INVESTIGATION OF THE FLAME-RETARDANT PROPERTY OF SILICA NANOPARTICLES RATIO IN THE PAPER COATING

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Abstract
Papers have a highly flammable property and can easily catch fire. This is a major disadvantage for paper and paper packaging materials. For this reason, this can be delayed or prevented by producing papers with high heat resistance. For this purpose, coating formulations containing 1%, 2.5%, 5% and 10% silica nanoparticles were prepared and applied on 80 g/m2 office paper. Chemical analyses of the coatings were made with ATR-FTIR. Surface contact angle and surface energy properties of coatings were measured using PocketGoniometer PGX+, gloss measurements of coated papers were carried out with BYK Gardner GmbH micro gloss and color measurements were determined using X-Rite eXact spectrophotometer. Also, absorbency, surface morphology, and limited oxygen index (LOI) of the coatings were determined. All papers were printed with Toyolife LF - 1600 process magenta commercial offset printing ink using an IGT C1 offset printability test device. As a result, it was determined that the contact angle increased and the printability improved. It has been observed that silica nanoparticles coated papers have flame retardant and very good hydrophilicity and their printability values are in accordance with ISO 12647-2.
***Keywords**: Paper coating, nanoparticles, silica, flame retardant*

Introduction

Paper is a porous fiber network with a smooth surface, optical properties, usually coated with various materials, which provide good printing performance. A coating formulation to be applied on paper consists of three main components. It contains mineral pigments to provide optical properties, latex binders for adhesion and strength properties, and polymer additives to adjust runnability during the coating process and to better tune coated paper properties (dispersants, biocides, pH controllers, dyes and foam controllers etc.) (Preston et al., 1993; Ortner et al., 2018; Wedin et al., 2006; Özcan et al., 2018).

Every process and component made during papermaking directly or indirectly affects its physical and surface properties, such as printability, gloss, opacity, fiber orientation, filler and fine content, sizing process, calender nip pressure and coating (Sharma et al. 2020; Ozcan, and Tutak, 2020). Paper surface coating is a process in which a layer with a smooth surface is obtained by coating cellulosic fibers and filling the gaps between them with binders (often starch and/or synthetic latex), pigments and other fillers. The surface coating process is followed by drying and polishing processes. These processes are done to obtain a paper with better sizing, printing and barrier properties (Sharma et al., 2020; Howard and Hodgson, 2015). In addition, surface sizing is an efficient way to improve the water repellency and mechanical properties of paper, which are closely related to the application performance of paper-based products (Ni et al., 2021).

Some products produced in the printing industry are used where high heat resistance is required. For example, when used with the flame-retardant paper in rare books in libraries, the burning of these books during a fire can be delayed. Besides, some products produced in the printing industry are also used at home. Such as printed packages, wallpapers, newspapers etc. are products of the printing industry. The flame-retardant feature of such products ensures that the fire can be extinguished before it increases, due to its delayed ignition feature in a possible fire (Ozcan et al., 2020).

Material and Methods

Coatings were prepared by using nano silica in four different ratios (1%, 2,5%, 5% and 10%) except natural starch. (10% Nano silica coating could not be prepared due to gelling of silica) All prepared coating formulations were applied on 80g/m^2 office paper. A K-Control laboratory rod coater used for coatings. After coating, the samples were air dried and conditioned according to TAPPI standards. Toyolife LF - 1600 process magenta ink was printed on the surface of papers with IGT-C1 offset tester according to ISO 12647-2 standard. X-Rite manufacturing standards are used for all spectrophotometric and densitometric measurements (according to 0/45º geometry with 2º observer angle with D50 light source in the range of 400–700 nm and 23°C +/- 1°C temperature, 40-60% RH). The difference between the colors of the prints is calculated according to the formula 1 (according to the CIEDE 2000 standard, ISO 13655). Gloss values were measured at 60° according to ISO 2813:2014 standard for printed papers and 75° according to TAPPI standard T480:2005 for unprinted papers. Surface tension values were measured according to ASTM D5946 method.

$$\Delta E^* = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad (1)$$

Results

Starch and different ratio of Nano silica used in coatings have shown different behaviors for CIEL*a*b*, surface contact angle and surface energy, paper and print gloss, limited oxygen index (LOI). The results obtained from the coatings and printings are presented in tables and graphics below.

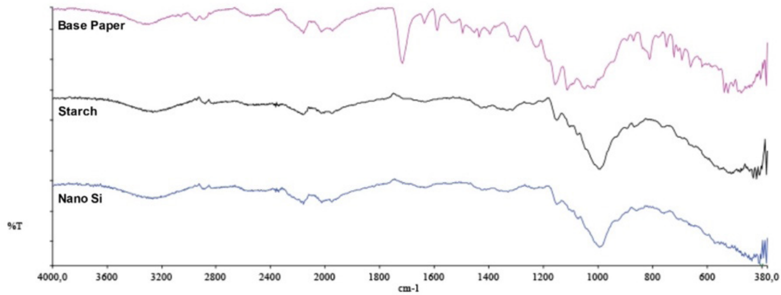

Fig 1. ATR-FTIR spectra of base paper, starch coated paper, silica nanoparticles coated paper

The strong absorption band at 3447 cm^{-1} of silica nanoparticles indicated that -OH on the surface of silica. The characteristic absorptions bands about 1100 cm^{-1}, 810 cm^{-1}, and 470 cm^{-1} were attributed to the asymmetric stretching vibration, symmetric stretching vibration, and bending vibration of Si-O-Si, respectively. When the starch coated papers spectra were examined the strong absorption peak at 3413 cm^{-1} was assigned to the hydrogen bonds association in -OH groups. The bands at 1168 cm^{-1} and 1071 cm^{-1} were attributed to the stretching vibration of C-O in C-O-H groups, and the band at 1026 cm^{-1} was attributed to the stretching vibration of C-O in C-O-C groups. The other characteristic absorptions of starch also appeared at 1463 cm cm^{-1}, 1408 cm^{-1}, and 860 cm^{-1}.

When the FTIR spectrum of the paper is examined, around 3400 cm^{-1} -OH bands belonging to cellulose the band at 2894 cm^{-1} is attributed to CH stretching vibration of all hydrocarbon constituents in polysaccharides. Typical bands assigned to cellulose were observed in the region of 1630 – 900 cm^{-1}. The peaks located at 1633 cm^{-1} correspond to vibration of water molecules absorbed in cellulose. The absorption bands at 1428, 1367, 1334, 1027 $cm^{-1}$and 896 cm^{-1} belong to stretching and bending vibrations of $-CH_2$ and -CH, -OH and C-O bonds in cellulose. The reason why the three spectra are very similar to each other is that the peaks of the paper main structure are much more dominant than the others. The results obtained are compatible with the literature (Tang et al., 2009; Hospodarova et al., 2018).

Table 1. Total surface energy and contact angle values according to ASTM D5946 method.

Coating type	**Contact Angle**	**Surface Energy (mj/m²)**
Base	8.8	35.5
Starch	42.6	49.7
1% Nano Silica	29.6	54.4
2.5% Nano Silica	24.2	56.3
5% Nano Silica	18.7	58.3

When looking at the contact angle and surface energy values obtained as a result of the measurement of the surface coatings, it was determined that the filling material used starch reduces the contact angle of the coating, but it increases the surface energy. In contrast to starch, the contact angle of the coating used %5 Nanosilica is the lowest, but it has the highest surface energy. In addition, as the Nanosilica ratio increased in the coating formula, the contact angle increased and the surface energy decreased.

Table 2. Paper Gloss and Print Gloss values

	Base	**Starch**	**1% Nano Silica**	**2,5% Nano Silica**	**5% Nano Silica**
Paper Gloss	3.04	10.7	4.84	5.96	6.33
Printing Gloss	5.92	13.44	5.73	6.24	5.85

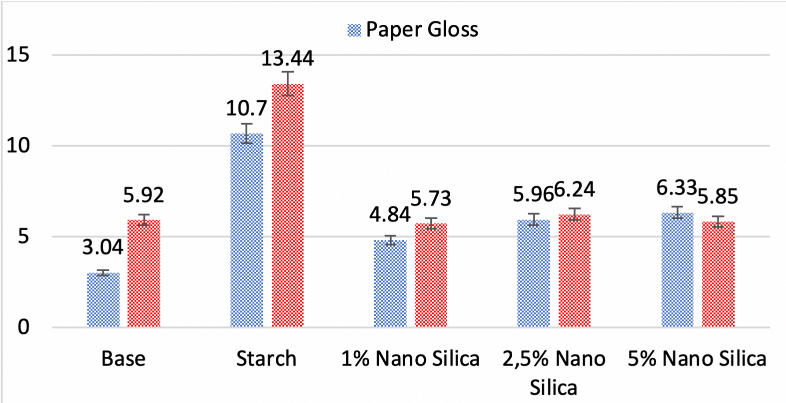

Fig 2. Paper gloss and printing gloss values

The starch applied on the base paper increases both the paper and the printing gloss. In nano silica applied coatings, although the gloss increased a little in both paper gloss and print gloss values, it remained at very low values compared to starch. This is because nano silica creates a roughness on the surface and this causes diffuse reflection and reduces the brightness. However, when starch is used, the increased gloss values are still higher than the untreated paper. This means increased attractiveness of the paper.

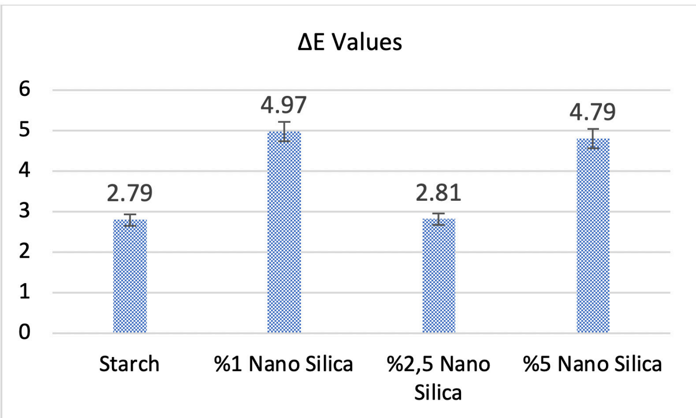

Fig 3. CIE L a*b* ΔE values*

When Delta-E values are compared according to printing parameters, it is seen that Starch and 2.5% Nano Silica ΔE values are lower than the other two coatings. According to ISO 12647-2, values below 5 are acceptable. This shows the acceptability of all coatings in terms of printing. This is because the added nano silica does not glow blue. Nanoparticles glow in different colors depending on their size. This is called the quantum effect. This quantum effect was also observed in the added nano silica. All ΔE values obtained are within the acceptable range specified in ISO 12647-2.

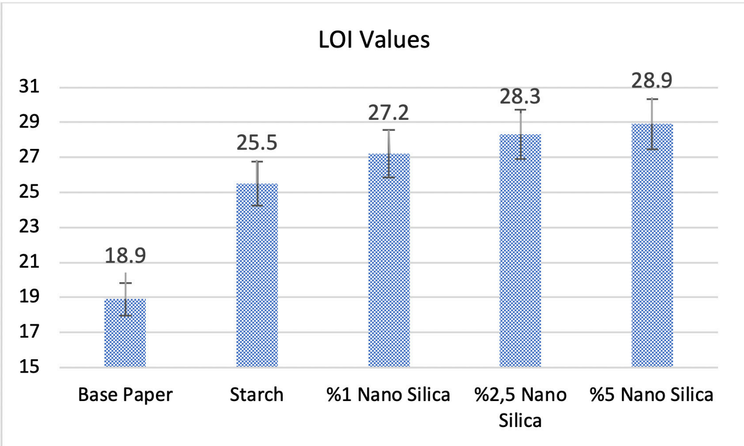

Fig 4. Limited oxygen index (LOI) values of Samples

The flame retardancy properties of nano silica added starch paper coatings were examined with LOI measurements. LOI is a widely used technique to determine the flame retardancy of coatings. LOI values of the coated papers are given in Figure 4. When the figure is examined, the flame retardancy feature is increased by adding nano silica. It was determined that the increase was slightly higher with increasing nano silica amounts. The reason for this increase is that the Si-O-Si bonds on the silica nanoparticle are resistant to increasing temperature and delay the ignition by forming an ash coating on the combustible surface. The obtained results are in line with the literature (Üreyen et al., 2020; Yuan et al., 2017).

Conclusions

While preparing the coating material, mixtures of 1 %, 2.5 % and 5 % were prepared and applied to the paper surface. However, nano silica particles added to the starch made the mixture into a gel after 5% and could not be used as a coating material.

Starch and Nano silica showed different behaviors both in the optical properties of the paper and in the printing properties.

According to the coating type, in the contact angle and surface energy values, it was determined that as the amount of nano silica in the coating increased, the contact angle decreased and the surface energy increased on the contrary. The low contact angle has a very important value for the offset printing system.

In paper and print glosses, coatings had a positive effect on both paper and print gloss. While paper gloss and print gloss starch coatings have an average of twice the value compared to Nano silica-containing coatings, the ratios are close to each other in Nano silica coatings, although the ratios vary.

When the printing color differences are examined, it has been determined that the printing ΔE values for all coatings are within the acceptable values. It can be said that Starch and 2.5% Nano Silica coatings are better than others.

There were positive changes in the flame-retardant values of the coatings of nano silica particles added to the starch. As the amount of nano silica in the coatings increased, its resistance to flammability also increased. This will ensure that the nano silica included coated papers to be used are more resistant to burning, especially for valuable documents and documents to be stored for a long time.

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