that, even though the ignition time was low, the best fire retardancy was presented by sample S2, which was coated with a mixture of sodium silicate and aluminium hydroxide. Other samples, such as S4–S6 had higher ignition time and similar burned area, but the paper layer was burned through, which could pose a potential threat of damaging the inside of the packaging. The sample S2 had a somewhat lower ignition time, but the burning was contained on the surface layer and no hole was observed in the fire application timeframe. According to this, sample S2 was chosen as the most appropriate sample for water barrier and fire retardancy protection. This sample was further tested for converting into packaging, with different tooling (creasing and cutting), and it was shown that the composite material is appropriate for converting into different packaging shapes (Fig. 1).

CONCLUSION

A pH neutral paper that fulfils the requirements of ISO 9706: 2014 and ISO 11108: 2016 standards for archival paper, regarding permanence and durability, was produced and used as a base material for developing multilayer composite packaging. The paper was coated with different combinations of water barrier as well as fire-retardant coatings and final multilayer material samples for storing CH objects were developed and tested. The analyses revealed that sample S2 (combination of styrene acrylic copolymer aqueous dispersion and coating of sodium silicate and aluminium hydroxide mixture) had the optimum properties. The coating combination resulted in four times lower WVTR rate, compared to that of the uncoated samples, and had a low burned area, with no fire penetrating through the material. Other samples also had lower WVTR rate and Cobb absorption rate. Interestingly, the lignin coated samples (combined with hydrostatin, sodium silicate+aluminum hydroxide and sodium silicate+carbonate) also achieved better values, compared to the uncoated sample, regarding WVTR and Cobb, and had relatively good results in fire retardancy (burned area) with high ignition times. The final S2 sample also proved to be suitable for converting into 3D packaging shapes, which opens up possibilities in further development of packaging with extended functionalities for CH objects.

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