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Microstructure, morphology and properties of printing paper laminated with polypropylene film

Adham Salimovich Rafikov[1], *Fazliddin Muhiddinovich Turaev*[2], *Anvar Abdugafarovich Djalilov*[2] *and Bekzod Shuxrat Ugli Ibodulloyev*[1]

[1]Tashkent Institute of Textile and Light Industry,
Department of Chemistry,
Shakhdjakhon Street 5, 100100, Tashkent, Uzbekistan
[2]Tashkent Institute of Textile and Light Industry,
Department of Technology of Printing and Packing Industry,
Shakhdjakhon Street 5, 100100, Tashkent, Uzbekistan

asrafikov@mail.ru
fazliddin5576@gmail.com
anvar-matbaa@mail.ru
bshibodulloyev@mail.ru

Abstract

To improve design, reduce wear, and extend service life, lamination involves applying a thin polymer film to paper or cardboard using hot melt adhesive or a solution. Moreover, hot melt adhesive bonds well to a fairly rough or matte surface. If the surface of the paper or cardboard is smooth or glossy, then molten high molecular weight polymer adhesive does not always penetrate its micropores. Due to differences in melting temperatures between the polymer adhesive and the polymer film, the polymer adhesive does not bond strongly enough to the polymer film. In this study, in order to increase the adhesive strength between paper and polymer film, glossy paper was laminated with polypropylene film using an adhesive solution of ethylene–vinyl acetate (EVA) copolymer. A polymer adhesive solution, unlike a melt, penetrates into the micropores of glossy paper and ensures strong adhesion of the polymer film to the paper surface. FT–IR spectroscopic studies of polypropylene, EVA copolymer, and laminated paper showed the absence of chemical interaction between them during the lamination process. As studies on SEM-EDS analysis have shown, the adhesion interaction between the polymer film and the adhesive occurs due to ethylene units, and between the paper and adhesive due to vinyl acetate units. In contrast to the industrial sample with hot melt adhesive, in the experimental paper sample, near the polypropylene film, micropores are filled with a polymer adhesive solution. Elemental analysis of torn layers of laminated paper shows the presence of polymer adhesive in the micropores of the paper layer. The adhesive strength between layers of laminated paper is 20 % higher, and the penetration force is 40 % greater than that of the industrial sample.

Keywords: laminate, paper and cardboard, polypropylene, ethylene–vinyl acetate copolymer, adhesion.

1. Introduction

Polymers in the form of a carrier of text and illustration information, protective film and layered materials, and adhesives are widely used in printing (Radermacher, 2016; Gregor-Svetec, 2022) and in packaging production (Riley, 2012). Large-scale industrial polyolefins, such as polyethylene and polypropylene, as well as their copolymers and derivatives (Posch, 2011), have long been used for laminating paper and cardboard. Lamination printing is the process of applying a thin polymer film to paper or other comparable substrates to enhance and protect a printed layer. It is used for covers of books, magazines, brochures, business cards and other printed products. Lamination is also used to produce various types of packaging materials and paper for insulating electrical cables (Furuse and Fuchino, 2014). Lamination refers to a printing finishing process in which a thin layer of plastic laminate is bonded to the surface of paper or cardboard using pressure and heat. Lamination has the following goals: improving design and appearance, increasing strength and other physical and mechanical properties, reducing wear and increasing the service life of printed products.

Laminates are typically applied to the front surface of book and magazine covers, but can be applied to both sides of the printed product. Laminate can have different thicknesses and degrees of gloss. Commercial printers use a combination of heat, pressure, tension and an adhesive to apply the laminated film.

The composition of the lamination film contains two main components: a polymer film and an adhesive layer. Polyethylene terephthalate (PET) (Charinee, et al., 2021), polybutylene terephthalate (PBT) (Repeta, et al., 2020), polyethylene (PE) (Galikhanov and Musina, 2012; Kibirkštis, et al., 2022), polypropylene (PP) (Furuse and Fuchino, 2014; Rousseau, et al., 2023) and polyvinyl chloride (PVC) (Pilipović, 2022) are often used as polymer films. Ethylene vinyl acetate copolymer (EVA) (Shih and Hamed, 1997; Paul, 2023; Li, et al., 2008; Moyano, et al., 2008; Rafikov, et al., 2022), polyurethane adhesive (Yan, et al., 2020; Stiene, et al., 2019), epoxy adhesive (Sharma, et al., 2023) or other adhesive material are used as the adhesive layer. The quality of the laminate depends on both the thickness and the ratio of components (Repeta, et al., 2018). The thickness of the polymer film for lamination ranges typically from 8 to 250 μm, which depends on the scope of application or the product. The polymer adhesive is attached to a polymer film either from a melt by hot extrusion or from a solution by spraying or rolling.

Lamination film with an adhesive layer can be applied to the surface of paper or cardboard using a hot or cold method (Prambauer, et al., 2016). In the first case, the treated surface, like the film itself, is heated to at least 70 °C. This causes the adhesive layer to melt, allowing it to bond with the sheet of the printed products. This method of applying a laminate coating is the most common. Most commercially available films are designed for hot application. Applying a PP film to a substrate using the hot method reduces processing time and pressure (Peng, et al., 2020). Cold-apply film is used for laminating documents and other papers, such as valuable archival records, for which exposure to high temperatures can be detrimental. In this case, the surface to be treated is covered with the lamination film and passed through a special press. Under the influence of high pressure, the adhesive applied to the layer of polymer film softens and the film adheres to the surface of the document.

In recent years, manufacturers have been inclined to use PP film for laminating book and magazine covers, which is more transparent than PE and PVC. Also, it is more elastic and cheaper than PET. As an adhesive polymer, preference is often given to EVA copolymer. The EVA copolymer shows a good adhesion to surfaces of non-polar polyolefin films due to ethylene units, and to the surface of paper due to vinyl acetate units. Printing enterprises of the Republic of Uzbekistan use PP laminating film with a layer of hot melt adhesive EVA copolymer made in China. This laminate is applied to the surface of paper and cardboard by hot pressing. During thermal exposure, PP and the EVA copolymer are in a highly elastic, almost liquid state, while paper, as an infusible material, remains in a solid state. If the paper is sufficiently porous, then the molten polymer adhesive penetrates into these pores and binds well to the paper. This lamination film does not have sufficiently high adhesion to the surface of smooth or glossy paper, since the high molecular weight polymer does not penetrate into the micropores of the paper. In this case, the adhesive solution has an advantage; a low-molecular solvent easily and quickly penetrates the micropores of paper, drawing the polymer along with it. The purpose of this study is to increase the adhesive strength between polymer film and paper by using an adhesive solution of EVA copolymer.

2. Materials and methods

2.1 Materials

Glossy paper with a grammage of 220 g/m^2 was selected for lamination tests. The laminating film used was a biaxially oriented polypropylene (PP) film with a thickness of 20 μm. For gluing PP film to paper, the colorless copolymer polyethylene vinyl acetate (PEVA) was chosen as granules. Xylene with toluene impurities (technical grade) was used as a solvent. As an analogue, we selected industrial PP film with an adhesive layer for laminating paper with a thickness of 24 μm.

2.2 Method for producing laminated paper

2.2.1 Preparation of PEVA adhesive solution

Several PEVA granules were placed in a glass with a lid, the calculated amount of solvent (1 g EVA, 10.46 g solvent) was poured on top, the lid was closed, and left for a day to swell. The contents were then vigorously stirred, slightly heated (70 °C) in a hot water bath until a homogeneous viscous solution was formed. Solutions with different concentrations of PEVA were obtained by diluting the original solution.

2.2.2 Applying adhesive to the surface of the PP film

Work with PP film was carried out using surgical gloves to prevent contamination of the surface of the film. A 0.1 mm thick adhesive solution was applied to the inner surface of the PP film using a squeegee device. The adhesive layer is dried under a fume hood at room temperature for 2–3 minutes.

2.2.3 Paper lamination

The lamination process was carried using an “A4 Exact LR-H001” installation by tanning layers of paper and PP film with PEVA adhesive under pressure from rollers at a temperature of 90–100°C. The width of the rollers was 20 cm. The diameter of the rollers was 3 cm and the speed of paper passing was 0.66 ± 0.04 m/min.

2.3 Testing the properties of laminated paper

The structure of the samples was analyzed using Fourier Transform Infrared Spectroscopy (FT-IR) with a Nicolet IN10 spectrometer from Thermo Fisher Scientific (USA), covering a scanning range of 500–4000 cm^{-1}.

The surface morphology and elemental composition of the samples were analyzed using a scanning electron microscope (JSM-IT200LA InTouchScope, Japan) equipped with an energy-dispersive spectroscopy (SEM-EDS) application.

The adhesive strength between the polymer film and paper was determined by the peel force (N) of the film using a Shimadzu AGS-X device. A sample of laminated paper measuring 10 × 5 cm was adhesived to the clamps of the device and the force required to completely tear off the film from the surface of the paper was determined.

The bending resistance of the paper was measured using an endurance testing machine (HD-A519-2) from Haida Equipment Co., Ltd. For this test, a strip measuring 150 x 12 mm was cut from a sample of laminated paper. The device was used to determine the number of double bends required to completely destroy the sample.

The resistance of the paper to piercing was determined using a bursting strength testing machine (HD-A504-2) from Haida Equipment CO., LTD. for a sample size of 130 × 100 mm.

3. Results and discussion

3.1 FT-IR spectra

Fourier transform infrared spectroscopic studies were carried out to clarify the nature of the interaction of PP film, PEVA adhesive and paper with each other. The obtained FT-IR spectra are presented in Figure 1.

The FT-IR spectra of the PP film show absorption bands characteristic for stretching (ν) and bending (δ) vibrations of C–H and C–C bonds: in the regions of 2949–2839 cm^{-1} for $\nu_{(C-H)}$; in the regions of 1456–1304 cm^{-1} and 528–459 cm^{-1} for $\delta_{(C-H)}$; and in the regions of 1359 – 809 cm^{-1} for $\nu_{(C-C)} + \delta_{(C-C)}$.

The FT-IR spectra of PEVA adhesive revealed absorption bands characteristic for stretching and bending vibra-

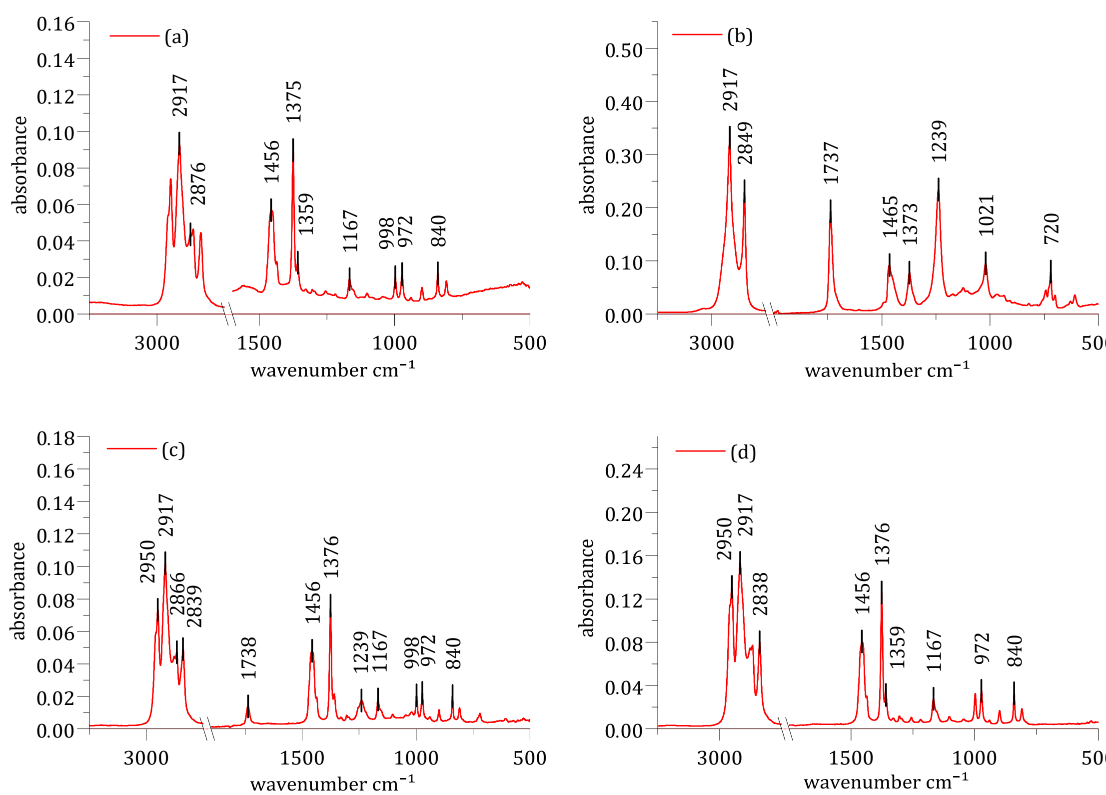

Figure 1: FT-IR spectra of PP (A), PEVA (B), PP-PEVA laminating film (C) and laminated paper (D)

tions of PEVA bonds: at 2917 and 2849 cm^{-1} for $\nu_{(C\text{-}H)}$; at 1737 cm^{-1} – $\nu_{(C=O)}$; at 1465, 1372 and 743–608 cm^{-1} for $\delta_{(C\text{-}H)}$; in the region of 1239–821 cm^{-1} for $\nu_{(C\text{-}O)} + \nu_{(C\text{-}C)} + \delta_{(C\text{-}O)}$.

In the FT-IR spectra of the PP film with PEVA adhesives, absorption bands of polypropylene and PEVA bonds were detected, including $\nu_{(C=O)}$ at 1738 cm^{-1}, but with lower intensity than in the adhesive itself.

In the FT-IR spectra of laminated paper, the previously observed absorption bands are retained, along with additional bands characteristic of cellulose, such as a low-intensity broad band $\nu_{(O\text{-}H)}$ at 3282 cm^{-1}.

The absence of obvious new absorption bands in the combined products indicates that during the lamination process there is no chemical interaction between the components, but an adhesive interaction.

3.2 SEM-EDS analysis

The SEM-EDS analyses were carried out to determine the surface morphology and cross-section of samples of PP film with PEVA adhesive, laminated paper, as well as to determine the nature of the interaction of the adhesive with paper and polymer film. Figure 2 shows a cross-section of a PP film with an adhesive layer. As can be seen from Figure 2, the industrial laminating film consists of three layers with a total thickness of 20–23 µm; the thickness of the adhesive layer is 6–10 µm. The laminating film prepared in this study consists of two layers with a total thickness of 26–29 µm; the thickness of the adhesive layer is 8–12 µm.

Figure 3 shows the fibrous-porous structure of the paper and the layer of polymer film on its surface. The thickness of the laminated paper together with the polymer film was 210–220 µm. In contrast to the industrial sample, the micropores of the experimental paper (near the PP film) are filled with a polymer adhesive solution. Apparently, the polymer adhesive solution seeps into the interfiber space of the paper, and at the same time partially dissolves the contact surface of the PP film. All this should lead to increased adhesive interaction between the surface of the paper and the laminating film. To confirm this, SEM-EDS analysis of each layer of laminated experimental paper was carried out (Figure 4). It can be seen that the energy dispersive spectra were taken from three scanned areas of the laminated paper. The first region refers to the cross section

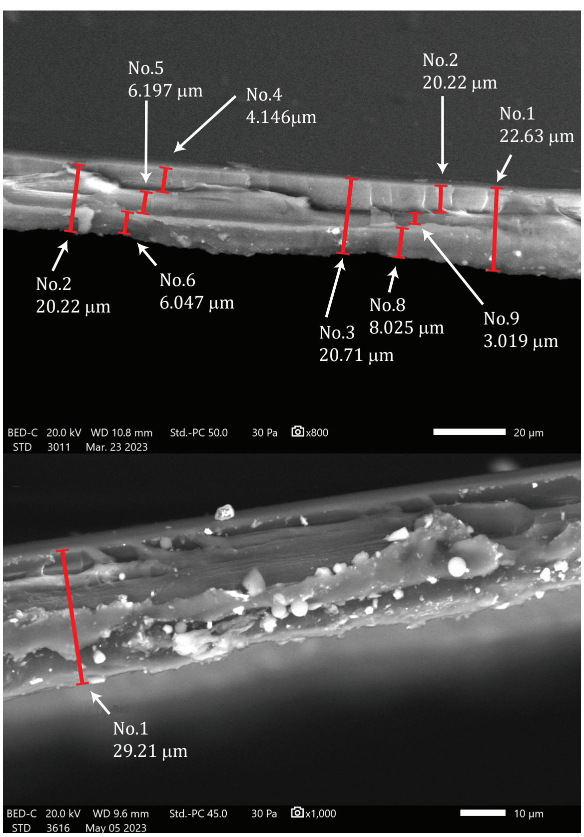

Figure 2: SEM image of the cross section of a PP – laminating film: (top) – industrial sample, (bottom) – experimental sample

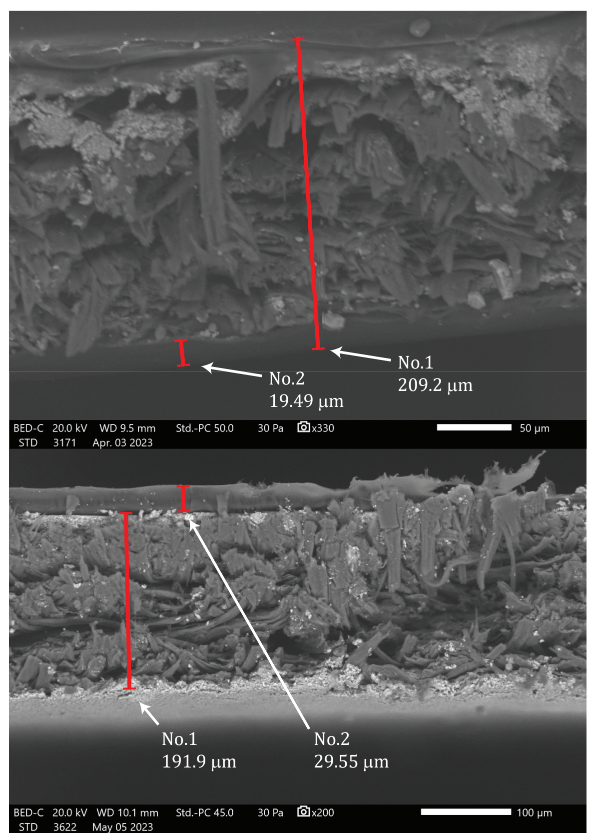

Figure 3: SEM images of a cross section of paper laminated with commercial (top) and experimental (bottom) PP film

of the PP film, where carbon atoms should be detected. It turned out that there is also oxygen in this area. Apparently, oxygen belongs to the PEVA, which confirms the previously stated assumption that some of it passes into the PP film as a result of partial dissolution. The second region contains carbon and oxygen atoms, in a ratio that approximately corresponds to PEVA. This confirms another assumption about the transition of the adhesive solution into the micropores of the paper. The mass ratio of carbon and oxygen in the third region corresponds to the composition of paper pulp.

SEM-EDS studies continued at the interface between paper and polymer film (Figure 6). The observed picture of the surface of the polymer film after forceful tearing under load provided information about the relationship between the forces of adhesion and cohesion in laminated paper. Traces of paper in the form of white spots are visible on the film interface. The elemental composition of the three areas of these stains is approximately the same, and corresponds to the composition of mineral-filled paper. Judging by the presence of large amounts of calcium, the filler is calcium carbonate or chalk. These stains are an agglomerate of chalk particles with cellulose fibers. The elemental composition of four more surface areas where there are no white spots was scanned. In these areas, carbon and oxygen atoms of approximately the same composition were found, which corresponds to the composition of PEVA. The results indicate that the adhesion forces of PEVA adhesive with PP film are much stronger than with paper; when torn, the adhesive almost completely transfers to the surface

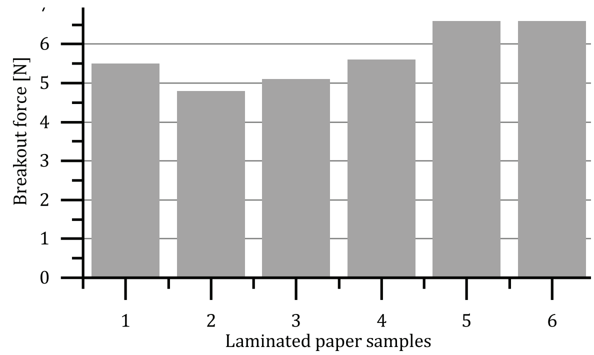

Figure 5: Breaking force of PP film from the paper surface: industrial analogue (1); experimental samples using PEVA adhesive solution with concentrations of 8 % (2), 9 % (3), 10 % (4), 11 % (5) and 12 % (6)

of the film. The adhesive forces of interaction between PEVA and the surface of the paper are comparable to the cohesive forces inside the paper. Moreover, a piece of paper comes off at the weakest link – in places where mineral filler accumulates.

3.3 Physical-mechanical properties

The following studies were carried out to determine the adhesive interaction forces between layers in comparison with the industrial analogue. Figure 5 shows the dependence of the breaking force between PP film and paper on the type of laminated paper and the concentration of PEVA adhesive solution. As can be seen from Figure 6, an increase in the concentration of PEVA

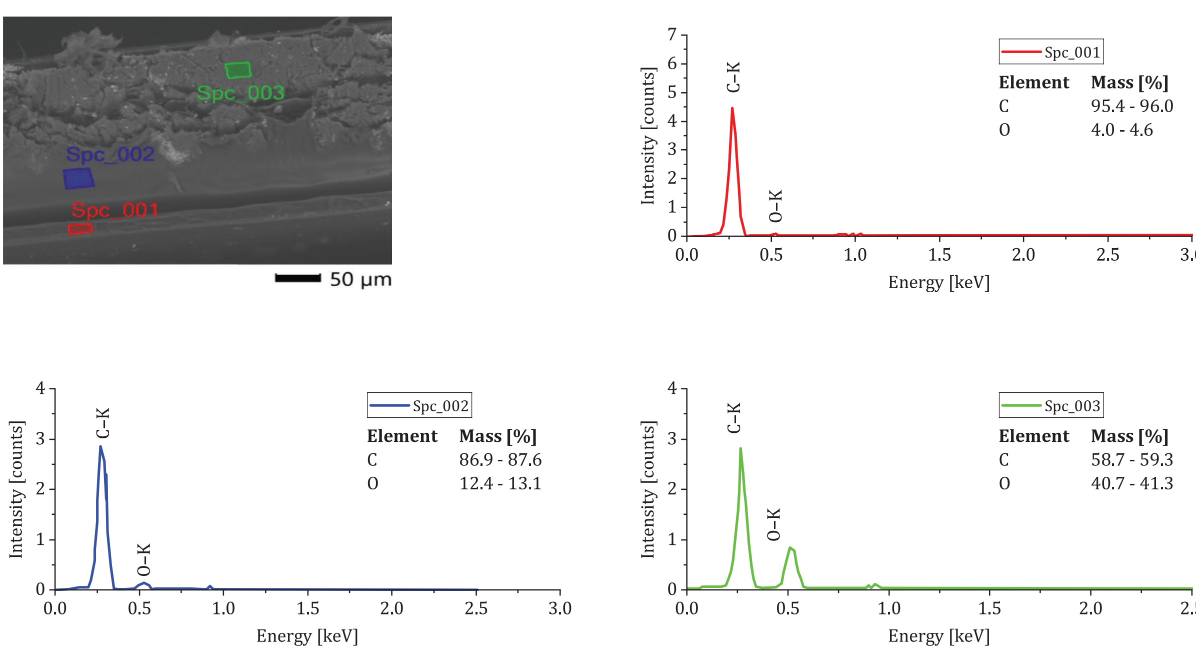

Figure 4: SEM-EDS analysis of layers of experimental laminated paper

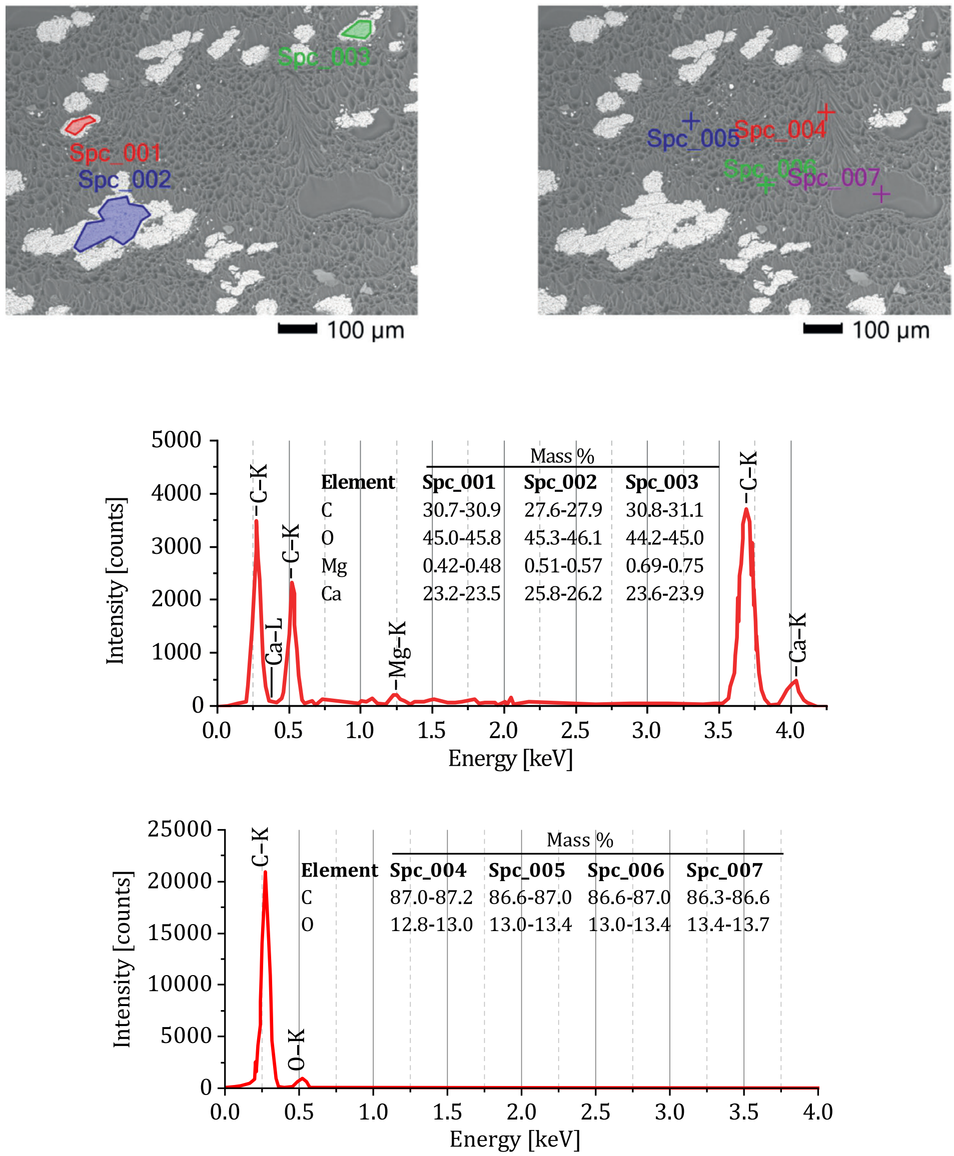

Figure 6: SEM-EDS analysis of the interface between PP film and paper of an experimental sample of laminated paper

solution to 11 %, the adhesive strength between the polymer film and paper increased. Moreover, the adhesion strength of the film in this sample was approximately 20 % higher than in the sample of the industrial analogue. These data confirm the assumption that the adhesive solution penetrated into the micropores of the paper. For a sample obtained using an 11 % solution of PEVA adhesive, some other important indicators of laminated paper were determined (Table 1).

As can be seen from Table 1, at the same grammage, the analogue and the experimental sample can withstand more than 100 double bends. The bursting pressure of the experimental sample is 1.4 times higher than that

Table 1: Physical-mechanical properties of laminated paper

Sample	Grammage [g/m²]	Bending resistance, number of double bends	Pressure resistance [kPa × m²/g]
Paper without lamination	220 ± 3	15	–
Industrial Aanaloge	240 ± 4	more than 100	3.68 ± 0.06
Laminated paper	245 ± 4	more than 100	5.12 ± 0.06

of the analogue. The data obtained shows the obvious advantages of laminating glossy paper with PP film using a PEVA adhesive solution.

4. Conclusion

Bonding smooth or glossy paper and cardboard to polypropylene film using an ethylene-vinyl acetate copolymer adhesive solution has significant advantages over gluing using hot melt adhesive. Due to the stronger adhesive interaction of the adhesive solution with both the surface of the paper and the surface of the polymer film. The solvent partially dissolves the polypropylene, which ensures strong adhesion of the film to the adhesive. At the same time, the solvent, together with the adhesive macromolecule, penetrates into the micropores of the paper, which ensures strong adhesion of the paper to the adhesive. Additionally, stronger adhesive interaction between the layers provides, in turn, better overall physical and chemical mechanical properties of the laminate. A direct comparison of the properties of an industrial paper–polypropylene laminate produced using hot melt adhesive and an experimental laminate with the same grammage showed the following: the force for tearing off layers, the number of double bends and the force for punching the experimental laminate are approximately consistently 20 – 40% higher than the industrial analogue.

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