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Biodegradable Flame Retardant Nanocomposites

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Abstract:

The use of polymers around the world has grown exponentially and is continuing to grow, which makes the production of new and improved polymers a significant priority. Polymers often burn quickly and release a large amount of smoke and heat, and they also drip excessively resulting in further fire propagation. The smoke produced from burning these polymers can contain toxic substances that potentially lead to serious health issues and environmental damage. For these reasons, reducing the propagation of fire is a necessity in polymer development. Along with good flame retardant properties, polymers must also retain decent mechanical properties in order to effectively be applied and utilized. Another important aspect of the development of polymers is sustainability. A substantial number of conventional flame retardant polymers are not biodegradable, and the accumulation of polymer waste can result in detrimental effects on the environment and local ecosystems. Therefore, it is important to discover environmentally-friendly, low-cost, and effective flame retardant additives that can be added to biodegradable polymers to produce an ideal mass-producible polymer.

Polyhydroxyalkanoate (PHA) and Polyhydroxybutyrate (PHB) are biodegradable polymers that have a low cost of production since they are made via microbial synthesis, which is a process that can be manipulated easily. However, these polymers have minimal flame-retardant properties which limit their use in industrial applications. Melamine polyphosphate (MPP), Ammonium polyphosphate (APP), and resorcinol bis (diphenyl phosphate) (RDP) were flame retardant additives that were used in this study, along with graphene to offset the decrease in mechanical properties caused by the addition of the flame retardants. In this study, UL-94 flammability tests, tensile strength tests, and TGA analysis were used to investigate the improvement of PHB by incorporating PHA to promote charring, MPP, and APP to add flame retardancy, and graphene, cellulose, sodium clay, and RDP/RDP clay to improve mechanical strength. A majority of compositions failed the UL-94 flammability test and the few that passed had very weak mechanical properties, however, many insights were made on the effects of the materials used in this study.

Keywords: Flame retardant, biodegradable, polymer, APP, MPP, RDP, cellulose, graphene nanoplatelets, UL-94, flame test.

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1. Introduction

As synthetic and natural polymers are increasingly incorporated into our daily lives, flammability hazards have started to cause greater concern. A majority of polymers have poor flame retardant properties and this has resulted in a significant loss of life and property due to fires. Polymers tend to burn rapidly and emit a large amount of smoke and heat, and they also drip excessively resulting in further fire propagation [1]. The smoke produced from burning these polymers can release toxic substances into the atmosphere that can lead to serious health issues and environmental damage [2]. Furthermore, safety requirements revolving around the fire resistance performances of polymers are becoming more stringent, and rightfully so. According to the World Health Organization (WHO) burns and fire-related damages/deaths constitute a major public health problem. This holds especially true in second and third-world countries, where almost 96% of all burn deaths occur; there are over 300,000 deaths per year due to fire-related burns alone. First-world countries such as the US have developed safer buildings and appliances that have kept the death rate due to fires low, but now another hurdle must be crossed to keep it that way [4]. Polymers are being used in industries ranging from construction to electronics to transportation, and it is an increasing necessity to design polymers that have limited flammability hazards to replace not only petroleum-based polymers but non-flame retardant polymers as well. Most polymers not only burn easily, but they also release combustible gasses and toxic fumes as they burn. These reasons constitute the importance of creating low-cost, biodegradable, and flame retardant polymers to reduce the loss of life and property due to fires worldwide. This is easier said than done, and it is very difficult to find and create perfect compositions of polymers to obtain the properties desired.

Increasing flame retardancy of polymers sounds simple on paper, but it is actually complicated as flammability hazards are composed of a combination of factors, including: ease of self-extinguishment, ignitability, flame propagation, smoke production, moke toxicity, and more. Different polymers have different weaknesses and flammability hazards which makes it challenging to find a single solution to increasing the flame retardant properties in all polymers. A multitude of flame retardants have been found and used to increase flame retardant properties in polymers but at the cost of a substantial reduction in mechanical properties, which results in the polymer becoming ineffective in its intended application. Additionally, some flame retardants, such as halogenated additives, have been shown to cause a detrimental impact on the environment. This narrows down the options even more as it is exceedingly difficult to find an ideal composition for a polymer that gives good flame retardant properties, retains sufficient mechanical properties, and is also environmentally friendly. Different flame retardants affect varied factors of flammability as well, so the potential combinations of compositions are immoderate. Thus, it is important for researchers to work together and build off known data to advance this increasingly emerging field of developing biodegradable and flame retardant polymers.

It has been found that Polyhydroxyalkanoate (PHA) and Polyhydroxybutyrate (PHB) are biodegradable polymers that have a low cost of production since they are made via microbial synthesis [3]. This means that the rate of production can be manipulated easily. These polymers, as expected, have been shown to be very flammable and therefore have limited usage. It is desirable to increase their flame retardant properties via the implementation of flame retardants and broaden their real-world applications. Melamine polyphosphate (MPP), resorcinol bis (diphenyl phosphate) (RDP), and ammonium polyphosphate (APP) are halogen-free flame retardants that have been shown to be environmentally friendly and also effective in limiting the flammability of polymers. They are relatively low cost and they also have good processability. However, the introduction of these additives leads to a significant reduction in the mechanical properties of the polymers, and so other substances must be looked at to incorporate into the composition. Cellulose, sodium clay, graphene, and RDP clay are all materials that could potentially be used in conjunction with the flame retardants listed above to compensate for the lowered mechanical properties.

In order to assess how these compositions affect the properties of the polymers, various tests and analyses must be done. The main flammability test that is paramount in determining the flame retardancy of a polymer is the UL-94 flammability rating test. In this assessment, the polymer is vertically ignited for 10 seconds over a cotton ball two times consecutively, assuming it self-extinguishes after the first flame application. Depending on the time it takes to self-extinguish, whether the cotton ball ignites, and whether the polymer drips, a flammability rating ranging from V-0 to V-2 is designated. A thermogravimetric analysis (TGA) is also a good test to determine the thermal stability of the polymer as it is heated. Finally, to analyze the effects of the additives on the polymers in relation to their mechanical properties, an impact strength test is necessary. These three tests allow for a good basic evaluation of the flame retardant and mechanical properties of polymers.

2. Materials and Methods

2.1 Materials

The materials used in this study, the type of material, and the supplier are all given in Table 1 below. PHA and PHB are the base polymers used in this study and these are both produced from bacteria. PHA and PHB were purchased from GoodFellow. PHB has a molecular weight of 500 kg/mol, a density of 1.250 g*cm^3, and nominal granular size of 5 mm. PHA has a nominal granule size of 3 mm. One of the flame retardants used was ammonium polyphosphate (APP) which was purchased in powder form from the Beijing Institute of Technology. The APP starts to degrade at a temperature above 300°C and produces ammonia and polyphosphoric acid [5]. Melamine polyphosphate is another flame retardant used and it was purchased in powder form from BOC Sciences. Resorcinol bis(diphenyl phosphate) (RDP) in liquid form was purchased from ICL located in Israel. Cellulose in powder form was purchased from Sigma-Aldrich. Sodium clay in powder form was purchased from Southern Clay Products, Inc. Graphene nanoplatelets (GNP) in powder form was purchased from XG Sciences, Inc. Lastly, RDP clay was made in the laboratory with 20% RDP and 80% Cloisite.

2.2 Polymer Sample Preparation

As depicted in Table 3, in the results section, 22 samples were made with varying compositions using materials such as PHA, PHB, APP, MPP, NA+ Clay, RDP, Cellulose, RDP clay, and graphene nanoplates. RDP clay was prepared with 20% RDP and 80% Cloisite which was combined in the Thinky Mixer at 2000 rpm for 8 minutes. For each sample, a specified weight percent composition was prepared based on 50 grams. The materials were precisely measured in grams using a My Weigh iBalance 201 Commercial Scale. The measured materials were poured into the C.W. Brabender and blended at 180°C and

Table 1. The materials used in this research study, along with what form the material was in and where the materials were acquired from.

Material	Type	Supplier
Polyhydroxybutyrate (PHB)	Granule	GoodFellow
Polyhydroxyalkanoate (PHA)	Granule	GoodFellow
Ammonium Polyphosphate (APP)	Powder	Beijing Institute of Technology
Melamine Polyphosphate (MPP)	Powder	BOC Sciences
Resorcinol bis(diphenyl phosphate) (RDP)	Liquid	ICL Group Ltd.
RDP Clay (20% RDP, 80% Cloisite)	Powder	Prepared in laboratory
Cellulose	Powder	Sigma-Aldrich
Na+ Clay	Powder	Southern Clay Products, Inc.
Graphene Nanoplatelets (H-5GNP)	Powder	XG Sciences, Inc.

a rotational speed of 100 rpm. The blended composition was cut into small pieces and placed in a mold. The scaffold was transferred to the Carver hot press and allowed to uniformly melt at 356°C. After the composition was fully melted, it was cooled to room temperature. The sample was carefully removed from the mold and went onto further testing.

2.3 Flame Retardant Testing

The flame retardant properties of the samples were analyzed by vertical UL-94 flammability testing, as shown in Figure 1. This procedure is done by exposing the sample to an open flame for 10 seconds and then removing the sample to observe its flame extinguishing properties. This step is repeated again to observe any changes in the extinguishing properties. Throughout this test, a cotton ball is placed underneath the sample to examine the dripping. In some cases, the dripping would transfer the flame to the cotton ball and cause it to ignite. Furthermore, after the tests are completed, the charring is observed. The results are analyzed based on Table 2.

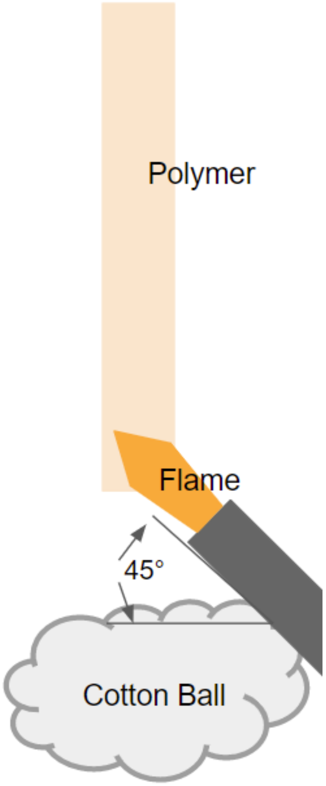
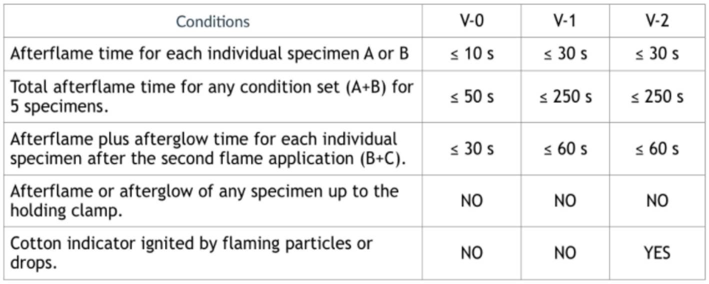


Figure 1. Visual representation of the Ul-94 flammability test setup.

Table 2. A table showing how results from the flame test were analyzed and flammability ratings were determined [6].



Conditions	V-0	V-1	V-2
Afterflame time for each individual specimen A or B	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame time for any condition set (A+B) for 5 specimens.	≤ 50 s	≤ 250 s	≤ 250 s
Afterflame plus afterglow time for each individual specimen after the second flame application (B+C).	≤ 30 s	≤ 60 s	≤ 60 s
Afterflame or afterglow of any specimen up to the holding clamp.	NO	NO	NO
Cotton indicator ignited by flaming particles or drops.	NO	NO	YES

2.4 Mechanical Testing

The polymers were prepared in the same method as discussed prior but were placed in a different mold with dimensions of 64 x 12.7 x 3.2 mm and a V-shaped notch. The samples from this mold were used for impact strength testing with the Tinius Olsen Pendulum Impact Tester which measures the impact resistance of the sample. The resilience or impact strength of the sample is calculated by dividing the impact value by the thickness of the sample (J/m).

2.5 Thermogravimetric and Derivative Thermogravimetry Analysis

Thermogravimetric Analysis (TGA) was conducted with the Thermogravimetric Analyzer to measure the weight loss over time as the temperature increases from 50°C to 600°C by 10°C/time. First, the machine is tarred and calibrated. Then, a small piece of the sample is cut off and placed on the scale in the machine and the test is begun. The results were plotted in a weight loss vs. change in temperature graph. The derivative weight loss as the temperature increases was also looked at: Derivative Thermogravimetry (DTG).

3. Results

3.1 Ul-94 Flammability Test Results

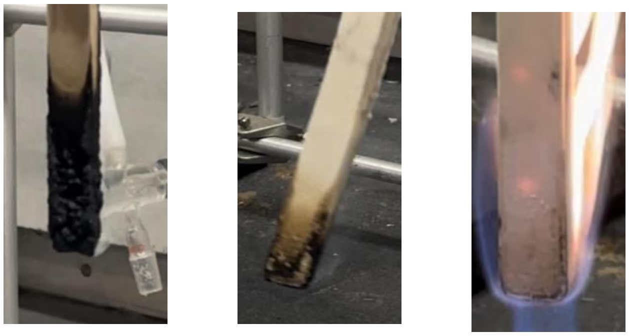
Table 3. Table above represents Ul-94 flame test results of all compositions prepared throughout the duration of this study. Various blends were made using PHA, PHB, APP, MPP, RDP, RDP Clay, Cellulose, Na+ Clay, and GNP.The majority of the samples prepared failed, but a select few combinations were successful.

Composition	Attempt 1 Extinguishing Time	Attempt 2 Extinguishing Time	Drip	Cotton ignited	Rate
APP					
80PHB/20APP	>30s	-	NO	NO	FAIL
90PHB/5PHA/5APP	< 10s	>1 min	YES	YES	FAIL
88.8PHB/4.7PHA/4.7APP/1.8Sodium Clay	> 30s	-	YES	YES	FAIL
88.8PHB/4.7PHA/4.7APP/1.8Cellulose	> 30s	-	NO	NO	FAIL
89.6PHB/4.7PHA/4.7APP/1Cell+RDP	> 30s	-	YES	YES	FAIL
87.6PHB/4.7PHA/4.7APP/1Cellulose	> 30s	-	YES	YES	FAIL
PHB+MPP					
85PHB/15MPP	> 30s	-	NO	NO	FAIL
60PHB/40MPP	<10s	>30s	NO	NO	FAIL
80PHB/19MPP/1RDP	> 30s	-	NO	NO	FAIL
80/PHB/19.5MPP/0.5RDP	<10s	>30s	YES	YES	FAIL
79.5PHB/20MPP/0.5RDP	<10s	> 30s	YES	YES	FAIL
79.7PHB/20MPP/0.3RDP	<10s	> 30s	YES	YES	FAIL
77PHB/22.5MPP/0.5RDP	<10s	> 30s	YES	YES	FAIL
75PHB/24.5MPP/0.5RDP	<10s	> 30s	YES	YES	FAIL
70PHB/20MPP/10RDP Clay	<10s	> 30s	NO	NO	FAIL
65PHB/25MPP/10RDP Clay	<10s	> 30s	NO	NO	FAIL
PHA+MPP					
80PHA/15MPP/5GNP	<10s	>30s	NO	NO	FAIL
80PHA/20MPP	1s	3s	NO	NO	**V-0**
PHA+PHB+MPP					
50PHB/25PHA/25MPP	<10s	<10s	NO	NO	**V-0**
48PHB/25PHA/25MPP/2GNP	<10s	27s	NO	NO	**V-1**
60PHB/20PHA/20MPP	<10s	> 30s	NO	NO	FAIL
70PHB/10PHA/20MPP	<10s	> 30s	NO	NO	FAIL

As seen in Table 3, there were three successful samples 80PHA/20MPP, 50PHB/25PHA/25MPP, and 48PHB/25PHA/25MPP/2GNP. The samples containing 80% PHB and the sample containing 50% PHB had a V-0 rating with no dripping. Despite the impressive flame retardant results, these samples were brittle. The mechanical properties of two out of the three samples were too weak to move on to impact testing as will be seen in the impact test results. When doing the flame tests of the various compositions made, even though most of them failed, a lot of important observations were made regarding the materials used. It is a collective goal for researchers in this field of study to build off research done by others, and we hope that our failed compositions are used as a baseline to create successful ones in the future.

It was found that PHA increased dripping when blended with APP, and that MPP was a much better flame retardant to use with PHB/PHA compared to APP. Furthermore, we experimented with Cellulose and Sodium Clay as additives to help decrease dripping and stabilize the molecular mixing of all the materials in the polymer. It was found that adding 1.8 w.t % Cellulose did in fact decrease dripping (adding 1 wt.% was not enough for the composition used), but the polymer still failed the flame test. Sodium clay also failed. Once we moved on to MPP as our primary flame retardant, we experimented extensively with compositions involving liquid RDP due to a prior study depicting the benefits of how liquid RDP synergizes with the dispersion of flame retardants such as APP [7]. It was noted that incorporating liquid RDP increased dripping and flammability as well, and this was presumably due to the fact that it did not disperse well in the polymer. Figure 2 shows a visual representation of the results of three flame tests, and it can clearly be seen that in the composition with liquid RDP, there are visible holes that definitely increased dripping during the flame test. We then moved on to RDP clay to see if the liquid state of the RDP was potentially to blame for the dripping. The RDP clay compared to liquid RDP had no dripping whatsoever, however, it still did not pass the flame test. Further research needs to be done on the method and amount of RDP to add to flame retardant compositions to obtain a beneficial synergistic effect.

Afterward, PHA was focused on as the main base polymer in the compositions. PHA had very good char formation with MPP and even achieved a V-0 Rating for an 80PHA/20MPP polymer. The char formation is shown in Figure 2 as well. However, it was very brittle and so it was necessary to compensate for the weak mechanical strength. Since PHB has significantly better mechanical properties than PHA, compositions were made that had majority PHB, some w.t. % PHA for charring, and MPP for flame retardancy. This led to the next successful V-0 rated flame retardant polymer: 50PHB/25PHA/25MPP. However, this polymer was still very weak and brittle, so GNP was incorporated into the polymers as a prior study showed the benefits graphene had on the mechanical properties of flame retardant polymers [8]. Finally, a V-1 rate flame retardant polymer that was relatively strong compared to the other flame retardant compositions was obtained: 48PHB/25PHA/25MPP/2GNP.



50PHB/25PHA/25MPP *80PHB/20MPP* *77PHB/22.5MPP/0.5RDP*

Figure 2. UL 94 Flame tests for 50PHB/25PHA/25MPP (left), 80PHB/20MPP (middle), and 77PHB/22.5MPP/0.5RDP (right).

3.2 Impact Testing Results

Impact test results represent the amount of energy necessary to break a sample of a specified width. The greater the value of resilience, the stronger the sample is against impact force. Figure 3 displays the impact test results of 100% PHB, 100% PHA, 66PHB/33PHA, and 48PHB/25PHA/25MPP/2GNP. Of these samples, PHB had the highest resilience of 116.1 J/m, however, this sample failed the flame test. Similarly, 66% PHB/33% PHA had the second highest resilience of 82.5J/m, but also failed the flame test. The compositions containing PHA were noticeably more brittle. These observations are confirmed by impact test results showing that pure PHA is the second weakest sample. The polymer with a composition of 48PHB/25PHA/25MPP/2GNP had the lowest impact resilience with 11.27 J/m. Despite the low resilience value, this sample had a V-1 flammability rating. All other samples that passed the flame test, were too brittle and cracked during the molding process and therefore, never got tested.

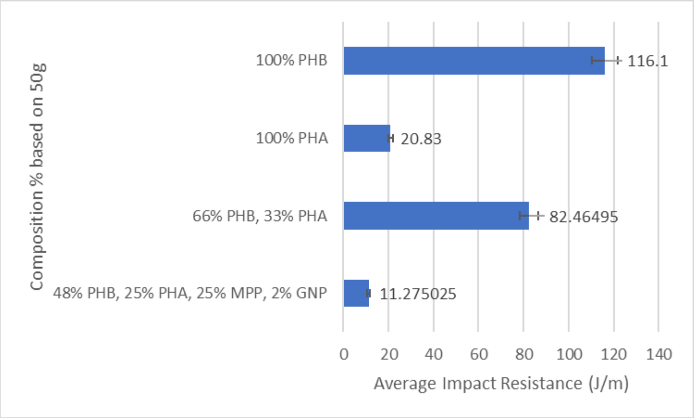


Figure 3. Average impact resistance in J/m for 100PHB, 100PHA, 66PHB/33PHA, and 48PHB/25PHA/25MPP/2GNP. The 2% GNP sample is the only sample that was able to pass a flame test with a V-1 rating. Other samples which passed the flame test were too brittle for impact testing. 100PHB, 100PHA, and 66PHB/33PHA failed the flame test.

3.3 Thermogravimetric Analysis

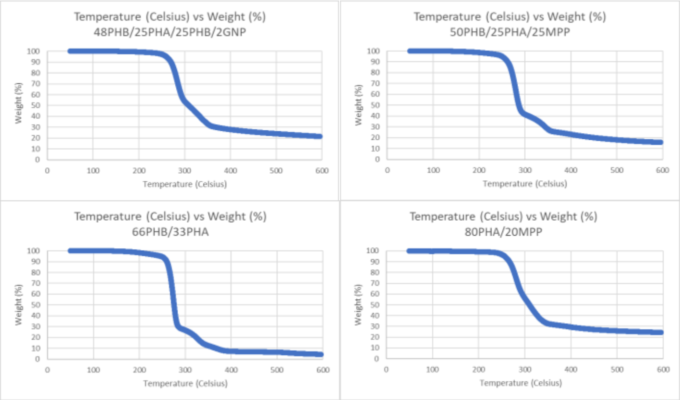


Figure 4. Temperature (Celsius) vs Weight (%) for 80PHB/20MPP, 48PHB/25PHA/25MPP/2GNP, 66PHB/33PHA, and 50PHB/25PHA/25MPP.

The temperature vs weight percent loss was determined using TGA analysis. The temperature was increased 10 degrees Celsius per minute from 50 C to 600 C. As seen in

Figure 4, clear differences can be seen in the results depending on the polymer composition. The 66PHB/33PHA composition had no flame retardant additives, and the graph was representative of that. The weight loss began at 167 C and there was near 0 w.t. % left at 600 C. The 80PHA/20MPP polymer showed much better thermal stability. The weight loss began at 238 C and there was more than 20 w.t.% of the polymer left at 600 C which is indicative of good char formation. In the 50PHB/25PHA/25MPP sample, the weight loss began at around the same temperature as the 66PHB/33PHA sample (167 C), however, the PHB/PHA sample had a steeper decline as temperature increased compared to 50PHB/25PHA/25MPP sample. There was also more w.t. % of the polymer left for the PHA/PHB/MPP sample at 600 C. The difference in the results of this sample compared to 80PHA/20MPP can be attributed to the char forming properties of PHA. Finally, for the last sample, 48PHB/25PHA/25MPP/2GNP, the weight loss began at 191 C and there was around 20% of the sample left at 600 C. Just adding 2 w.t. % GNP led to a substantial increase in thermal stability of the polymer compared to 50PHB/25PHA/25MPP. Further experiments still need to be performed in order to find the most ideal ratio of GNP to add.

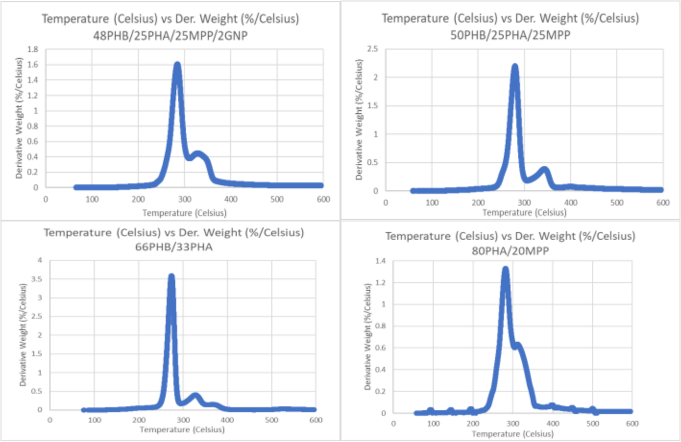


Figure 5. Temperature (Celsius) vs Der. Weight (%/Celsius) for 80PHB/20MPP, 50PHB/25PHA/25MPP, 66PHB/33PHA, and 48PHB/25PHA/25MPP/2GNP.

The temperature vs derivative weight percent loss was also looked at in the DTG analysis. This data gives the temperature at which the greatest change in weight loss occurred, or in other words, at what temperature the polymer underwent the most degradation. Figure 5 shows the visual representations of this data, but Table 4 shows the T_{peak} of each of the samples. As expected, 66PHB/33PHA had the lowest T_{peak}, and the other three samples had remarkably close values of around 283 C. The 48PHB/25PHA/25MPP/2GNP had the highest T_{peak} value of 286 C, beating 50PHB/25PHA/25MPP and 80PHA/20MPP with their values of 280 C and 282 C, respectively.

Table 4. Tpeak values of 66PHB/33PHA,48PHB/25PHA/25MPP/2GNP, 80PHB/20MPP, and 50PHB/25PHA/25MPP.

Polymer Sample	**T_{peak} (Celsius)**
66PHB/33PHA	273 C
80PHA/20MPP	282 C
50PHB/25PHA/25MPP	280 C
48PHB/25PHA/25MPP/2GNP	286 C

Overall, it was evident that the addition of GNP did seem to have a synergistic effect with MPP and PHB/PHA and increased thermal stability.

4. Conclusion

Various blends were made using PHB, PHA, APP, MPP, cellulose, RDP, RDP clay, Na clay, and graphene. A significant number of samples failed the Ul-94 flammability rating test, but a few samples passed. The flame test results suggest that MPP was a better synergistic flame retardant than APP for PHA and PHB. The introduction of MPP led to better thermal stability.

The few samples that passed the flame test were too brittle for mechanical testing. Specifically, samples with a high PHA content were brittle but had better thermal stability. PHA resulted in substantial char formation and reduced flammability compared to PHB. PHB had better mechanical properties compared to PHA, but PHA exhibited better flame retardancy. An ideal ratio of the two remains to be determined.

A small amount of graphene also offered good thermal stability. A 2-1 ratio of PHB and PHA, along with the implementation of graphene, resulted in a V-1 rated sample that was strong enough to be tested, but was found to be mechanically weak. Graphene is a good addition in polymers with MPP to increase mechanical properties without drastically lowering flame retardancy.

Implementation of liquid RDP led to increased dripping and flammability, whereas RDP clay had no dripping, but still failed the flammability test. Ineffective dispersion of RDP in the polymer resulted in the formation of holes in the sample. Liquid RDP was found not to disperse well with MPP and PHB/PHA, RDP clay was concluded to be a better option when it comes to incorporating RDP in the sample. Ideal compositions involving sodium clay and cellulose were not found.

Overall, even though a perfect composition giving good flame retardancy and mechanical properties was not found, a significant number of new insights were made on the synergistic properties between our selected materials.

5. Acknowledgements

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