

Enhancing the Flame Retardancy of Low Concentrations of Biodegradable Poly(vinyl alcohol) Hydrogels with Resorcinol Bis(diphenyl phosphate)

Jalaj Mehta¹, Lauren Stiefel², Yuan Xue³, Miriam Rafailovich³

¹Hauppauge High School, Hauppauge, New York, 11788,

²Samuel H. Wang Yeshiva University High School for Girls, Holliswood, New York, 11423,

³Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, 11794

Flame retardant components are necessities to a firefighter's protective gear, such that more eco-friendly advancements in this technology have become more pertinent in an effort to better ensure the safety of both firefighters and victims in fire. Conventionally, flame retardants have been created from only slightly biodegradable superabsorbent polymers with extremely high water content [1]. Generally these superabsorbent polymers are derived from acrylic acid and acrylamide and unless these are oligomers it is likely that they are not biodegradable [2,3]. In lough of these facts the primary goal of this research was to synthesize a biodegradable hydrogel flame retardant that is as efficient as its less environmentally friendly equivalents.

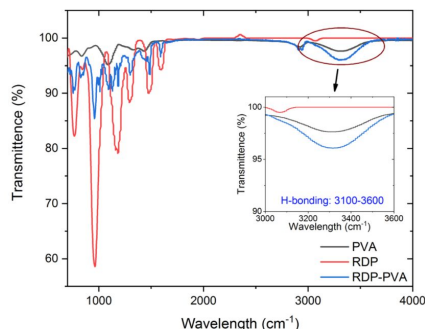
To create the hydrogel samples we used a cyclic freezing and defrosting procedure consisting of 24 hours in a -20 degree Celsius freezer and then 1 hour of defrosting at room temperature 3 times for each set of samples. Our samples consisted of various concentrations of starch, resorcinol bis(diphenyl phosphate)

(RDP), and RDP-coated starch suspended/dissolved in multiple bases that were created through the addition of poly(vinyl alcohol) (PVA) and RDP-coated PVA in deionized water. The samples created can be seen in Figure 1.

	Control	5% RDP	16.67% RDP-Starch
1% PVA	A	B	C
1% RDP-PVA	D	E	F
2% PVA	G	H	I
2% RDP-PVA	J	K	L
4% PVA	M	N	O
4% RDP-PVA	P	Q	R

Fig. 1- Hydrogel make up and concentration of each sample

Starch and RDP were chosen as a result of their performance as flame retardants and chemicals with excellent charring both in our preliminary testing with gelatin based hydrogels and in previous literature. We also suspected that the free hydroxyl groups on starch and the double bonded, outstretched oxygen on RDP would interact well, likely through hydrogen bonds, with the surface of the PVA molecules in the PVA based hydrogel. The PVA was also chosen as a result of its positive performance and flame retardant properties along with strong mechanical properties and flexibility in literature [4,5,6]. All the samples were 5 grams and we created 3 identical versions of each solution for testing with Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), burn tests and Rheometry. FTIR revealed the interactions between the gel and the



particles in each sample, TGA identified the degradation of the samples in relation to temperature, the burn tests helped us compare the effectiveness of each sample in terms of charring, temperature, and amount of gel/skin remaining. Rheometer tests gave us in depth information on the mechanical properties of our gels, the most important being whether they were shear thinning or thickening.

Fig. 2- FTIR spectrum of RDP/PVA We derived from the FTIR results in Figure 2 that hydrogen bonds were present in the PVA and RDP-PVA, and learned that the gels were mainly shear-thinning through the rheological studies. Overall samples *R* and *O* performed the best in terms of the completeness of the char layer formed, the lowest max temperatures, both being below 65°C (the temperature for a burn to almost instantaneously be second degree), the amount of gel remaining with *R* having .60 grams of gel remaining and *O* having .51 grams remaining. Additionally these two samples displayed clear shear-thinning which is useful for flame retardants. Compared to previous results, our gels are better while still retaining their biodegradable nature, as they keep the temperature under 65 degrees celsius for longer than 200 seconds [7]. With the knowledge that the hydrogels synthesized in this experiment behave in the ways described and that 4% RDP-PVA with RDP-Starch hydrogels and 4% PVA with RDP-Starch hydrogels perform the best, in future studies we aim to test additional concentrations of RDP-PVA, starch, RDP-starch, and PVA to determine the optimal combination for a flame retardant.

1. Introduction

Firefighters have a high risk of skin burns when trying to save the lives of civilians. 2,835 United States firefighters suffered from burn-related injuries in 2017 alone [8]. The current flame retardant fabrics are not capable of protecting firefighters' faces and skin. There is currently no published research on flame-retardant hydrogel used for skin protection, which, if successfully developed, would help to protect firefighters from potential burns. The hydrogel must also be non-toxic and non-irritating on human skin. Commercial flame retardants used on non-living surfaces are toxic and irritate skin, therefore a new non-toxic hydrogel is needed for application on human skin.

In recent years, many efforts have been made to further eliminate toxic chemicals in intumescent fire-retardants, a system that includes a carbonizing agent and an acid source to catalyze char formation [9]. Several alternatives have been used, one of which is starch. Starch consists of a plethora of adjoining glucose units, and possesses thermal stability and charring capabilities. [10]. Starch is inexpensive, environmentally- friendly, biodegradable, and can be found in various crops like corn, wheat and rice [11]. Therefore, starch had been successfully incorporated into fire retardants to enhance their performance [12].

Resorcinol bis (diphenyl phosphate), RDP, a biodegradable phosphate with fire retardant properties, has been recently used to replace other toxic phosphates [13]. It suppresses flames by promoting surface charring through dehydration and esterification [14]. However, RDP is a liquid with high mobility, so attaching it to surfaces with hydroxyl groups, like cellulose and MMT-clay will reduce its bubbling under high temperature [15]. Another important property that fire retardants applied on skin must possess is the ability to be adhesive to human skin. Creating an adhesive hydrogel with a high hydrophilicity to human skin will address this issue. Poly(vinyl alcohol, or PVA, solutions was mixed with the RDP and went through a cyclic freezing and defrosting process to form hydrogels. PVA has a relatively simple structure with a hydroxyl group, and it physically cross links after undergoing a cyclic freezing and defrosting cycle [16].

This research presents a non-toxic and non-irritating method of protecting human skin from fire. The hydrogels demonstrated hydrophilicity, thermal stability and excellent rheological

performances. Combined with its non- toxicity, these hydrogels have the potential to save the skin and lives of firefighters.

2. Materials and Methods

2.1 Materials

The RDP and PVA used in this research was purchased from ICL (Israel Chemicals Ltd.) Industrial Products and its brand name is Fyrolflex RDP ®. The All Deionized (DI) water used was generated from a Milli-Q® Water Purification System.

2.2 Preparation of RDP- coated starch and RDP- coated PVA

To prepare the RDP-coated starch, RDP and starch were weighed with a Mettler Toledo XPE204 analytical balance in a 3:7 weight ratio. After the mixture was placed in a 200 mL beaker and stirred with a metal spatula for 5 minutes, the beaker was placed in a Hotpack vacuum oven for 10 minutes and kept under 40 °C. The powder was then centrifuged three times with an ARE-250 THINKY for additional homogenization. The centrifuge spun at 750 rotations per minute (rpm) for 5 minutes, and then sped up to 2000 rpm for 10 seconds. The mixture was then transferred back into the beaker and kept in the Hotpack vacuum oven at 60 °C for 24 hours. The RDP-coated PVA was prepared by mixing RDP and PVA in a 1:4 weight ratio, and then heating it and centrifuging the mixture the identical to the RDP-coated starch was prepared.

2.3 Hydrogel preparation

The RDP-coated PVA prepared in 2.2 was separated and each sample was mixed with different volumes of DI water to create different concentration solutions of RDP-coated PVA. Additionally, the same concentration solutions were created with non-coated PVA and DI water. The concentrations were 1%, 2% and 4% PVA solutions in DI water, and 1%, 2% and 4% RDP-coated PVA solutions in DI water. Once these concentrations were made in 200 mL beakers, and the beakers were placed them on a hot place to increase the solubility of the DI water to dissolve all of the PVA and RDP- coated PVA. After 4 hours on the hot plate, the solutions were removed and fixed percentages of RDP and the RDP-coated starch prepared in 2.2 were added, while leaving one sample of each PVA and RDP-coated PVA without any addition to create a control. Figure 1 depicts the make up and concentration of each sample.

These samples were poured into petri dishes, and they were put through a cyclic freezing and defrosting cycle to form hydrogels. The petri dishes were placed in a freezer at -20°C for 24 hours, and then taken out of the freezer to defrost at room temperature for 1 hour. They were then placed in the freezer for another 24 hours, and taken out to defrost. This cycle was repeated once more, until gel like structures were formed. Many of the lower concentration PVA gels, like the 1% and 2% gels didn't completely gelatinize in this process, so they weren't tested in the flammability assessments.

2.4 Flammability assessments

To test the samples, each hydrogel prepared in 2.3 was placed on a thin layer of sheep skin membrane in a 2cm x 2cm x 0.5cm aluminum tin. The sheep skin membrane was cut to 2cm x 2cm to fit the bottom of the tin, and the gelatinized hydrogel sample was placed on top. Each hydrogel sample gelatinized differently; Some became complete gels while some had a thin layer of gel on top and the non gelatinized liquid underneath. A Bernzomatic Fat Boy blowtorch fueled with propane was used to burn the gels for 3 minutes, and observed how they charred. Figure 3 depicts the device I engineered a device to measure the temperature under the sheep skin membrane as the torch heated the gel. The pan was mounted on the stand using three spring clamps to fixed positions, and the distance between the surface of the samples and the tip of the blowtorch was 5cm.



Fig. 3- Device used to perform burn tests.

I analyzed the time it took for each gel to reach 40°C , 60°C and 80°C , and recorded the maximum temperature of each gel after a 180- second burn time using an Omega Thermocouple.

2.5 Further Sample Study

Tests were performed to better understand how the structure of the gels affected the way they performed in the flammability assessments described in 2.4. Thermal Gravimetric Analysis (TGA) is a method through which the thermal degradation properties of a material is discerned. The temperature a material is exposed to is slowly increased and the deterioration of the material is observed. The test was performed on a TGA/SDTA851 (Mettler Toledo, USA), and was heated from 35°C to 750°C at a rate of $10^{\circ}\text{C}/\text{minute}$ under 20 mm/min nitrogen flow. The

results were graphed, and the first derivative of the graph was included. The peaks on the derivative of the curves represent the points of fastest degradation and the flat lines represent periods of charring. This is important, because measuring which samples char fastest will help ascertain which samples will perform better on the flammability assessments, and how to improve the flame retardancy of the best performing samples. I performed Rheological studies on the samples using a Bohlin Gemini HR Nano rheometer (Malvern Instruments, UK) to determine whether each sample demonstrates shear-thickening or shear-thinning properties. The steady shear rate measurements were carried out in the shear rate range from 0.001 to 10 s⁻¹. The data was graphed, and if the curve on the graph was concave down, it is likely shear-thinning, while a positive concavity is likely shear-thickening. Additionally, A Thermo Scientific Nicolet 6700 (Thermo Fisher Scientific, USA) Fourier-transform Infrared Spectroscopy was utilized to characterize the presence of hydrogen bonds between the RDP and the PVA. A calibration for the background noise is done before the actual tests. Each spectrum is an average result of thirty-two scans at a resolution and all tests are done at room temperature.

3. Results and Discussions

3.1 Flammability assessments:

After the flammability assessments described in 2.4 were performed and the data was gathered, conclusions were drawn about the ability of each sample to perform as a fire retardant hydrogel. Only the samples that formed at least a thin layer of hydrogel were tested because the goal of this research was to create a fire retardant hydrogel, and if there was no gel formed after the cyclic freezing and defrosting process, then this sample could not be used. Figure 4 demonstrates which samples were used in the burn tests; An “X” indicates that those samples weren’t tested, and a “□” indicates that those samples were tested. Only the 4% PVA and 4% RDP-coated PVA samples gelatinized enough for testing.

	Control	5% RDP	16.67% RDP-Starch
1% PVA	X	X	X
1% RDP-PVA	X	X	X
2% PVA	X	X	X
2% RDP-PVA	X	X	X
4% PVA	□	□	□
4% RDP-PVA	□	□	□

Fig. 4- Table of which samples were tested in the flammability tests

Figures 5 and 6 are examples of the variety of the gelatinization of samples when they were in the aluminum tins. Figure 5, the left image, wasn't burned in the flammability assessments because of its liquidy consistency, while Figure 6, the image on the right, was tested because of its gel-like structure. The gels with higher concentrations of PVA tended to gelatinize better, so only the 4% PVA and 4% RDP-PVA samples were tested. After the gels were tested, some trends were observed:



Fig 5&6- Picture of a liquid- like gel that wasn't burned in the flammability assessments on the left, and a completely gelatinized hydrogel on the right that was burned in the burn tests.

1. The non-coated PVA samples tended to gelatinize better than the RDP-coated PVA samples, and mostly performed better in the burn tests. As seen in Figure 7, the 4% PVA solution with no RDP or RDP-starch performed better than the 4% RDP-coated PVA solution with no RDP or RDP-starch. It took longer for the sheep skin membrane to reach the temperatures of 40°C, 60°C and 80°C, which could give burning skin more time to be extinguished and prevent higher degree burns. The non-coated PVA control sample also reached a lower maximum temperature than the RDP-PVA control sample. This same trend was noticed for the PVA and RDP-PVA samples with 16.67% RDP-starch. This

statement isn't entirely true for the PVA and RDP-PVA samples with 5% RDP, but the times at which both samples reached 40°C, 60°C and 80°C were relatively close, and the maximum temperature reached by both samples was close as well.

Sample	Time at 40-degrees Celsius	Time at 60 degrees Celsius	Time at 80 degrees Celsius	Highest Temperature
M	24 seconds	37 seconds	52 seconds	308 Celsius
N	29 seconds	67 seconds	127 seconds	256 Celsius
O	48 seconds	-----	-----	58.2 Celsius
P	10 seconds	25 seconds	46 seconds	320 Celsius
Q	18 seconds	70 seconds	140 seconds	236 Celsius
R	34 seconds	140 seconds	161 seconds	232 Celsius

Fig. 7- Table of the time it takes for each sample to reach temperatures of 40°C, 60°C and 80°C, as well as a record of the maximum temperature reached after the 3 minute burn test.

- The samples with 16.67% RDP-coated starch tended to perform better in the burn tests than the control samples with just PVA and RDP-PVA and the samples with 5% RDP added to them. Figure 8 records the weight of the gel before the burn test, and compares it with the amount of char after the burn test. After the 3 minutes, the gel completely charred over. A calculation of the percent of original gel remaining after the burn test was calculating. The two samples that had the least gel lost were the 4% PVA and 4% RDP-PVA with the 16.67% RDP-starch. The amount of gel left after the 3 minute burn period is significant because the more char remaining, the more char there is between the flame and the skin, the more the skin is protected from burns.

Sample	Weight of gel pre burn test	Weight of gel post burn test	Percent gel remaining	Percent gel lost
M	3.79 grams	.01 grams	.264%	99.72%
N	3.88 grams	.01 grams	.258%	99.74%
O	3.90 grams	1.12 grams	28.7%	71.3%
P	2.92 grams	0 grams	----	100%
Q	2.28 grams	0 grams	----	100%
R	5.60 grams	.16 grams	2.86%	97.1%

Fig 8- Percent of weight lost from each gel after burn test

Figures 9 and 10 are images of the best performing sample, sample O, before and after the burn test. This sample, consisting of 4% PVA and 16.67% RDP-PVA, took the longest amount of time to reach the temperatures of 40°C, 60°C and 80°C and had the lowest maximum temperature after the 3 minute burn time, as shown in Figure 7.

After the burn test, the top layer completely charred over, protecting the skin underneath.

After the char layer was peeled on this sample, the entire sheep skin membrane was still underneath. On the samples without RDP-starch, the gels didn't protect the skin membrane throughout the duration of the burn test, and there was minimal skin remaining.

Figure 11 shows the pictures of each sample after the burn tests. The samples with the 16.67% RDP-starch had the most char remaining after the burn test, and the samples with the 4% PVA tended to have more char than the 4% RDP-PVA samples.



Fig. 9 & 10- Figures 9 & 10 are sample O, the best performing sample. Sample O had 4% PVA with 16.67% RDP-starch. Figure 9, left, is an image of the gel before the burn test, while Figure 10, right, is an image of the same sample after the 3 minute burn test.







	Control	5% RDP	16.67% RDP-starch
4% PVA			
4% RDP-PVA			

Fig. 11- Pictures of each sample after the burn test.

3.2 Rheology analysis:

Rheological Studies reveal whether a material demonstrates shear-thickening or shear-thinning properties. If the curve is concave down, it is likely shear-thinning. All the samples possess shear-thinning properties, but two samples—4% PVA,

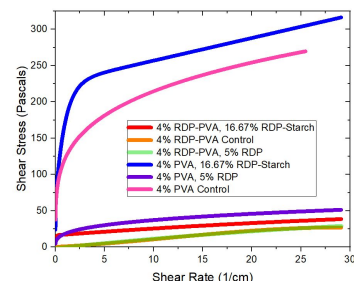


Fig. 12- Rheology analysis

16.67% RDP-Starch and 4% PVA control-- were observed to have a much larger amount of shear-thinning.

3.3 Thermogravimetric Analysis Data:

The RDP-PVA did not perform significantly better than the regular PVA hydrogel in the TGA tests and both charred at similar temperature marks, as depicted in Figure 13. The RDP-Starch performed significantly better than the regular starch in terms of heat resistance and charring, as shown by Figure 14. The second layer of char for the RDP-starch was formed well before the second layer of char for regular starch.

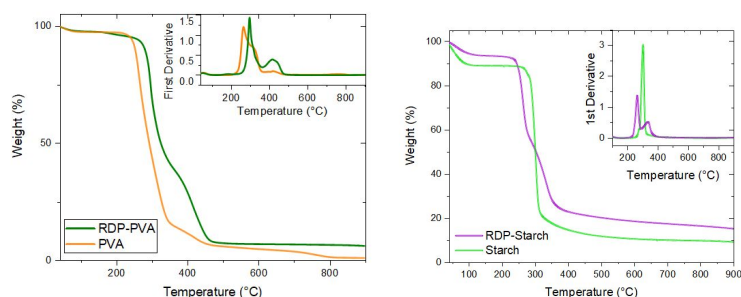


Fig. 13 & 14- Thermogravimetric analysis data. Figure 13 graphs the relationship between RDP-PVA and PVA, while Figure 14 depicts the relationship between RDP-starch and starch.

3.4 Fourier Transform Infrared Spectroscopy Data Analysis:

The FTIR graphs presented as Figures 15 and 16 revealed the interactions between the gel and the particles in each sample. These graphs present evidence of the hydrogen bonding in each of these tested samples: PVA, RDP, RDP-PVA, starch, RDP and RDP-starch.

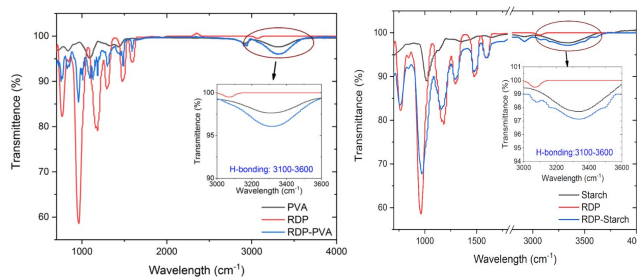


Fig. 15 & 16- FTIR data revealed the interactions between the gel and the particles in each sample.

3.5 Thermal Protective Performance:

The thermal protective performance of the PVA/RDP-Starch Hydrogel (Sample O) was

calculated and compared to the control (Sample M), a commercially available product (Fireice), and the Stoll Curve (second degree burn curve) to determine its efficacy. Sample O far outperformed all other samples including the commercially available FIREICE with a time below the Stoll Curve of 108 seconds as compared to the times of 34.8 seconds and 53.3 seconds respectively for the control and FIREICE[Figure 17].

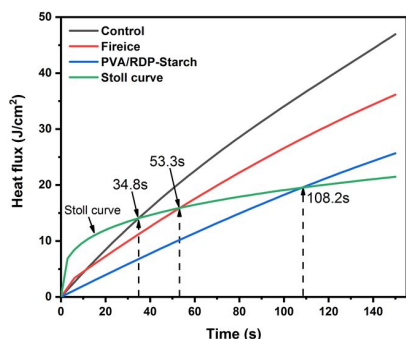


Figure 17-TPP data showed the relationship between commercially available products, the best performing hydrogel, and a control sample with the Stoll Curve.

4. Conclusion

In conclusion, this research has shown that there is a non-toxic way to protect human skin from burning. The hydrogels possessed RDP, a known fire retardant and PVA. They went through a cyclic freezing and defrosting process to gelatinize the samples. The best working sample, the sample with a 4% PVA solution with 16.67% RDP-starch, never rose above 60°C, the temperature at which human skin receives second degree burns. Additionally, in TPP tests the hydrogel out performed the commercially available FIREICE while staying below the Stoll Curve for 108 seconds. The Rheology, Thermogravimetric Analysis and Fourier Transform Infrared Spectroscopy data all supported the data that the burn exemplified. The tests explained certain trends in the data, and why some samples formed thicker char layers than others. This hydrogel research could be further developed to save firefighters' and other applicants' lives by protecting their skin from burns.

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- [1] "Ultimate Biodegradation of Ingredients Used in Cleaning Agents." *ScienceDirect*, Elsevier Science B.V., 19 Oct. 2007, www.sciencedirect.com/science/article/pii/B9780444516640500206.
- [2] "US5087513A - Flame Retardant Film and Composite Containing Superabsorbent Polymer." *Google Patents*, Google, patents.google.com/patent/US5087513A/en.
- [3] "Iranian Polymer Journal - Home Page." *Iranian Polymer Journal - Home Page*, journal.ippi.ac.ir/.
- [4] Cheng, Zhihan, et al. "Sustainable, Low Flammability, Mechanically-Strong Poly(Vinyl Alcohol) Aerogels." *Polymers*, MDPI, 5 Oct. 2018, www.ncbi.nlm.nih.gov/pmc/articles/PMC6403961/.
- [5] Bright, Danielle A., et al. "Resorcinol Bis(Diphenyl Phosphate), a Non-Halogen Flame-Retardant Additive - Bright - 1997 - Journal of Vinyl and Additive Technology - Wiley Online Library." *Journal of Vinyl and Additive Technology*, John Wiley & Sons, Ltd, 16 Apr. 2004, onlinelibrary.wiley.com/doi/pdf/10.1002/vnl.10184
- [6] "Improved Flame-Retardant and Tensile Properties of Thermoplastic Starch/Flax Fabric Green Composites." *Carbohydrate Polymers*, Elsevier, 16 Mar. 2017, www.sciencedirect.com/science/article/pii/S0144861717302928.
- [7] "Fire-Resistant Hydrogel-Fabric Laminates: A Simple Concept That May Save Lives." *ACS Applied Materials & Interfaces*, pubs.acs.org/doi/abs/10.1021/acsami.5b10538.
- [8] Fahy, R. F., LeBlanc, P. R., & Molis, J. L. (2017). Firefighter fatalities in the United States. Quincy, MA: NFPA.
- [9] Ma, H., & Fang, Z. (2012). Synthesis and carbonization chemistry of a phosphorous–nitrogen based intumescent flame retardant. *Thermochimica Acta*, 543, 130-136. doi:10.1016/j.tca.2012.05.021
- [10] Wang, J., Ren, Q., Zheng, W., & Zhai, W. (2014). Improved Flame-Retardant Properties of Poly(lactic acid) Foams Using Starch as a Natural Charring Agent. *Industrial & Engineering Chemistry Research*, 53(4), 1422-1430. doi:10.1021/ie403041h,
- [11] Wang, Y., Su, Q., Wang, H., Zhao, X., & Liang, S. (2018). Molded environment-friendly flame-retardant foaming material with high strength based on corn starch modified by crosslinking and grafting. *Journal of Applied Polymer Science*, 136(11), 47193. doi:10.1002/app.47193
- [12] M.n., P., & Song, J. (2018). Fabrication and characterisation of starch/chitosan/flax fabric green flame-retardant composites. *International Journal of Biological Macromolecules*, 119, 1335-1343. doi:10.1016/j.ijbiomac.2018.07.006
- [13] Wu, K., Hu, Y., Song, L., Lu, H., & Wang, Z. (2009). Flame Retardancy and Thermal Degradation of Intumescent Flame Retardant Starch-Based Biodegradable Composites. *Industrial & Engineering Chemistry Research*, 48(6), 3150-3157. doi:10.1021/ie801230h
- [14] Shao, N., Xue, F., Hou, L., Li, D., Gao, Y., & Zhu, X. (2019). Effects of ternary potassium containing intumescent flame retardant coating on the combustion and thermal degradation properties of reconstituted tobacco sheet. *Thermochimica Acta*, 678, 178310. doi:10.1016/j.tca.2019.178310
- [15] Pack, S., Kashiwagi, T., Cao, C., Korach, C. S., Lewin, M., & Rafailovich, M. H. (2010). Role of Surface Interactions in the Synergizing Polymer/Clay Flame Retardant Properties.

Macromolecules,43(12), 5338-5351. doi:10.1021/ma100669g

[16] Christie M. Hassan, Nikolaos A. Peppas et al., “Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods” Biopolymers · PVA Hydrogels, Anionic Polymerisation Nanocomposites pp 37-65, *Advances in Polymer Science*”, 20 October 2000, https://link.springer.com/chapter/10.1007/3-540-46414-X_2.