THE USE OF ENCAPSULATED AMMONIUM POLYPHOSPHATE IN THE PRODUCTION OF FLAME RETARDANT PAPER

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Abstract
Papers have extreme burning and ignition properties due to their natural extractsToday, it has become a necessity to provide late flammability properties to valuable papers such as money, checks, promissory notes. It is desired that the additives used to provide late flammability materials do not emit harmful gas. In this sense, the use of additives containing phosphate is increasing. Encapsulation allows a material to be protected by natural effects or to be dispersed more homogeneously in the dispersion medium. In this study, ammonium polyphosphate, known for its flame retardancy property, was encapsulated with an easy method and it was investigated whether it provides a late flammability feature on papers.
For this purpose, microencapsulated ammonium polyphosphate was prepared by in situ polymerization with glycidyl methacrylate (GMA) and polyurethane as the shell material, respectively. The chemical structure of microcapsules illuminated with Fourier transform infrared spectroscopy (FTIR), and size of microcapsules were determined with scanning electron microscopy (SEM). Paper coating formulations containing starch binder and encapsulated ammonium polyphosphate in different ratios (0,1,3,5,7.5) were prepared and coated onto office paper. Color (with spectrophotometer), gloss (with glossmeter), contact angle (with goniometer) and flame retardancy (with LOI) properties of coated papers were measured. Offset test prints were made on the coated papers produced with IGT C1 and the changes in color and gloss of the coating were determined. As a result, ammonium polyphosphate was successfully encapsulated by in situ polymerization. It was concluded that as the amount of microencapsulated ammonium polyphosphate increased, the flame retardancy property increased and there was no decrease in printability.
Keywords: *Coating, Printability, Microcapsulation, Ammonium polyphosphate, Flame retardancy*

Introduction

In the paper industry, as in other industries, circular production and biocompatibility is an increasingly important concept. It is expected that the environmental effects of the new features brought to the paper will be at the lowest level with the continuous increase in the desired features from paper. Some of the properties required from paper can be listed as smooth surface properties, printability, gloss, mechanical resistance properties, and resistance to heat and moisture. Recently, the importance of fire-resistant papers has been increasing especially in valuable papers, librarianship and wallpapers. Although the flame-retardant feature is not new in paper or polymer-based materials, this feature is traditionally gained with toxic substances that have environmental effects. Two methods can be used for flame retardant property in papers (Li and Wu, 2012). The first method is to add a flame retardant to the formulation in paper production. However, homogeneous distribution is very important in this method, otherwise it will not gain flame retardant property and there may be other problems (Ozcan et al., 2020). In addition, in this method, it functions as a flame retardant filler and causes printing problems by negatively affecting the flexibility of the paper. The second method is to make a single or double-sided coating on the paper. Besides being a very practical method, since a very thin film layer is applied to the surface, it does not cause problems in flexibility and printing problems do not occur.

Microencapsulation is a rapidly developing and growing technology that is being used in many sectors today. It can be defined as the coating of a material with a uniform film in the form of microparticles. Microcapsules consist of two parts, the core and the shell. The core consists of an active substance that can be solid, liquid or gas, while the shell protects the core material and is made of natural or synthetic polymers. The purpose here is to keep the core material in a suitable shell, to protect it from some environmental effects, and to extend its usage or durability life (Kandirmaz et al., 2020).

In recent years, there are studies showing that many polymers such as polypropylene, polyethylene, acrylonitrile butadiene styrene and Nylon 6 are used as flame retardants (Xia et al., 2008; Xie et al., 2006; Venkatram et al., 2018; Bee et al., 2018; Rezvani Ghomi et al., 2020). Ammonium polyphosphate (APP) is a material with a high phosphorus content that yields phosphoric acid, N2 and ammonia when heated. Therefore, it can be used for flame retardancy of many organic polymers (Qu et al., 2014).

Material and Methods

Materials

Ammonium polyphosphate, cyclohexane, glycidyl methacrylate, benzoyl peroxide and butanone were purchased from Sigma-Aldrich, Germany. Starch was obtained from Merck, Germany. Process magenta ink was purchased from TOYO ink Co., Turkey. In this study, 80 g/m^2 office papers were used for coatings. Papers were obtained from UPM, Finland.

Methods

The fabrication of microencapsulated ammonium polyphosphate was seen in Figure 1. Encapsulated ammonium polyphosphate produced in accordance with the procedure described by Yang et. al., 2021. 200 g ammonium polyphosphate and 500 mL cyclohexane were loaded into a 1000 mL three necked reaction flask at 50 °C with stirring 1000 rpm for 20 minutes. After 25 g glycidyl methacrylate was transferred the reaction flask continued mixing for half an hour, then the temperature was increased to 80 °C. 0.4 g benzoyl peroxide was solved in 50 mL of butanone, and the resulting mixture was added to the reaction flask at this temperature and allowed to stir overnight. The resulting mixture was cooled to room temperature, washed with butanone, and dried in a vacuum oven at room temperature.

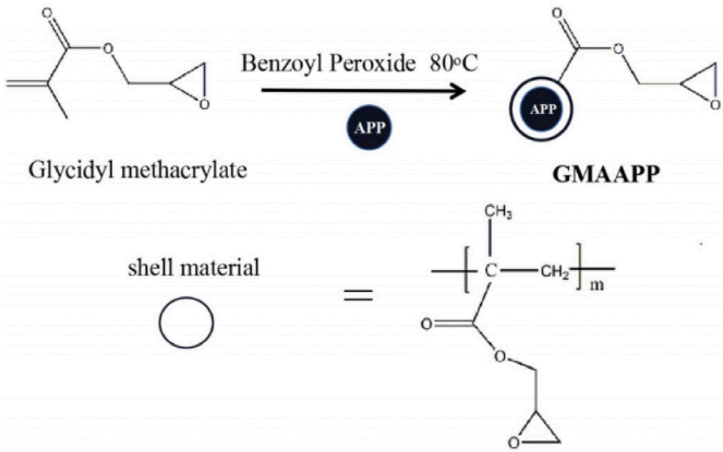

Fig 1. The encapsulation process of ammonium polyphosphate

100 g Polyether polyol (LY-4110), 1 g triethylenediamine, 2 g Silicone oil foam stabilizer and 3 g triethanolamine and 5 g distilled water and synthesized encapsulated ammonium polyphosphate were added intı reaction flask. And the flask was stirred vigorously. After 150 g Polymethylene polyphenyl polyisocyanate was added to the mixture. The mixture was turned to White. The resulting precipitate was filtered. And then matured in an oven at 80 °C to complete the polymerization reaction.

The contents of the formulations prepared in order to provide flame retardancy properties to office type papers by using the obtained capsules are given in Table 1.

Table 1. Formulation of coatings

Sample	Starch (g)	Water (g)	Capsulated Ammonium polyphosphate (g)
F0	7.5	92.5	0
F1	7.5	92.5	1
F2	7.5	92.5	3
F3	7.5	92.5	5
F4	7.5	92.5	7.5

In the preparation of the coating formulation, a mixture of 7.5 % starch and water was first prepared and mixed for about 15 minutes at 90 °C. The formulations were prepared by cooling the mixture to 55 °C and adding encapsulated ammonium polyphosphate at different rates. The obtained paper coating formulations were coated with a laboratory type K303 Multi-coater (RK Print Coat Instruments Ltd, United Kingdom) with using Mayer Rod 2, at room temperature onto amount of 0.1 g/m^2 to one side of 80 g/m^2 paper at a speed of 2 m/min. The average thickness of the coatings was set to 3 µm. The color, gloss contact angle-surface energies of the obtained coatings were determined by X-Rite eXact spectrophotometer and BYK Gardner glossmeter, PGX goniometer respectively.

Uncoated and enhcapsulated ammonium polyphospate coated papers were printed with IGT C1 test printing machine using equal amounts of process magenta ink (DIN ISO 2846-1). Printing parameters; 300 N printing pressure and 0.2 m/s printing speed. The ink film thickness of all printed samples was measured as 8 µm. The color measurements of the prints on different coated paper were made by CIEL*a*b* method using X-Rite eXact spectrophotometer according to ISO 12647-2:2013 standard. The measurement conditions of the spectrophotometer are determined as a polarization filter with 0°/45° geometry with 2 observer angles with D50 light source in the range of 400-700 nm. The difference between the colors of the different prints was calculated according to formula below according to the CIE ΔE 2000 ISO 13655 standard.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (1)$$

The gloss measurements of coated papers were carried out with BYK Gardner GmbH micro gloss 75° geometry in accordance with ISO 82541:2009, and the gloss measurements of prints with BYK Gardner GmbH micro Tri-gloss 60° geometry in accordance with ISO 2813:2014.

The flammability characteristics of composites were determined by LOI. The LOI values of the coatings were measured by using a Fire Testing Technology (FTT) type instrument.

Results

In order to determine whether ammonium polyphosphate is encapsulated or not, the FTIR spectrum of both ammonium polyphosphate and encapsulated ammonium polyphosphate was examined and given in Figure 2. Ammonium polyphosphate is shown in black and the spectrum of encapsulated ammonium polyphosphate is shown in red. When the spectrum is examined, N-H stretching vibration can be clearly seen at 3200 cm^{-1}. In addition, P-O and P=O can be seen at 1100 cm^{-1} and 1250 cm^{-1}. Besides, the peaks at 1020 cm^{-1} and 805 cm^{-1} are PO2 and P-O-P asymmetric stretching peaks, respectively. In the encapsulated ammonium polyphosphate, in addition to these peaks, the stretching peak of the C=0 bond was observed at 1730 cm^{-1}, while the C=C at 1640 cm^{-1} disappeared. This shows that the encapsulation was successful. The results are consistent with the literature (Tang et al., 2014).

Figure 3 shows the SEM photograph showing the particle sizes of ammonium polyphosphate and microencapsulated ammonium polyphosphate. The particle sizes of ammonium polyphosphate and microencapsulated ammonium polyphosphate are around 10 µm. However, the surface of the clean and smooth ammonium polyphosphate became rougher by encapsulation. The results are in line with the literature (Chen et al., 2015).

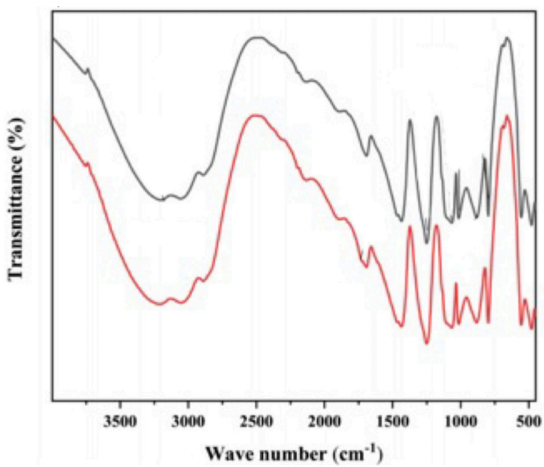

Fig 2. FTIR spectrum of ammonium polyphosphate and encapsulated ammonium polyphosphate

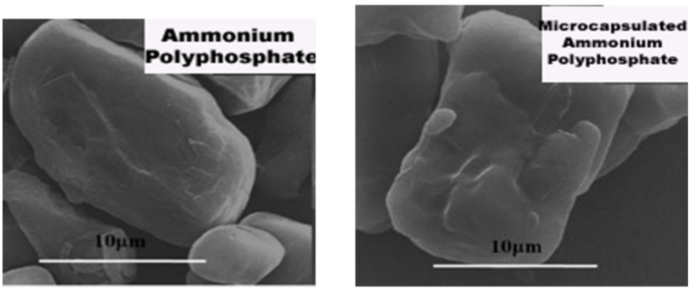

Fig 3. SEM images of ammonium polyphosphate and encapsulated ammonium polyphosphate

Coatings containing encapsulated ammonium polyphosphate were prepared in the compositions in Table 1 and coated on the paper surface without any problems. The thicknesses of the resulting coatings were set to 3 µm. One of the main parameters for printing on the obtained papers is the establishment of the relationship between the ink and the substrate without any problems. This is a relationship that depends on the surface energy and the contact angle. In this sense, the contact angles and surface energies of the papers were measured and given in Table 2 in order to be able to print without problems. When Table 2 was examined, it was determined that the contact angles of all coatings containing encapsulated ammonium polyphosphate were lower than the coating containing only starch. When the literature is examined, it has been observed that the contact angle of the coatings containing ammonium polyphosphate decreased due to the -NH4 contact angle groups on the ammonium polyphosphate, and the contact angle of all coatings to which the ammonium polyphosphate was added decreased up to 10° (Zheng et al., 2014a). For this reason, the materials become weakly resistant to water and moisture. For this purpose, it was aimed to use encapsulated ammonium polyphosphate in our study. As seen in Table 2, the contact angle decreased in coatings containing encapsulated Ammonium polyphosphate. However, it appears to have considerably higher water resistance and contact angle than this unencapsulated ammonium polyphosphate. As the amount of flame retardant material in the coating increases, the contact angle decreases more. In short, coatings to which ammonium polyphosphate added can be better printed with water-based inks and are water-labile, while coatings containing encapsulated polyphosphate have been made water-resistant and more suitable for oil-based ink. The results are consistent with the literature (Zheng et al., 2014b).

Table 2. Contact angle and surface energies of coatings

Sample	Contact Angle (°)	Surface Energy (mJ/m^2)
F0	72.3	38.9
F1	51.0	42.7
F2	49.6	45.9
F3	40.0	52.7
F4	35.5	58.4

The flame retardancy properties of microencapsulated ammonium polyphosphate content 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 encapsulated ammonium polyphosphate into the F0 coating, which shows extremely flammable properties. As the amount of encapsulated ammonium polyphosphate in the content increased, the fire resistance increased and reached approximately double in the coating containing 10%. Ammonium polyphosphate gives the composite material a flame retardant property with the formation of ash, which causes a decrease in mass and heat transfer between the solid phase and the burning surface. Similar results can be seen in the literature (Savaş and Doğan, 2018).

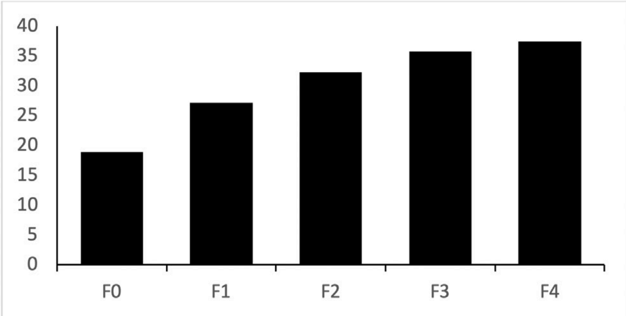

Fig 4. LOI values of coated papers

Table 3 shows the CIEL*a*b* color, gloss and color differences of the encapsulated ammonium polyphosphate coated paper. Untreated base paper was used as reference. When the color differences were examined, it was determined that the F0 starch coated paper color shifted slightly to yellow compared to the base paper. This is an expected result (Wang et al., 2021). It was determined that when encapsulated ammonium polyphosphate was added to the coating formulations, the color shifted to a small amount of blue. This is due to the color of the added ammonium polyphosphate and is an expected result. The color change (ΔE) is in the range about 0.44-1.35. It is also within the acceptable reference range according to ISO 12647-2:2013. When the gloss values were examined, it was determined that all coatings were at least 4.5 times glossier than the base paper. This is due to the fact that the roughness on the paper surface is covered by the coating and the diffuse reflection is prevented. Thus, the papers became glossier. The results are similar to the literature (Chinga and Helle, 2003).

Table 3. Color and gloss values of flame retardant paper coatings

Sample	L*	a*	b*	ΔE_{00}	Gloss
F0	95.46	2.91	-10.21	Standard	5.7
F1	95.31	2.87	-8.45	1.27	28.2
F2	95.28	3.02	-10.84	0.44	27.5
F3	94.93	3.17	-11.34	0.85	27.2
F4	94.41	3.49	-11.82	1.35	26.9

Offset test prints were made on coated papers containing encapsulated ammonium polyphosphate in different ratios, and color and gloss characters were examined and given in Table 4. When the color character is examined in Table 4, it is determined that the results are parallel to the non-printed papers. In other words, it was determined that the coating containing starch slightly shifted the color of the paper to yellow, while the coatings containing encapsulated ammonium polyphosphate slightly shifted the color to blue. The results obtained are compatible with the literature (Ozcan et al., 2020). Since the ΔE differences in the unprinted papers are tolerated by the magenta ink in printing, the color difference has decreased in the prints. The color differences of the prints on all coatings are within the tolerance limits according to ISO 12647-2. When the gloss values were examined, parallel results were obtained. The reason for the decrease in gloss of all prints is that the pigment in the ink distributes the light slightly. Thus, surface roughness and diffuse reflection increased, gloss decreased.

Table 4. Color and gloss values of printed papers

Sample	**L***	**a***	**b***	ΔE_{00}	**Gloss**
F0	47.24	73.94	-3.55	Standard	1.9
F1	47.09	73.86	-1.63	0.92	19.8
F2	46.87	74.05	-3.94	0.42	17.6
F3	46.75	74.21	-3.47	0.50	17.2
F4	46.38	74.59	-3.95	0.82	16.6

Conclusions

In this study, ammonium polyphosphate was encapsulated to make flame retardant coatings more resistant to water. It has been proven by FTIR that the capsules were successfully synthesized, and the size of the capsules obtained was measured by SEM at 10 µm. Starch-based coating formulations were prepared with the obtained capsules and successfully coated on the office paper surface. The contact angle and surface energy of the coatings were measured. The contact angle of ammonium polyphosphate in the literature has been increased by encapsulation, so that the coated papers produced can be printed with oil-based offset ink. When the LOI properties of the coatings containing encapsulated ammonium polyphosphate in the coatings were examined, it was determined that the paper gained flame retardancy property and the property increased with the increasing ammonium polyphosphate ratio. When the color properties of the coated papers were examined, it was measured that the color difference decreased even more with the prints where the color shifted to blue very little. It was determined that the surface became smooth and the gloss increased with the coatings made. As a result, papers that can be printed with oil-based ink with high flame retardancy properties have been successfully produced with encapsulated ammonium polyphosphate.

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