DNA AS A NATURAL FLAME RETARDANT ADDITIVE FOR COMMERCIAL POLYMERS

by
JENNA HARRIS TOWSLEE

Submitted in partial fulfillment of the requirements for the degree of
Master of Science

Department of Macromolecular Science and Engineering
CASE WESTERN RESERVE UNIVERSITY

May, 2017

CASE WESTERN RESERVE UNIVERSITY

SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis of

JENNA HARRIS TOWSLEE

candidate for the degree of

Master of Science*

Committee Chair

JONATHAN K. POKORSKI

Committee Member

DAVID A. SCHIRALDI

Committee Member

GARY E. WNEK

Date of Defense

March 29, 2017

*We also certify that written approval has been obtained

for any proprietary material contained therein.

TABLE OF CONTENTS

LIST OF FIGURES

ACKNOWLEDGEMENTS

Many thanks to my advisor, Dr. Jonathan Pokorski, for his support in my undergraduate and graduate research endeavors. He has been instrumental in my development as a scientist and engineer. Also, thank you to Parker Lee for his mentoring during my early undergraduate years and his advice and guidance throughout this graduate project. I would also like to acknowledge Sergey Isarov for his contributions to the LDPE portion of the project and Dr. João Maia for the use of his group’s processing equipment. Finally, thank you to my friends in the Case Western Reserve Polymer Science and Engineering Department, especially the members of the Pokorski research group past and present.

DNA as a Natural Flame Retardant Additive for Commercial Polymers

Abstract

by

JENNA HARRIS TOWSLEE

The flame retardant properties of deoxyribonucleic acid (DNA) were investigated in melt-processed low-density polyethylene (LDPE) and polystyrene (PS). DNA showed increased compatibility with the LDPE polymer matrix relative to industrially used intumescent melamine polyphosphate (MPP). Addition of DNA to polymer substrates resulted in a significantly smaller compounding torque relative to MPP samples. Furthermore, DNA in both substrates reduced burn distance during horizontal burn testing at loading levels above 5% w/w and 10% w/w for LDPE and PS respectively. PS samples subjected to larger scale mixing with repeated heat processing had comparable flame retardant properties to single step compounded samples. This research both broadens the field of green flame retardant additives and highlights the capacity of DNA to act as an all-in-one intumescent flame retardant additive in large-scale commodity polymer applications.

CHAPTER 1

INTRODUCTION

Modern commercial products must pass stringent tests prior to being put on the market. These tests ensure consumer safety as well as minimize risk to the company producing the products. As the use of polymers has become increasingly prevalent, an area of growing concern is fire safety which has initiated the development of burn testing standards. Many safety testing organizations, including Underwriters Laboratories (UL), the International Organization for Standardization (ISO), and the American Society for Testing and Materials (ASTM), have published standards that define the level of fire resistance a polymer needs for a given classification.

There are different levels of flame resistance described by the standards which allows for differentiation between fire-resistant materials for specific applications based on the stringency of the inflammability requirement. For example, UL-94 outlines 6 levels of resistance including, from lowest to highest flammability requirement, horizontal burn (HB), vertical burn (V), and surface burn (5V). Materials that meet these standards are suitable for small attended appliances and most decorative items, unattended portable appliances, and large or immobilized objects, respectively. The standards of multiple safety testing organizations have largely been harmonized so results can give an indication of the overall regulation compliance level of a material, however specific testing methods may vary so independent testing for each organization is required [1].

In their neat state, most commodity polymers are too flammable to pass even the least stringent of these burn tests. Therefore, flame retardant additives or coatings must be added to the polymer before it can be incorporated into a fire-resistant product. While inflammable coatings may seem to be an easy solution, it is impractical for products that may experience wear, deformation, and abrasion. In this scenario, the coating would be damaged exposing the unmodified polymer to any potential ignition source. To overcome the limitations of this method, flame retardant additives are often incorporated into the bulk polymer during processing.

1.1 Commercial Flame Retardants

The most common commercial flame retardant additives are halogenated compounds, metal hydroxides, and polyphosphates. The unique chemical structure of each of these three additives gives rise to a different mechanism to stop flame spread in polymers. Understanding these basic mechanisms will help determine how novel flame retardants are able to impart flame resistance to polymeric substrates.

Prior to describing the fire prevention methods of each material, the needs of a fire must first be discussed. There are three things that combine to create a fire: heat, oxygen, and fuel. Together they make the fire triangle, shown in Figure 1.1, which effectively illustrates the fact that when any of these key components are removed a fire cannot occur or will die. All flame retardants act by removing one or more of these components, protecting the material from ignition and

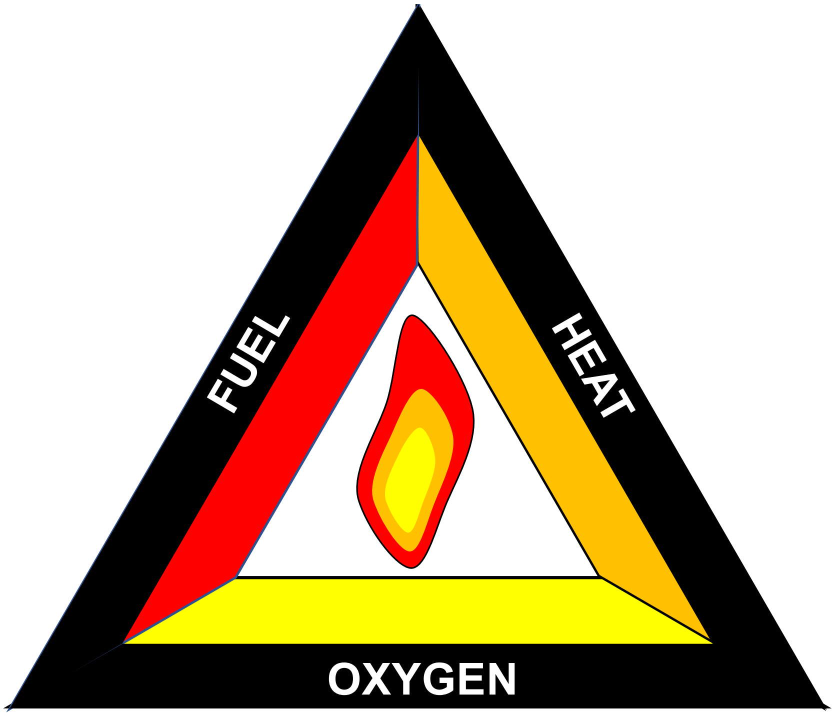

Figure 1.1. Visual representation of the fire triangle.

prolonged burning. In light of this information, the actions of each class of commercial flame retardants can be explored.

Halogenated compounds, usually polybrominated molecules, were formerly one of the more common flame retardants. They lend flame resistance by eliminating the heat for the fire. When polymers burn, the chains undergo pyrolysis, releasing small volatile radicals which can exothermically react with oxygen and water in the air. The energy released from these radicals reacting results in more pyrolysis, propagating the fire. While polybrominated molecules do not prevent the decomposition of the polymer chains, they do release radicals upon heating due to the thermally-labile carbon halogen bond which breaks at similar temperatures to those of polymer degradation [2][3]. These radicals quench those released by the polymer preventing their exothermic reactions from continuing the fire, essentially causing the fire to extinguish.

Unfortunately, halogenated flame retardants have several drawbacks. First, researchers have studied people’s exposure levels to these compounds in highly fireproofed areas, such as airplanes, and found that they are several orders of magnitude higher than normal [4]. These measurements indicate that the additives leach out of the polymers they are intended to protect which would decrease the fire resistance of the material. In addition, in 1997 polybrominated compounds were found to be human carcinogens as well as bioaccumulatory. Halogenated flame retardants also accumulate in the environment and give off toxic byproducts when burned including dioxins and corrosive hydrogen halides, potentially endangering people and other materials nearby [2][5]. Since these discoveries, these compounds are starting to be phased out of use as additives.

In an effort to move away from halogenated compounds, researchers turned to the two other classes of flame retardants, metal hydroxides and polyphosphates. Metal hydroxides, such as aluminum hydroxide, stop flame spread by eliminating both the heat and access to fuel. Metal hydroxides endothermically degrade into water and metal oxides. Not only does the flame retardant degradation take energy away from the fire, but the water produced also cools the combusting surface. In addition, the metal oxide formed during additive decomposition forms a char over the polymer, preventing oxygen from reaching the fuel and putting out the fire. However, metal hydroxides are only effective at high loading levels of up to 65 wt%, which will negatively impact the mechanical properties of the polymer being protected [2].

Polyphosphates, such as melamine polyphosphate (MPP), are also still used commercially, often in conjunction with other additives or flame retardants [6][7]. Polyphosphates are part of a category of flame retardants known as intumescents, which are materials that swell when they are heated. When heated, the phosphate groups become acidic and catalyze condensation reactions between active sites on polymer chains in the substrate, leading to the formation of a char layer at the combusting surface. The melamine decomposes simultaneously, releasing inert nitrogen gas and causing the char layer to expand. The barrier formed both prevents oxygen from reaching the polymer fuel and minimizes the escape of the byproducts of combustion, effectively killing the fire [8]. In addition, a small molecule carbon source is often added to react with the polyphosphate and generate carbon dioxide, increasing the char formation and barrier properties during burning [7].

However, like halogenated flame retardants, MPP has also been found to bioaccumulate and breaks down into neurotoxic products when it degrades under environmental conditions [2][8][9]. Therefore, it is necessary to find non-toxic alternatives to these commercially used flame retardants that not only provide good flame resistance, but also maintain the mechanical properties of the polymer.

1.2 DNA: A Natural Flame Retardant

As health and environmental effects are becoming a larger focus in industry, research has turned toward natural flame retardants as possible replacements for common commercial additives. Some natural materials have been investigated for this purpose. One example are alginate-clay aerogels which, when coated onto polyurethane foams, have been found to impart flame resistance [10]. However, few natural materials have been directly used as additives in commodity polymers. Therefore, alternative green additives capable of bulk incorporation are needed.

A promising natural flame retardant is deoxyribonucleic acid (DNA), found by the Malucelli group in Italy to possess flame retardant properties [11][12]. These capabilities were first demonstrated using a DNA solution as a coating for cotton cloth, which was then able to completely extinguish itself after being lit [11]. After seeing the success of DNA in this capacity, the reaction of pure DNA to heat

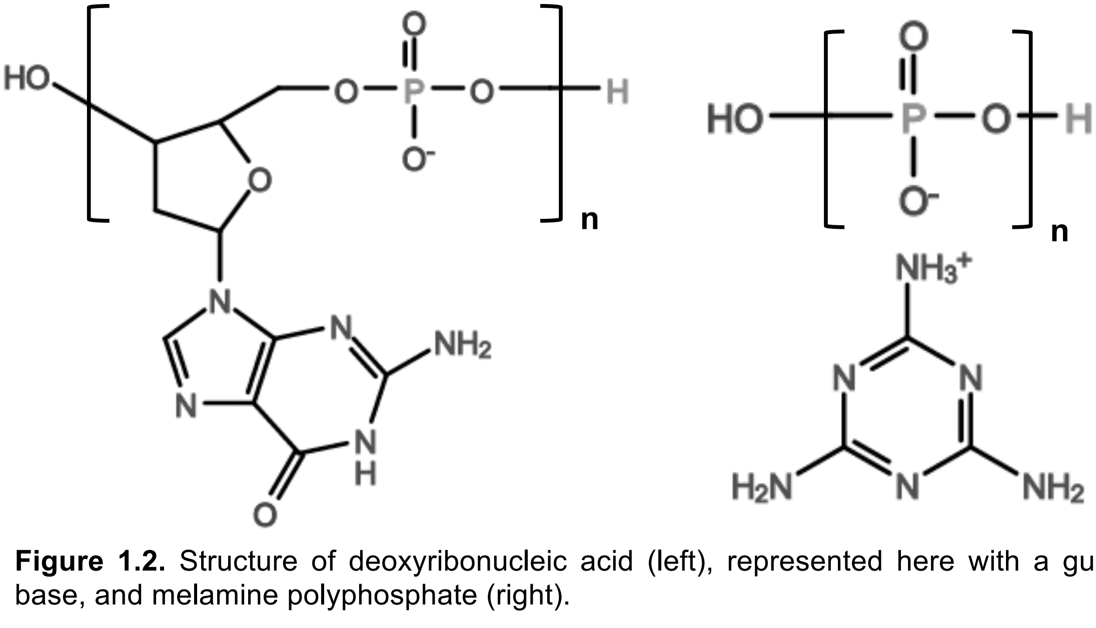

Figure 1.2. Structure of deoxyribonucleic acid (left), represented here with a guanine base, and melamine polyphosphate (right).

exposure was briefly explored. DNA was determined to act like an intumescent flame retardant, showing char formation and a significant increase in volume upon heating, much like MPP [13].

That DNA possesses intumescent properties is not surprising when the structure is compared with that of MPP, as seen in Figure 1.2. Both compounds have a phosphate group in the backbone as well as a nitrogen containing aromatic ring. These features contribute to the flame retardant properties by increasing char formation and thickness as well as diluting the oxygen around the fuel with released nitrogen gas. Furthermore, DNA has a carbon ring within its backbone, a structure not present in MPP. This additional carbon acts in a similar manner to the small molecule carbon source sometimes added to polymer/MPP formulations to generate of carbon dioxide and further dilute oxygen on the polymer surface [13].

DNA has also been incorporated into a polymeric system of ethylene-vinyl acetate (EVA) as both a coating and a bulk additive. It was determined that both methods prevent flame spread in a similar manner to DNA coated cotton cloth [14]. Furthermore, this study demonstrated that DNA can be melt blended with a polymer without significantly damaging its flame retardant properties and that the DNA distributes more homogenously within the polymer matrix than ammonium polyphosphate (APP), a comparable intumescent.

Within this research, commercial variables of the polymer blend, such as its processing properties, have not been explored. For DNA to become a commercially viable product it must not only perform as well as a synthetic flame retardant, but also have similar processing and final product properties, such as torque generation and tensile modulus. While there is currently a drawback to commercial DNA use, namely the high price of purified DNA, the technology for large scale DNA extraction from agricultural waste sources is improving which is likely to bring the cost down into a range comparable with synthetic flame retardants [15].

DNA is a promising natural replacement for current flame retardants as it acts as an all-in-one flame retardant, eliminating the need for additives and simplifying the production process. Additionally, it has been shown to be effective at levels that promote economic feasibility and the maintaining of mechanical properties. Here the processability, thermal properties, mechanical properties, and flammability of DNA and MPP containing low-density polyethylene (LDPE) and polystyrene (PS) melt blended with varying loading levels of DNA and MPP will be explored. Determining the results of incorporating DNA into commercial polymers is a critical step towards future applications of DNA as a green flame retardant.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Melamine polyphosphate (Hangzhou JLS Flame Retardants), Deoxyribonucleic acid powder from herring sperm (<50 bp degraded, Sigma-Aldrich), STYRON® 615APR polystyrene (DOW Chemical), Low-density polyethylene 503A (MFI 2, DOW Chemical).

2.2 Processing Methods

2.2.1 Twin Screw Extrusion

A Thermo Haake Minilab Microcompounder with a 2mm x 5mm rectangular die, in conjunction with a roll off system, was used for the creation of all burn strips. Low density polyethylene (LDPE) or polystyrene (PS) samples with DNA or MPP additives at 5, 10, 20, 30, or 40 wt% were processed at a screw speed of 80 rpm with a compounding time of 2 minutes. The LDPE/MPP and the LDPE/DNA samples were compounded at 165°C and 145°C, while the PS samples were processed at 170°C. Average torque measurements were collected for each compounding run.

2.2.2 Batch Compounding

PS samples with MPP or DNA additive loading at 5 or 10 wt% were compounded using a Thermo Haake Rheomix OS Lab Mixer. For all samples, the cell temperature was set to 170°C with a screw speed of 80 rpm. Samples were mixed for 3 minutes. After compounding, PS blends were extruded into strips for burn testing using the twin screw extrusion procedure described previously.

2.2.3 Polystyrene Tensile Sample Preparation

Compounded polystyrene materials from either batch mixing or Minilab compounding were pressed into sheets using a Carver Model C Heated Press. The blend was heated for 5 minutes at 160°C with no pressure, then 5000 pounds of force was applied for 5 minutes. The sheet was then cut into .918 rule (33mm x15mm) dog-bone tensile bars.

2.3 Thermal Analysis

A TA Instruments Q100 DSC was used to perform differential scanning calorimetry (DSC) on LDPE and PS. A T-Zero aluminum pan in the closed configuration was used for all samples. The heating rate was 10°C/min over the range of -50°C to 225°C. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 TGA under a nitrogen or air atmosphere for all starting materials and compounded samples. A drying step at 100°C was implemented for 10 minutes prior to heating at 10°C/min to 700°C.

2.4 Sample Characterization

2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The infrared spectra of samples were collected using a SpecAgilent Cary 630 FT-IR spectrometer. Attenuated total reflection (ATR) mode was used to collect spectra from 650-4000 cm^{-1} with a resolution of 8 cm^{-1}. Spectra from LDPE samples were collected from the internal surface while those for PS were collected from melt pressed sheets.

2.4.2 Tensile Testing

LDPE and PS samples from the MiniLab extrusion process or melt pressing, respectively, were loaded into a MTS 2525 ReNew 5565 electromechanical extensometer with a 1 kN load cell. LDPE samples 10 cm in length were tested using an initial gage length of 2.5 cm and a strain rate of 20 mm/min. PS dog-bones had an initial gage length of 1.5 cm and were strained at a rate of 1 mm/min. Five replicate values each for elongation at break and tensile modulus were collected for each loading level of each material.

2.5 Burn Testing

The flammability of 13 cm samples of each loading level and material was evaluated in a UL-94 Horizontal Burn (HB) test modified from the ASTM D635-14 procedure. The samples were placed on a wire mesh grid and exposed to flame on one end for 10 seconds. The burn distance and flame spread rate (FSR) for four replicates of each sample were recorded.

CHAPTER 3

FLAME RETARDANT ADDITIVES FOR LOW DENSITY POLY(ETHYLENE)

3.1 Processability of Polymer Additives

The processing temperatures for LDPE were chosen based on the DSC trace of LDPE, shown in Figure 3.1, and the TGA thermograms of MPP and DNA, included in Figure 3.2. The melting point of the LDPE is around 110°C indicating the minimum processing temperature would need to exceed that value. However, processing at that low of a temperature would be impractical as the melt viscosity would require too large of an energy input.

Therefore, the TGA thermograms of the additives were used to choose a specific temperature. While MPP is stable past 200°C, DNA undergoes a small mass loss at 170°C, which could indicate that degradation is beginning to occur. Although this change was not seen to heavily influence additive properties, the

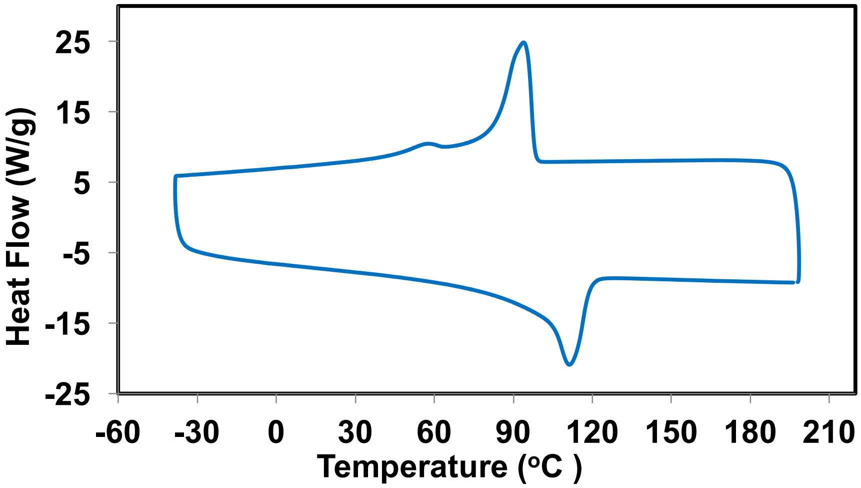

Figure 3.1. DSC trace of neat low-density polyethylene

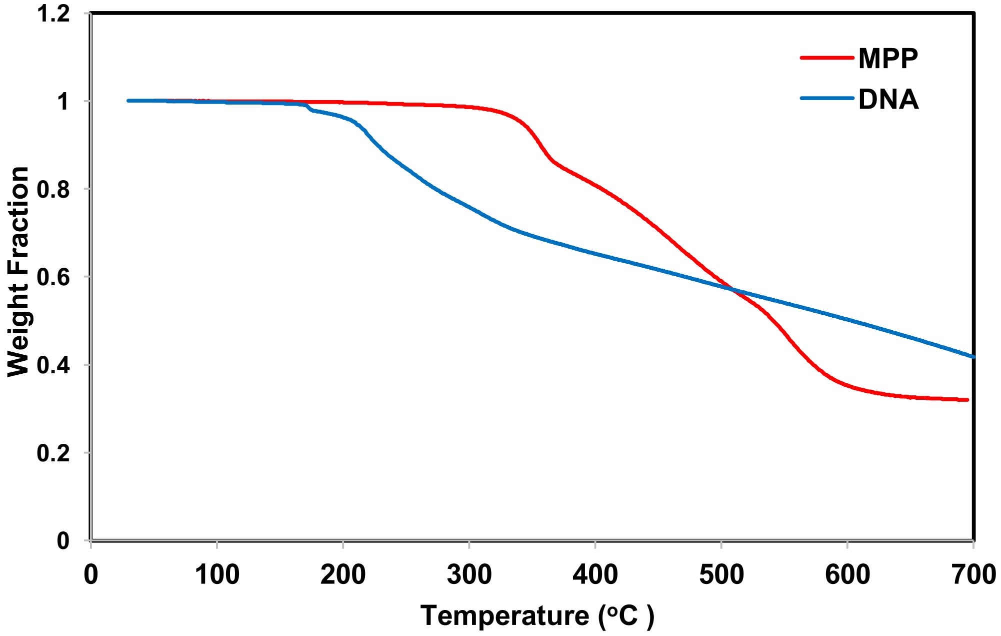

Figure 3.2. TGA thermograms of unmodified additives

processing temperature for DNA was chosen to be 145°C to ensure that the compounded samples contained DNA with its original structure that was melted enough for adequate mixing. As MPP is more stable, its processing temperature was raised to 165°C to decrease melt viscosity and compounding torque and improve sample consistency after extrusion. Residence time was selected as 2 minutes to prevent premature heat or shear induced degradation of either additive as this could negatively impact flame retardant properties.

During compounding using a small-scale twin screw extruder, the additives both appeared to be fully mixed with the LDPE matrix. No macroscopic aggregation or unmixed powder were seen in any sample after processing and extrusion. Upon closer examination, however, it was determined via EDS-SEM imaging and interior surface appearance after fracture that the DNA disperses more fully in the LDPE, especially at higher loading levels where MPP undergoes aggregation [16].

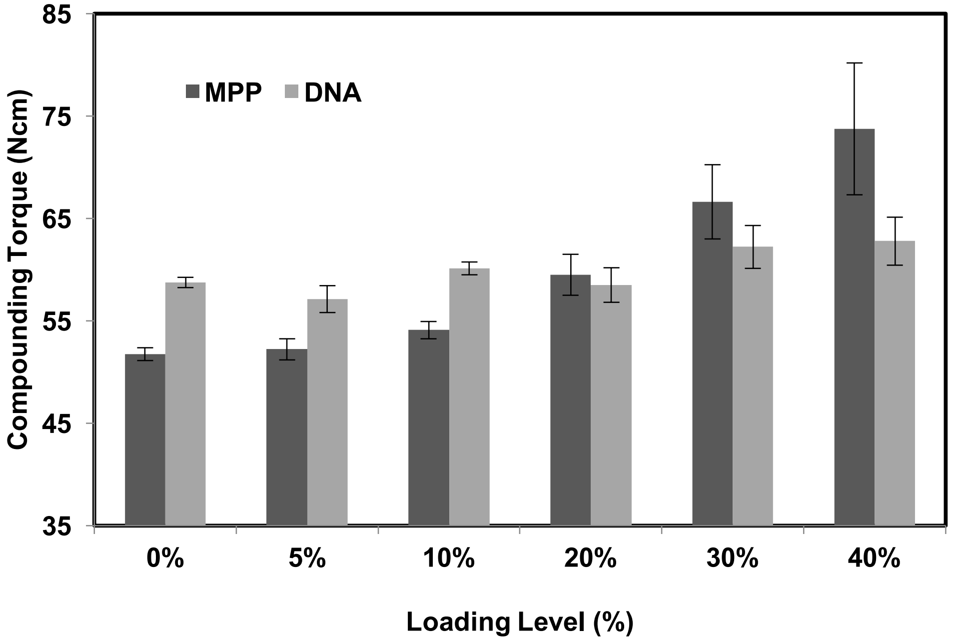

Figure 3.3. Compounding torque for LDPE with various loading levels of MPP and DNA as additives.

The torque data collected during compounding, presented in Figure 3.3, also shows a significant difference between LDPE with DNA versus MPP as an additive. Despite the lower processing temperature for the LDPE/DNA samples, the compounding torque is equivalent to that of MPP at a loading level of 20% and lower at higher loading levels indicating good compatibility between the DNA and the LDPE matrix. Furthermore, the addition of small amounts of DNA causes a slight decrease in compounding torque, whereas addition of MPP only leads to an increase in the required processing torque.

3.2 Effect of Loading Level on Mechanical Properties

Once it was confirmed that DNA could be incorporated into an LDPE matrix under similar processing conditions to MPP, the mechanical properties of the samples were =compared. Both modulus and elongation at break, shown for different loading levels in Figures 3.4 and 3.5 respectively, showed similar trends for both LDPE/MPP and LDPE/DNA samples.

As loading level increases, the modulus of the sample increases while the elongation at break decreases. This is the expected behavior for a reinforcing filler, indicating that both DNA and MPP behave as such. However, DNA shows improved modulus over MPP at high loading levels as well as a larger elongation at break at intermediate loading levels. These improvements likely come from the ability of DNA to disperse in the LDPE matrix. Since it does not aggregate as much,

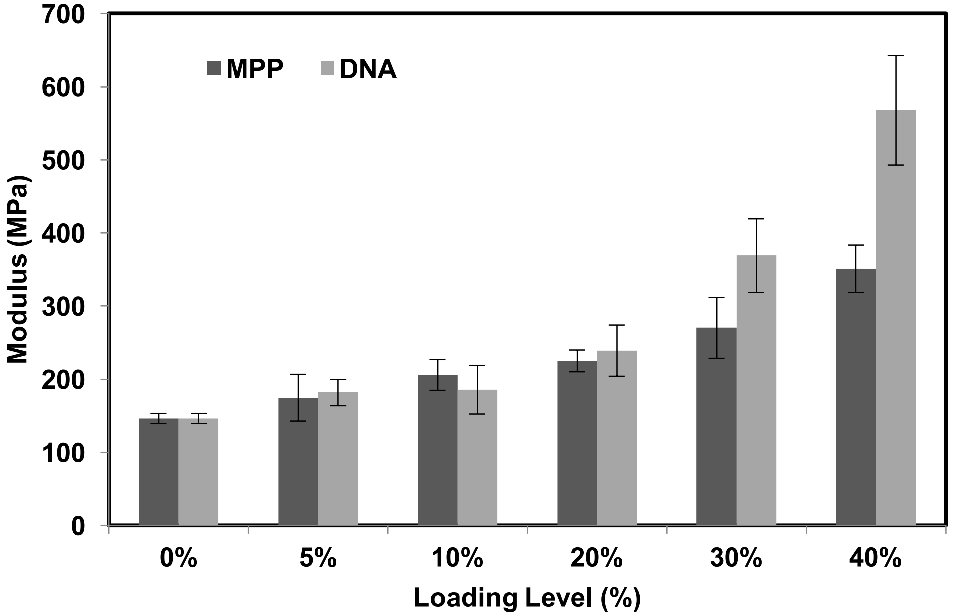

Figure 3.4. Tensile modulus as a function of loading level for MPP and DNA in an LDPE matrix.

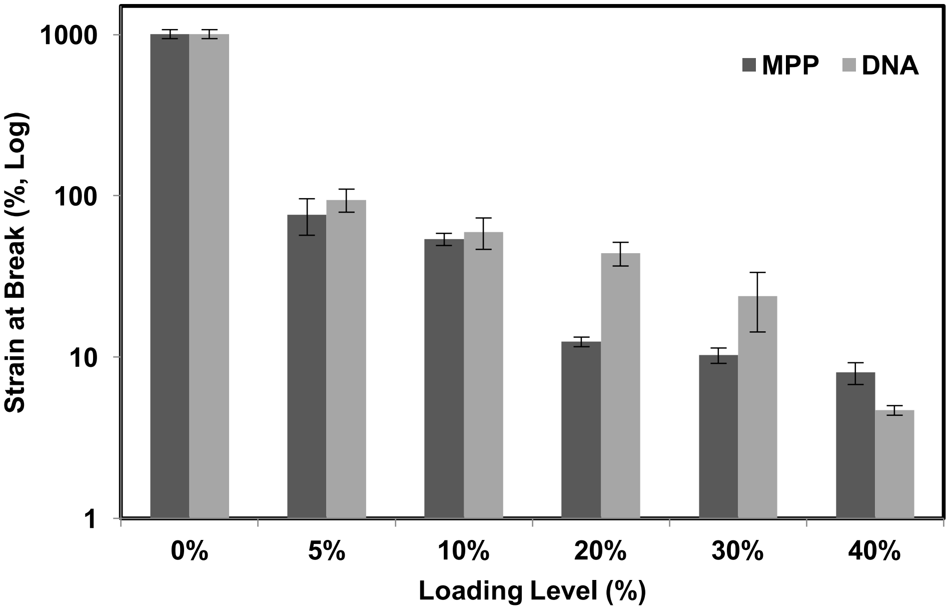

Figure 3.5. Elongation at break for various loading levels of MPP and DNA in an LDPE matrix.

DNA is able to effectively reinforce the entire sample without introducing weak points in the polymer matrix that are likely to cause failure. As intumescent flame retardant additives are generally incorporated into commercial polymers at loading levels of 15-25%, the good mechanical properties of LDPE/DNA samples in this range indicate the potential for commercial use.

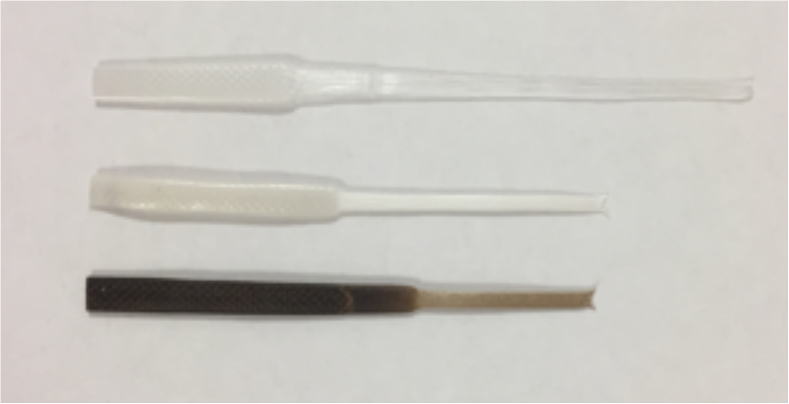

Figure 3.6. Neat LDPE (top), LDPE/MPP 5% (middle), and LDPE/DNA 20% (bottom) tensile samples strained until break.

In addition, both DNA and MPP samples are able to undergo drawing in a manner similar to that of neat LDPE during tensile testing. As can be seen in Figure 3.6, both samples also show signs of strain induced crystallization evidenced by the narrowing of the tested sample and, in the case of the DNA sample, by the lightening of the strained portion of the test sample.

3.3 Effect of Loading Level on Flammability

Flammability testing was performed on all samples to determine the effectiveness of the additive at imparting fire retardant properties to the flammable LDPE matrix. After ignition and removal of the heat source, the DNA promoted self-extinguishing capabilities in all samples at loading levels 10% and above, while MPP required a loading level of 20% before any tested samples self-

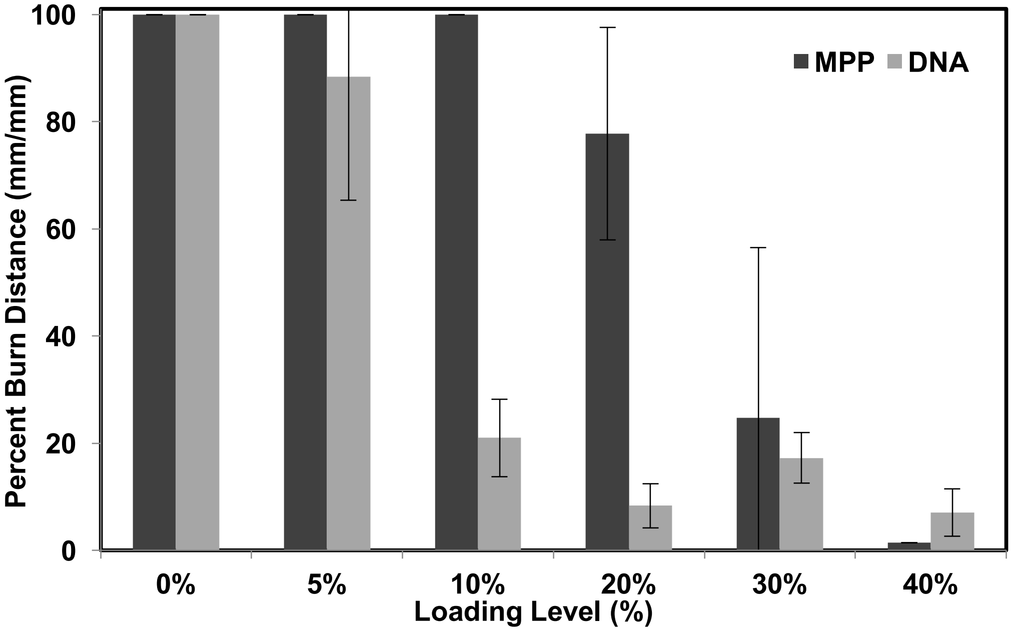

Figure 3.7. UL-94 HB test burn distances for LDPE/MPP and LDPE/DNA samples of different loading levels.

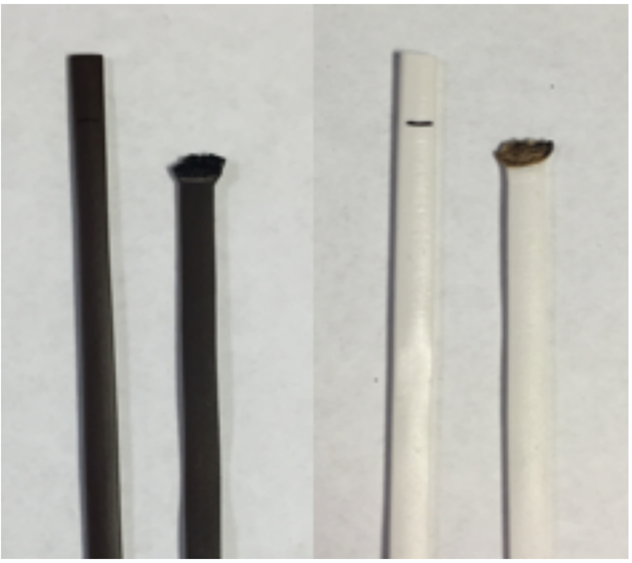

Figure 3.8. LDPE/DNA (left) and LDPE/MPP (right) burn strips before and after burning. Both samples are at a loading level of 30%.

extinguished. This is evidenced by the percent burn distances of all tested loading levels seen in Figure 3.7. In addition, the MPP samples have a much higher degree of error than DNA at 20% and 30% loading levels, indicating that the flame retardant properties of DNA are more consistent than those of MPP, possibly due to the addition carbon source present in the DNA backbone that is absent from MPP.

The char remaining after burn testing, pictured in Figure 3.8, also shows a benefit of using DNA over MPP. The DNA char is more plastic in appearance and feel whereas the char on the MPP samples has a powder-like consistency with no remnants of the original properties of the LDPE matrix. The pattern of charring is similar between LDPE/MPP and LDPE/DNA samples with both flame retardants showing intumescent properties, including black carbon char formation and gas evolution during burning, as expected from their similar structures.

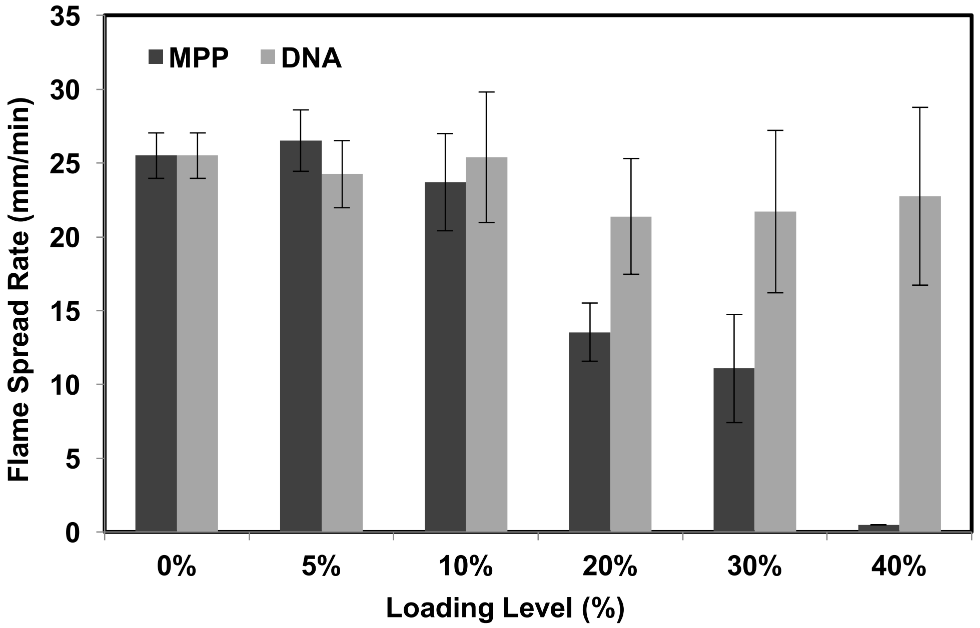

Figure 3.9. UL-94 HB test flame spread rate of LDPE/MPP and LDPE/DNA samples at varying loading levels.

The flame spread rate, however, has a different trend than the burn distance data. Displayed in Figure 3.9, this data shows that, while DNA decreases burn distance and promotes self-extinguishment at lower loading levels than MPP, it is not as effective at slowing the progression of the flame along a sample. In all likelihood, this is because the shorter burn distances at higher DNA loading levels do not allow for accurate measurements of the flame spread rate.

3.4 Additional Sample Analysis

Sample loading level was calculated using the char yield at 700°C from thermogravimetric analysis under nitrogen. TGA thermograms for all loading levels can be seen in Figure 3.10. The extracted values for char yield and the calculated

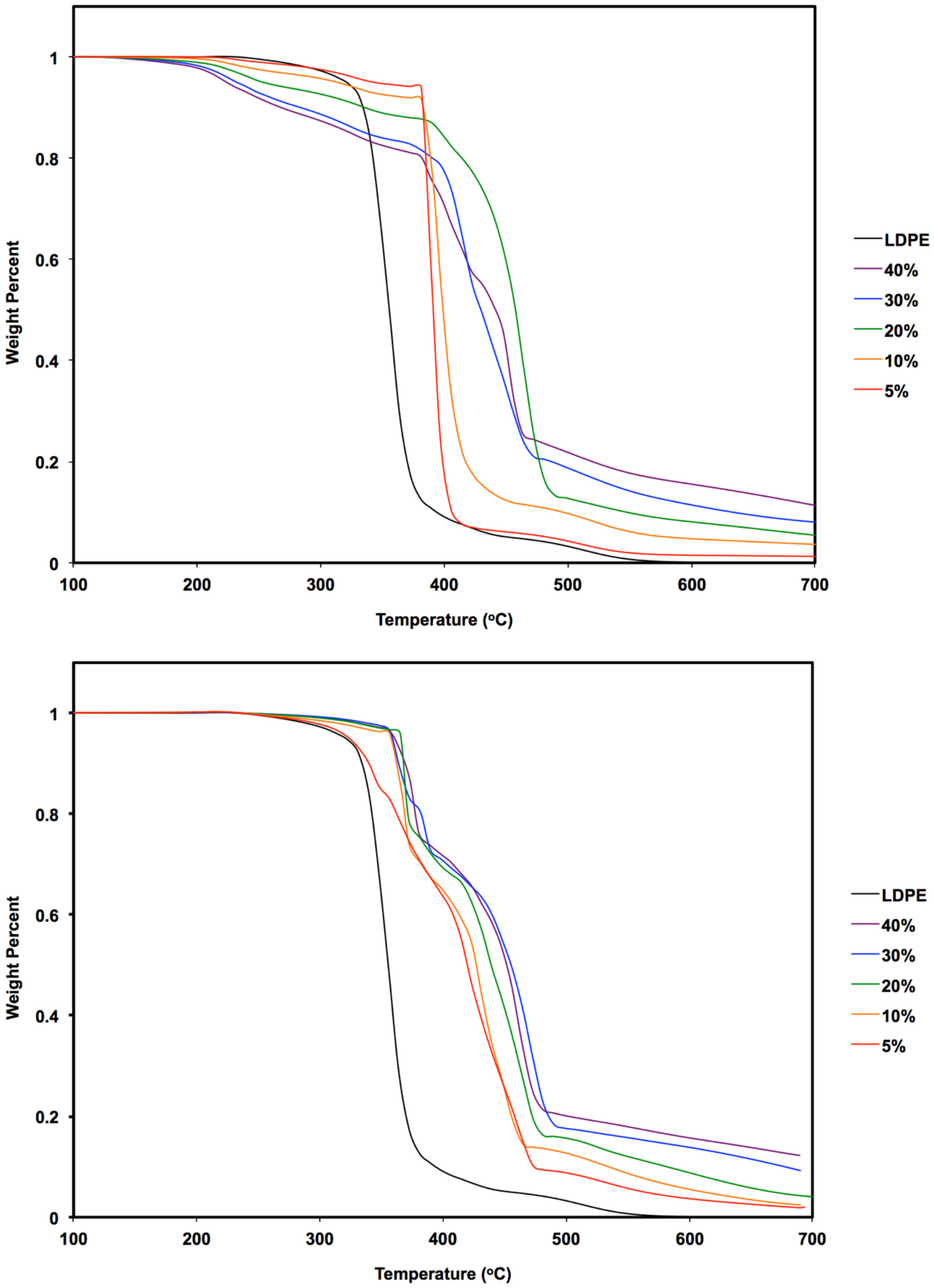

Figure 3.10. TGA thermograms of LDPE with DNA (top) and MPP (bottom) additives at various loading levels [16].

	Char Yield (%)		**Loading Level (wt%)**	
	MPP	DNA	MPP	DNA
5%	1.5	2.1	4.3	5
10%	3.8	4.5	10.9	10.8
20%	6.4	8.6	18.3	20.6
30%	9.1	13.8	26	33.1
40%	11.9	16.7	34	40
100%	35	41.7	100	100

Figure 3.11. Char yield and loading levels of samples based on TGA analysis.

loading levels can be seen in Figure 3.11. The loading level was calculated from char yields because all residue at 700°C was assumed to be additive as LDPE is completely degraded by around 550°C. Loading was shown to be repeatable in this small-scale test with few deviations occurring from the expected loading levels. DNA loading levels were largely determined to be higher than the actual loading level, possibly due to early onset char formation or overall substrate protection from the DNA. In this case, the lower degradation start temperature and the large degradation temperature range provide positive contributions to the thermal properties of the blend.

FT-IR analysis was also performed on samples before and after burn testing to explore the chemical changes that take place in the additives and matrix during burning. Full spectra as well as enlargements of the fingerprint region for each additive can be seen in Figure 3.12. In the MPP spectra, it can be seen that the C-H peaks at ~2900 cm^{-1} are no longer present in the char. This indicates that the

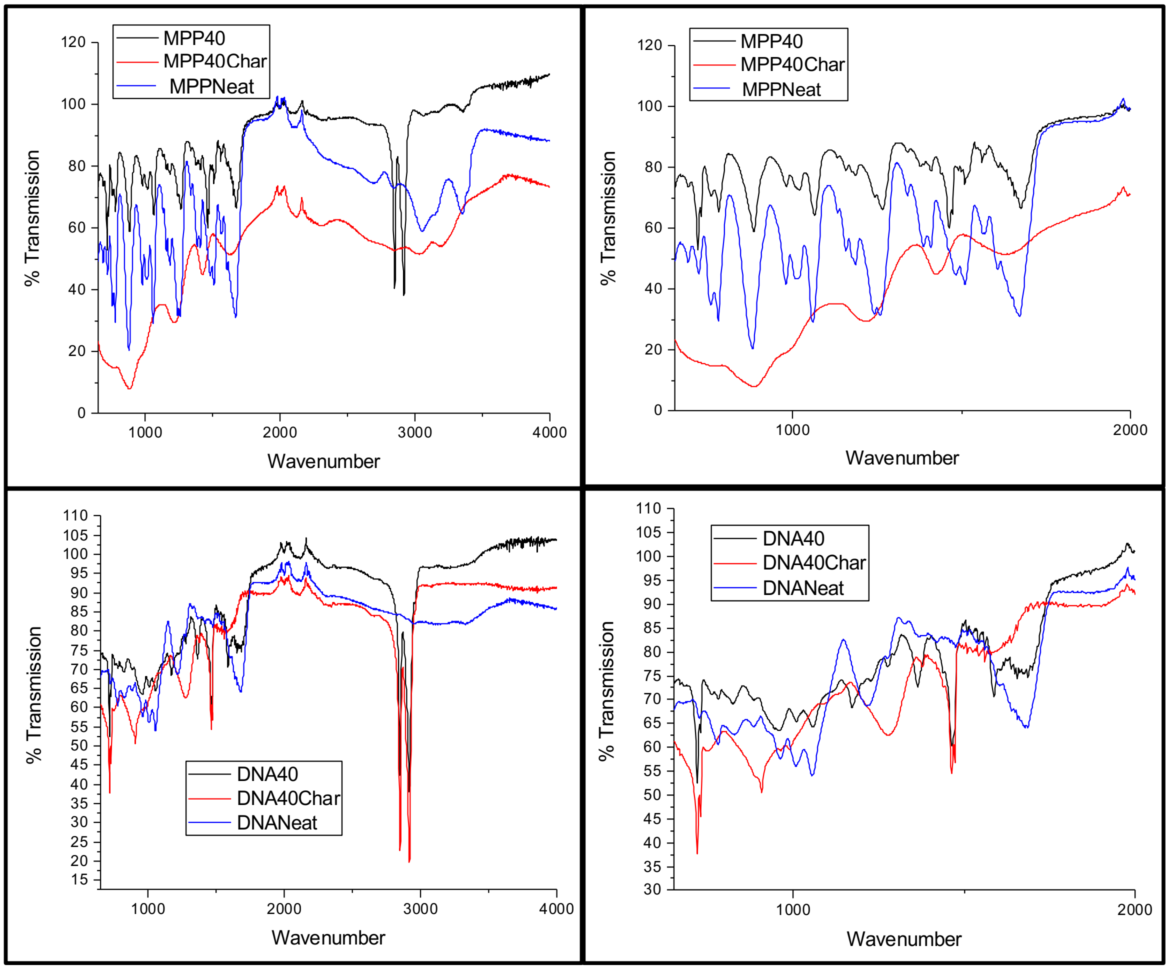

Figure 3.12. FT-IR spectra of 40% LDPE/MPP (top) and 40% LDPE/DNA (bottom). Fingerprint regions of the full spectra have been enlarged (right).

LDPE matrix was entirely consumed during burning. Furthermore, the MPP fingerprint region, which is clearly visible in the LDPE/MPP blend, is not present in the char meaning the flame retardant additive was consumed by the fire and chemically converted into the char layer as expected.

The DNA char, however, maintains the C-H peaks from the LDPE at ~2900, 1460, and 720 cm^{-1}, showing that more of the polymer matrix is preserved through the flame retardant action of DNA than of MPP. The presence of these peaks also supports the more plastic-like char seen during burn testing. The similarities between the fingerprint regions of the additives and the LDPE/additive blends should also be noted as they indicate successful incorporation of the additive without significant chemical change, a property which is important for effective flame retardant action.

CHAPTER 4

FLAME RETARDANT ADDITIVES FOR POLY(STYRENE)

4.1 Processability of Polymer Additives

Prior to compounding, DSC was performed on the neat polystyrene to ensure that the melting point was within an acceptable range and to determine the appropriate processing temperature. Any melting point above 200°C would cause too much degradation in the additives during processing, particularly the DNA, which undergoes significant weight loss at 220°C as determined by TGA. The melting point for PS-615 was determined to be 165°C based on the DSC thermogram, which is shown in Figure 4.1. From this information, 170°C was chosen as the processing temperature for both twin-screw extrusion and compounding as well as batch mixing. Although higher temperatures could have

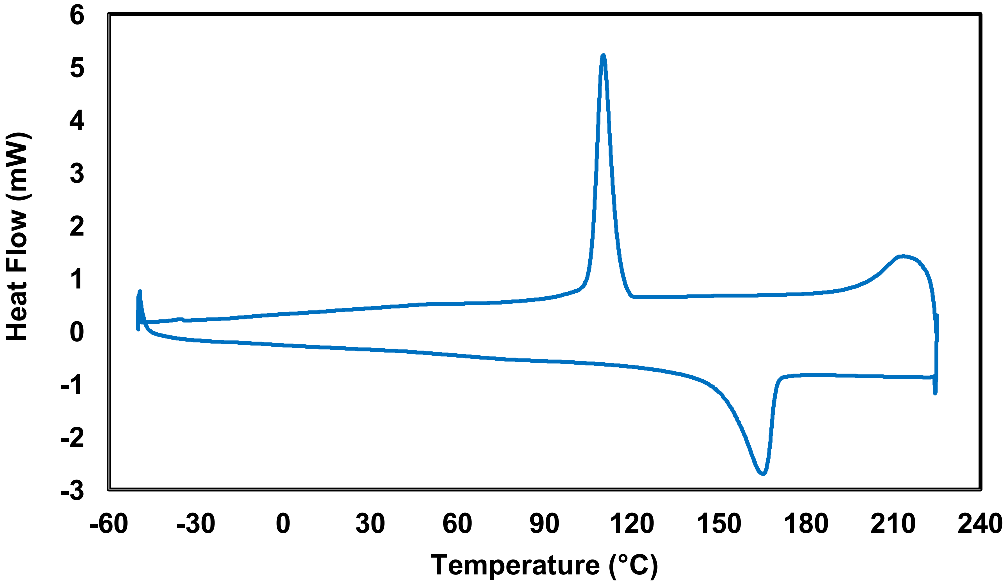

Figure 4.1. DSC trace of neat polystyrene-615.

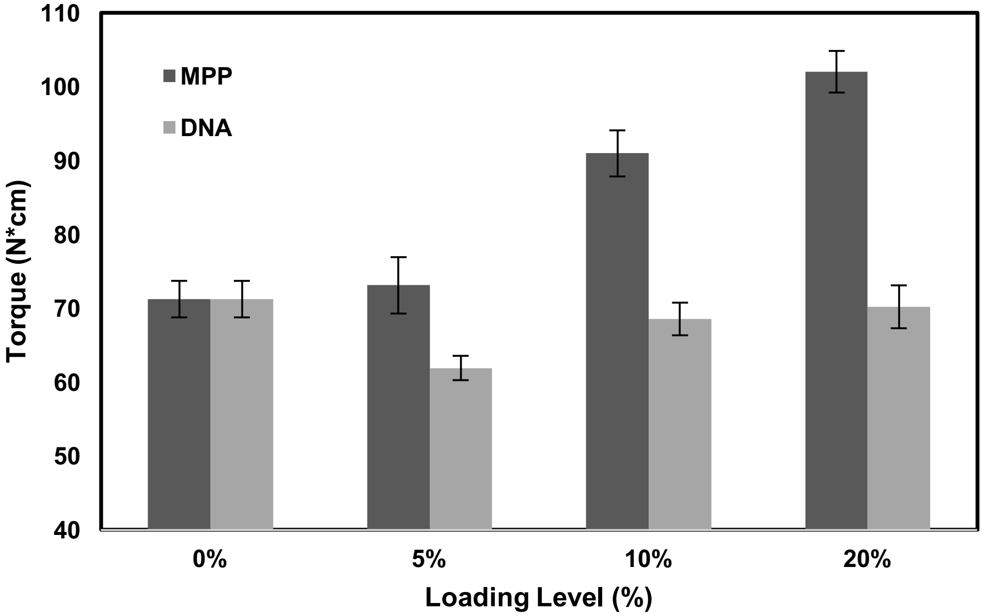

Figure 4.2. Torque generation during small-scale twin screw extrusion compounding of polystyrene.

been used to decrease the melt viscosity, the lower temperature did not generate unreasonable torque levels and was therefore selected to prevent unnecessary degradation.

PS/MPP and PS/DNA blends displayed similar trends to LDPE in the changing equilibrium compounding torque at different loading levels. However, since both PS/MPP and PS/DNA were compounded at the same temperature, the torque changes are even more significant. At all 3 loading levels measured, PS/DNA blends had a lower compounding torque than neat PS, indicating that DNA may be having a plasticizing effect on PS. In contrast, the compounding torque for PS/MPP significantly increases with increasing loading levels. Therefore, in a compounding system such as this, mixing PS with DNA will take less energy than mixing it with an equivalent amount of MPP.

4.2 Effect of Loading Level on Mechanical Properties

For PS samples, dog-bone tensile bars were cut from melt pressed sheets. Representative tensile bars for PS samples are pictured in Figure 4.3. Sample thickness was approximately 1mm. The modulus of both PS/MPP and PS/DNA blends increased with loading level, as shown in Figure 4.4, indicating that both additives also act as reinforcing fillers in a PS matrix. Like in LDPE, both additives lead to similar increases in modulus at low to moderate loading levels. Although this seems contradictory to the incomplete mixing seen in PS/MPP samples, it can be explained by the process used to make the tensile bars. During the melt pressing process, the large aggregates are obvious within the sheets and can be avoided when cutting tensile bars, thereby only utilizing the more homogenous regions.

Elongation at break shows a similar trend to the modulus with both MPP and DNA causing a decrease with increasing loading level as shown in Figure 4.5. It should be noted that at the 10% loading level, the average strain at break for PS/DNA is higher than that for PS/MPP, however the difference is not significant.

Figure 4.3. PS tensile bars of 10% PS/DNA, 5% PS/DNA, 10% PS/MPP, and 5% PS/MPP from left to right.

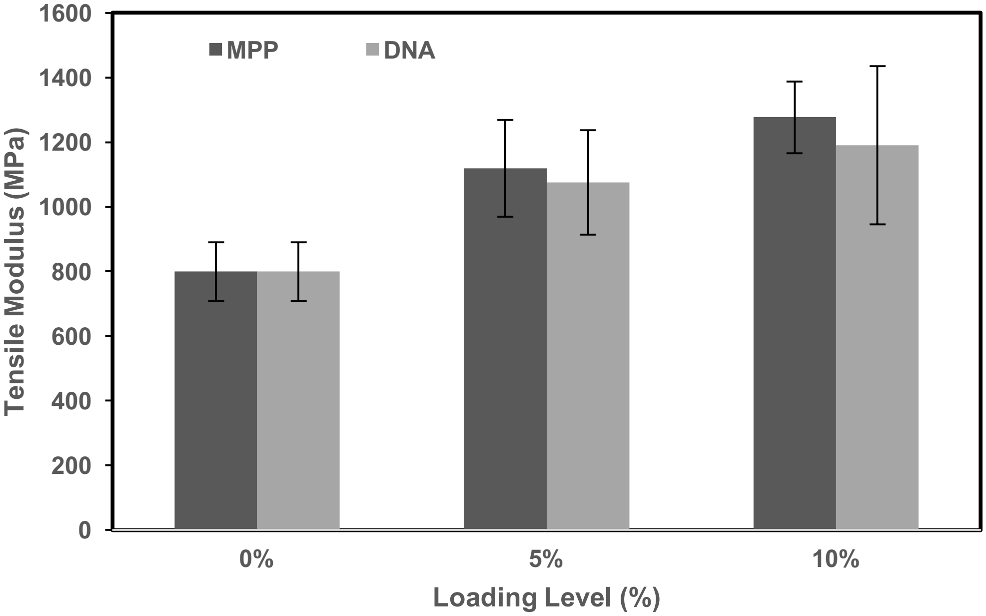

Figure 4.4. Tensile modulus as a function of loading level for MPP and DNA in an PS matrix.

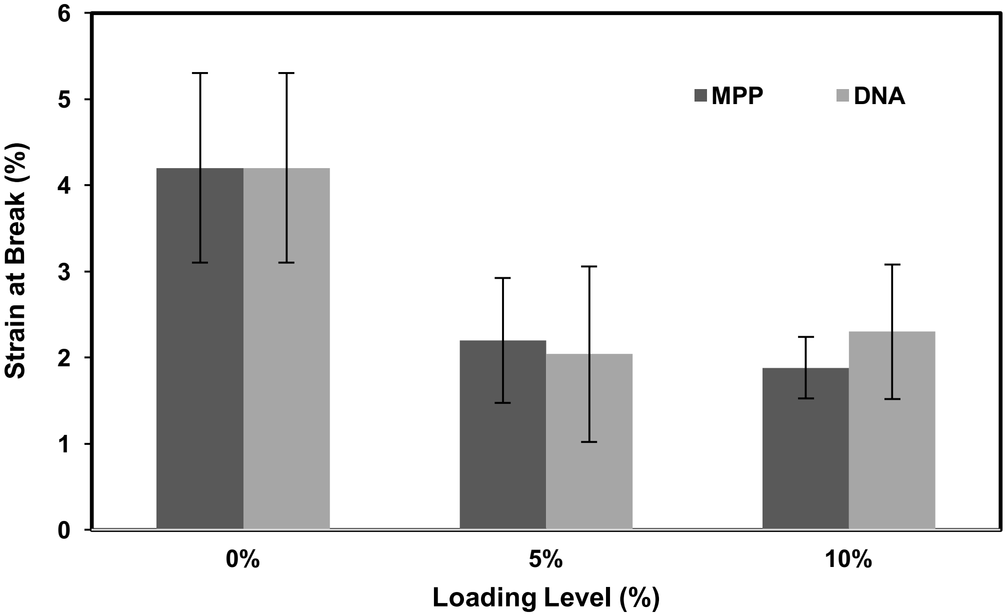

Figure 4.5. Elongation at break for various loading levels of MPP and DNA in an PS matrix.

4.3 Effect of Loading Level on Flammability

Here the flammability of the twin-screw extruded PS samples will be described and the effect of batch mixing the blends will be discussed in the next section. In a PS matrix, neither MPP nor DNA successfully promote self-extinguishment at a 5% loading level, as seen in Figure 4.6. At 10% loading, both additives promote self-extinguishing in some samples but not others, giving rise to the large error in burn distance measurements. This inconsistency could also indicate that the minimum loading level required for effective flame retardant properties is just above 10%, so small differences in loading level between samples would have profound changes in the amount of sample consumed before the flame was extinguished. Once 20% loading is reached, however, both MPP and DNA lead to flame extinguishment in all samples tested.

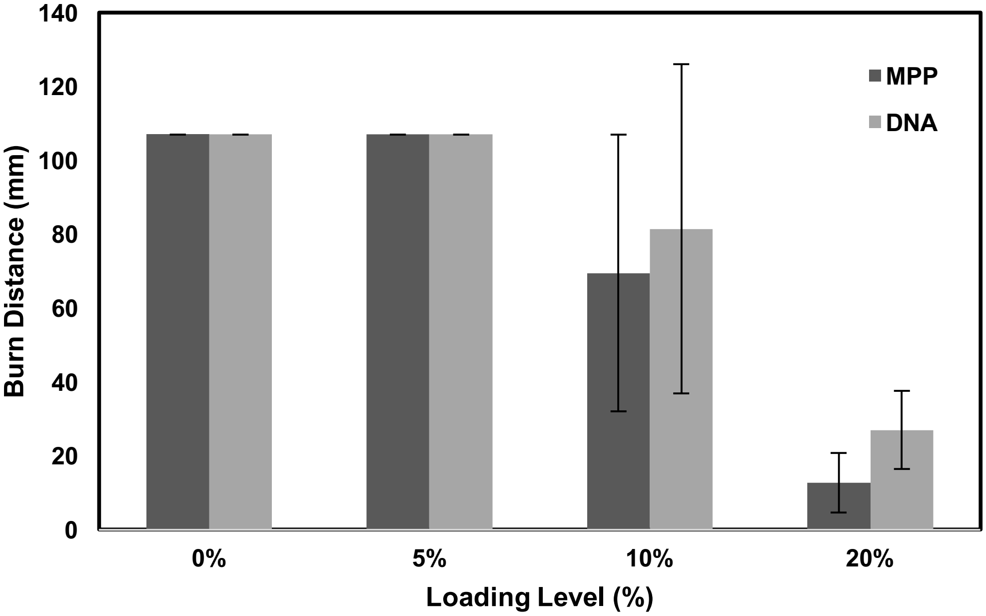

Figure 4.6. UL-94 HB test burn distances for PS/MPP and PS/DNA samples of different loading levels.

The flame spread rate of both PS/MPP and PS/DNA samples showed a similar trend with increasing loading levels leading to lower flame spread rates, as seen in Figure 4.7. However, while PS/MPP logically decreases at all loading levels, 5% PS/DNA has a flame spread rate that, within error, is the same as near PS. At 10% it decreases to below the value for neat PS and by 20% loading the flame spread rate is comparable to that of PS/MPP indicating that the higher value at 5% may be an anomaly alleviated by further testing.

Unlike in LDPE, the burn fronts on the PS samples were not consistent between PS/MPP and PS/DNA samples. Samples with DNA burned in a normal manner, with the burn front advancing through the entire cross-section of the strip at once. Samples containing MPP however, often burned on only one face of the sample. For instance, in Figure 4.8 an MPP sample is pictured that only burnt on the top half of the strip. Other samples have been seen to burn up only one side

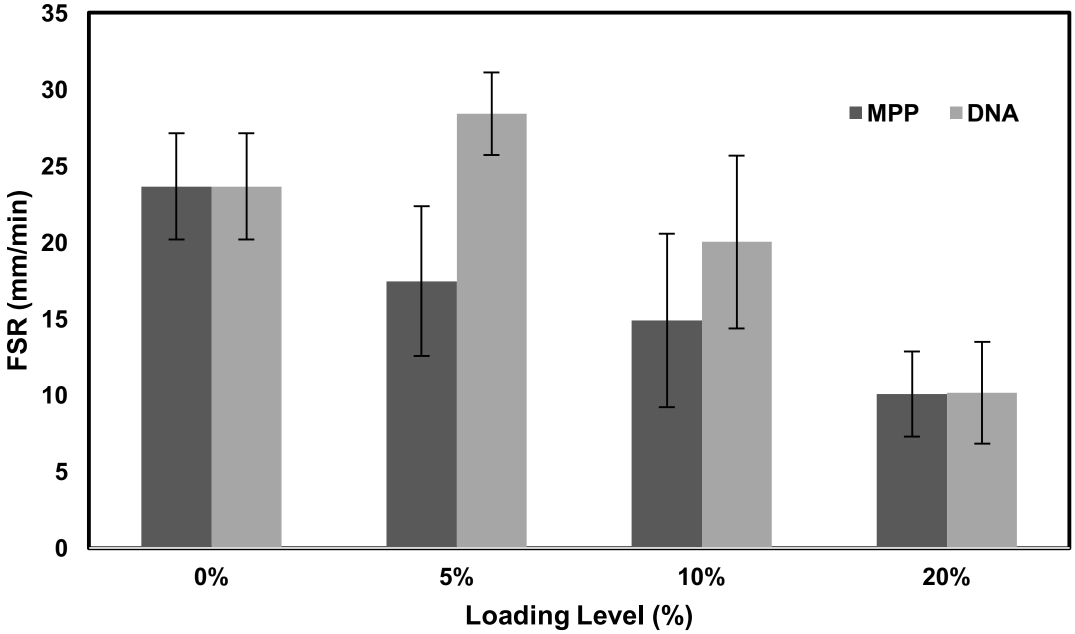

Figure 4.7. UL-94 HB test flame spread rate of PS/MPP and PS/DNA samples at varying loading levels.

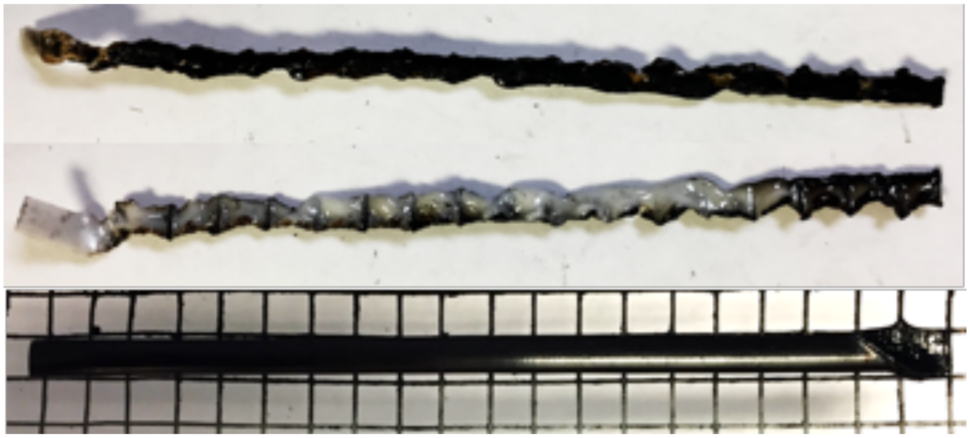

Figure 4.8. Samples after burn testing. 5% PS/MPP top face (top), 5% PS/MPP bottom face (middle), 10% PS/DNA (bottom).

as well. This could potentially be a result of the inhomogeneity of the additive. Both intumescent additives created a black char and gas formation could be seen during burning, particularly in the PS/DNA samples. The DNA containing blends also produced a more plastic-like char compared to the PS/MPP samples.

4.4 Additional Sample Analysis

Loading level was determined through TGA char yield for all samples. Minimal variation was observed between loading in batch mixed and twin-screw

	Char Yield (%)		Loading Level (wt%)	
	MPP	DNA	MPP	DNA
5%	1.4	1.7	4	4.1
10%	3.9	4.3	11.1	10.3
20%	7.8	7.6	22.3	18.2
100%	35	41.7	100	100

Figure 4.9. Char yield and loading levels of PS samples based on TGA analysis.

compounded samples. Representative char yields for both PS/MPP and PS/DNA are included in Figure 4.9.

Neither DNA nor MPP calculated loading levels were consistently above or below the expected loading level. This means that the char likely does not retain any of the PS substrate, as DNA did for LDPE, and variation in loading levels comes from actual changes in additive content. That DNA does not protect the PS substrate as well in thermal testing is a contributing factor to the decrease in flame retardant properties of PS/DNA as compared to LDPE/DNA. It should also be noted that PS-615 has a higher initial degradation temperature than either additive so increasing loading level results in a decrease in the temperature of the first weight loss event for each material as seen in the TGA curves in Figure 4.10.

4.5 Effect of Batch Mixing on Material Performance

As batch mixed samples underwent different processing conditions before testing, they can be used to explore the effect of repeated heat processing on the mechanical and fire related properties of PS/MPP and PS/DNA. In industry, polymers with pre-dispersed additives are often supplied in granule or pellet form for use in extrusion. This requires the formation of a master batch of polymer that will later be heat processed again before use. A commercial flame retardant needs to be capable of withstanding multiple heat processing steps without losing its fire retarding properties.

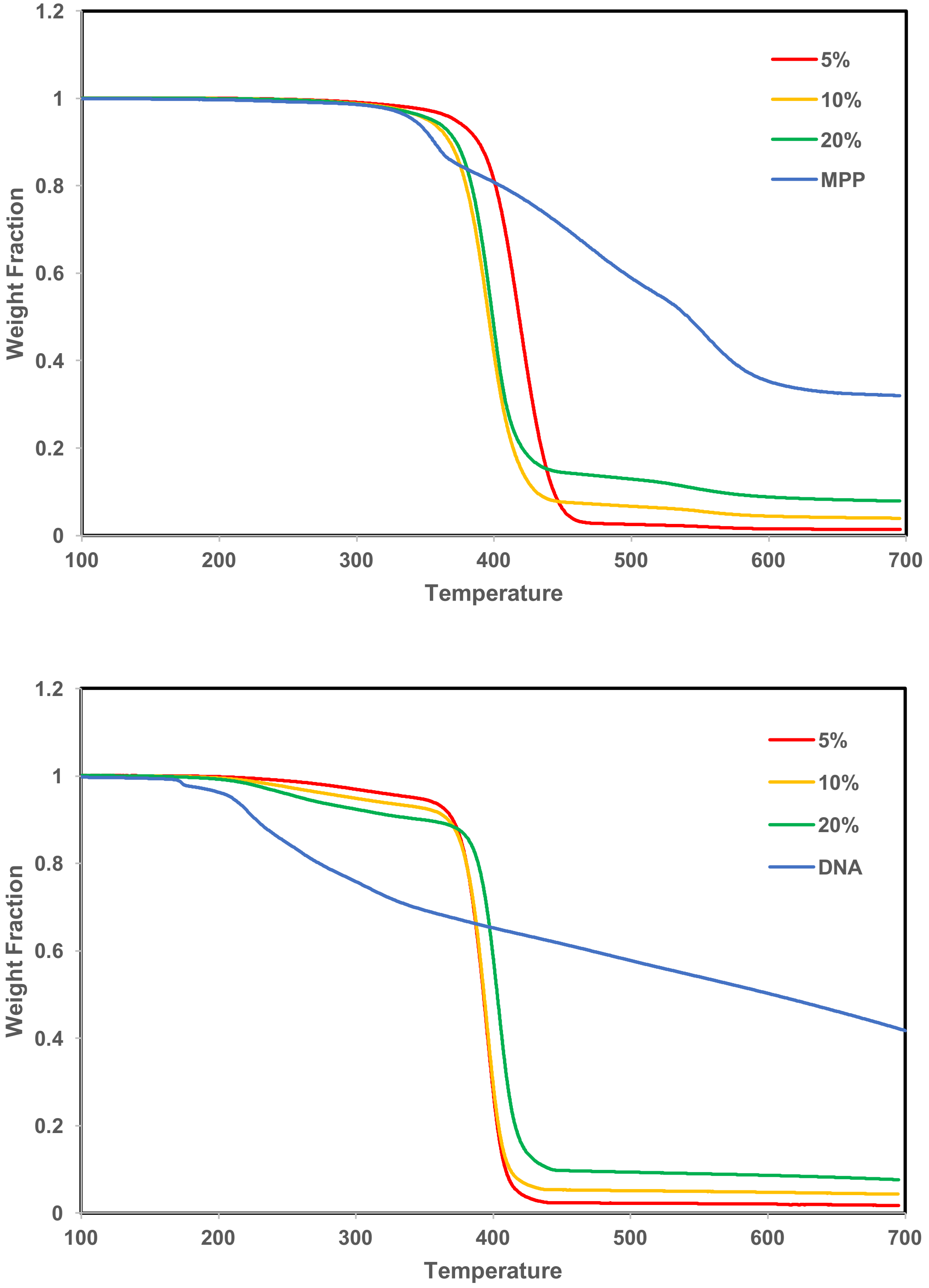

Figure 4.10. TGA thermograms of PS with MPP (top) and DNA (bottom) additives at various loading levels.

4.5.1. Processing Properties

When batch mixing the PS the equilibrium torque cannot be easily compared between samples as shear heating within the mixing cell leads to a unique temperature profile for each sample. Instead, the torque profile and temperature curves over the 3 minute mixing time, included as Figures 4.11 and 4.12, will be evaluated for each sample loading level. When the polymer and additive are introduced into the system, the temperature of the cell drops as expected since the material absorbs energy to melt. This also corresponds to the maximum torque for the system as the PS and the additive are initially mixing. At 5%, the final temperature is slightly higher, 176.5°C versus 175.4°C, and equilibrium torque is lower, 6.8 compared to 8.4 Ncm, for the PS/DNA than for the PS/MPP which indicates both additives have similar mixing properties at this loading level although DNA may show better incorporation. These values are

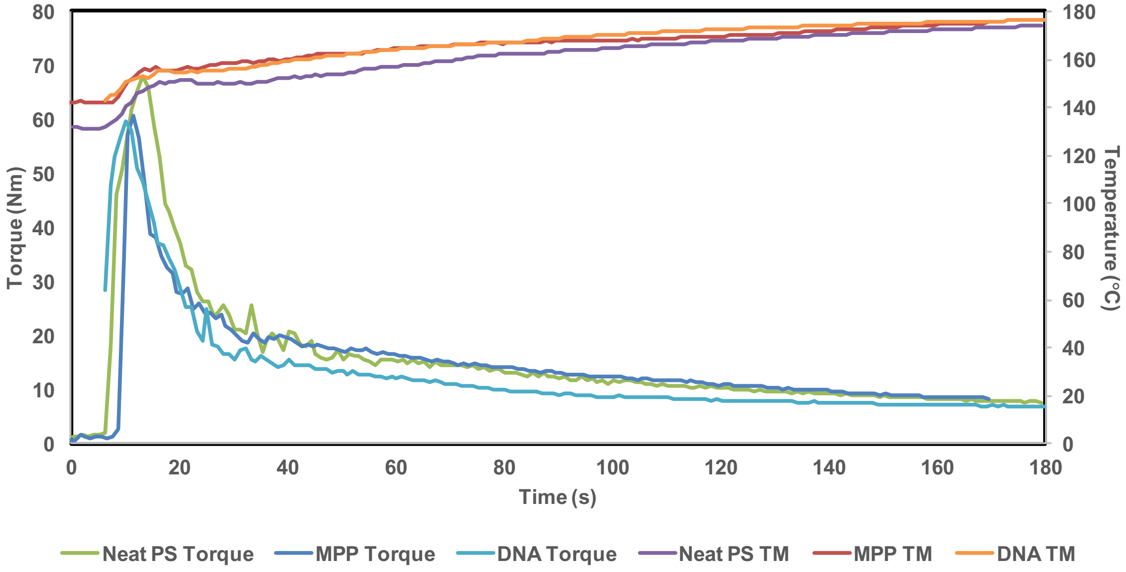

Figure 4.11. Batch mixing torque and temperature profiles for neat PS and PS/MPP and PS/DNA samples at a 5% loading level.

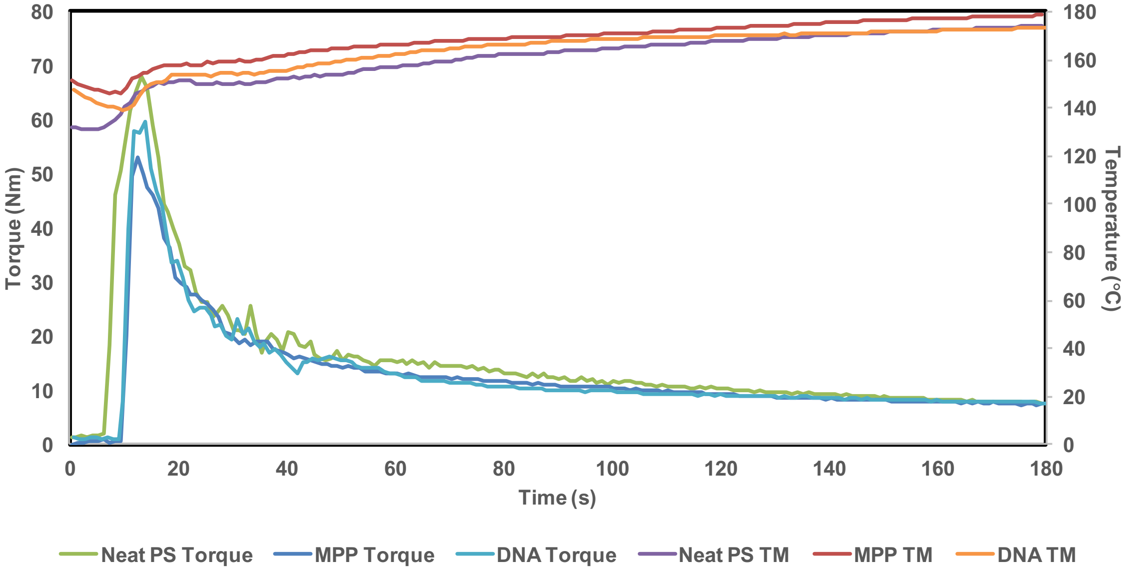

Figure 4.12. Batch mixing torque and temperature profiles for neat PS and PS/MPP and PS/DNA samples at a 10% loading level.

similar to those for neat PS, 174.3°C and 7.7 Ncm, with PS/DNA having a lower and PS/MPP having a higher equilibrium torque value. This agrees with the torque changes seen during twin-screw extrusion.

The 10% loading level shows a similar pattern to the 5%, with PS/MPP having a higher temperature than the PS/DNA by 5°C but only a slightly smaller torque. Overall, PS/DNA and PS/MPP appear to have similar properties when batch mixing. However, visually the MPP incorporation into the PS matrix is inferior to that of DNA, as aggregates of MPP powder can be seen after the compounding process is complete. These aggregates are not present after mixing with DNA.

After extrusion of the batch mixed material, no differences are visible between the batch mixed (MPPB and DNAB) and twin-screw compounded (MPPML and DNAML) burn strips as evidenced by the Figure 4.13. Color and

Figure 4.13. Extruded burn strips of PS/DNA (left) and PS/MPP (right). Each set is one strip each 5% ML, 5% Batch, 10% ML, 10% Batch from left to right.

consistency are similar indicating full mixing occurred during the extrusion process despite the aggregates in the MPP samples after batch mixing.

4.5.2 Mechanical Properties

Prior to tensile testing, both the batch mixed and the twin-screw compounded samples underwent multiple rounds of thermal processing, the first during compounding and the others during melt press cutting of the tensile bars. Since the thermal exposure was the same for both sets of samples, it was expected that the mechanical properties would also be consistent. However, this was not true for either the modulus or the elongation at break as shown by Figures 4.14 and 4.15 respectively. While both processing methods lead to the same general trends at a 5% loading level, with PS/MPP having a slightly higher modulus and elongation at break than PS/DNA, the mean values are not consistent. When batch

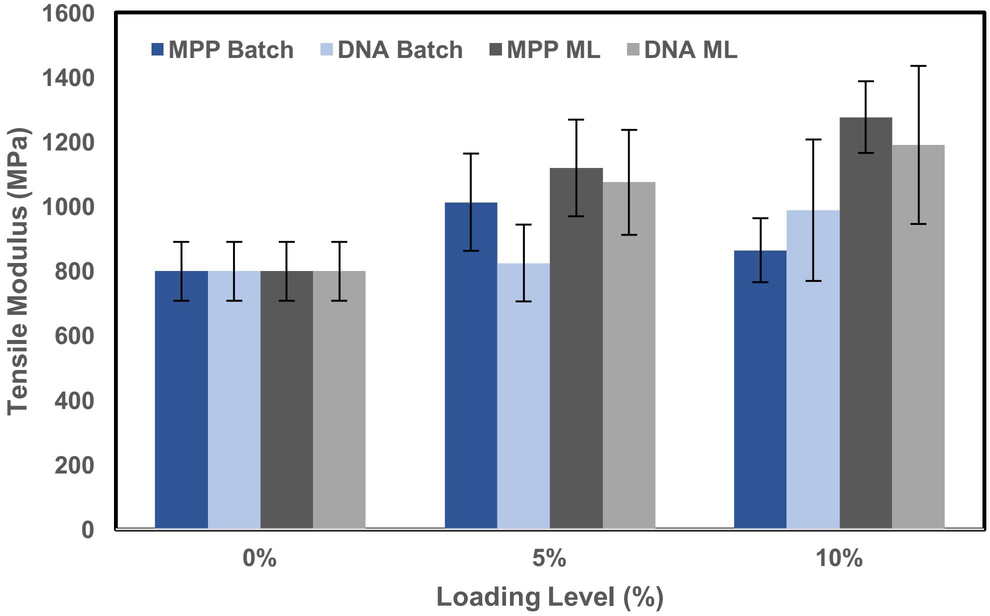

Figure 4.14. Tensile modulus as a function of loading level for MPP and DNA in a batch mixed (Batch) and twin-screw compounded (ML) PS matrix.

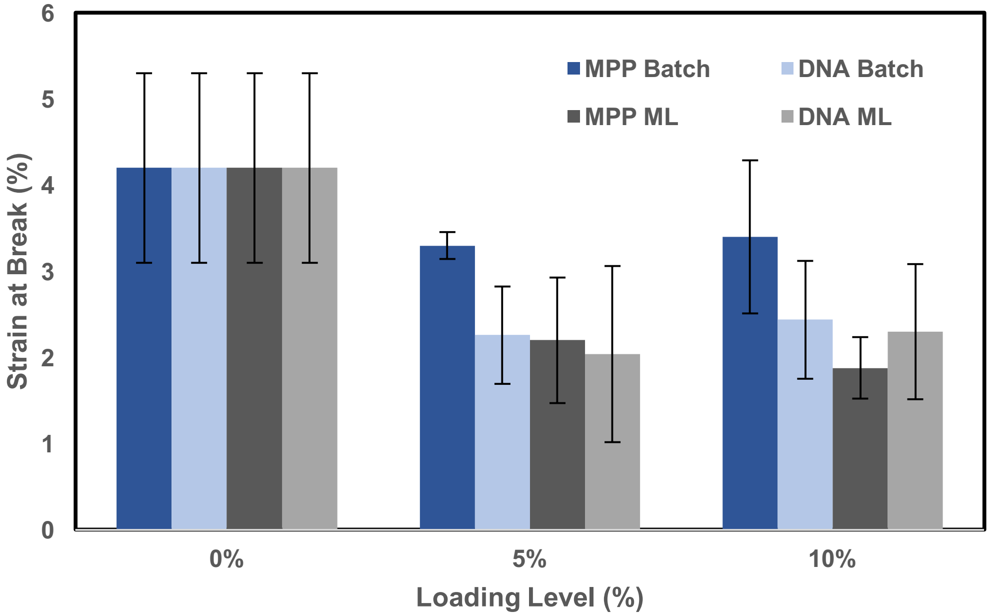

Figure 4.15. Elongation at break as a function of loading level for MPP and DNA in a batch mixed (Batch) and twin-screw compounded (ML) PS matrix.

mixed, the average elongation at break increases, while the average values for modulus decrease. This could be caused by the longer exposer to shear within the batch mixer breaking down the additives into smaller molecules which then have a plasticizing effect on the PS matrix. At 10% loading the differences between the batch mixed samples and the twin-screw compounded samples are even more pronounced with the same increase in elongation at break and decrease in modulus observed.

4.5.3 Flammability Testing

During sample preparation for flammability testing, batch mixed samples were reprocessed in the twin-screw extruder to enable extrusion of burn strips. As prolonged or repeated heating may have a negative effect on the stability of DNA,

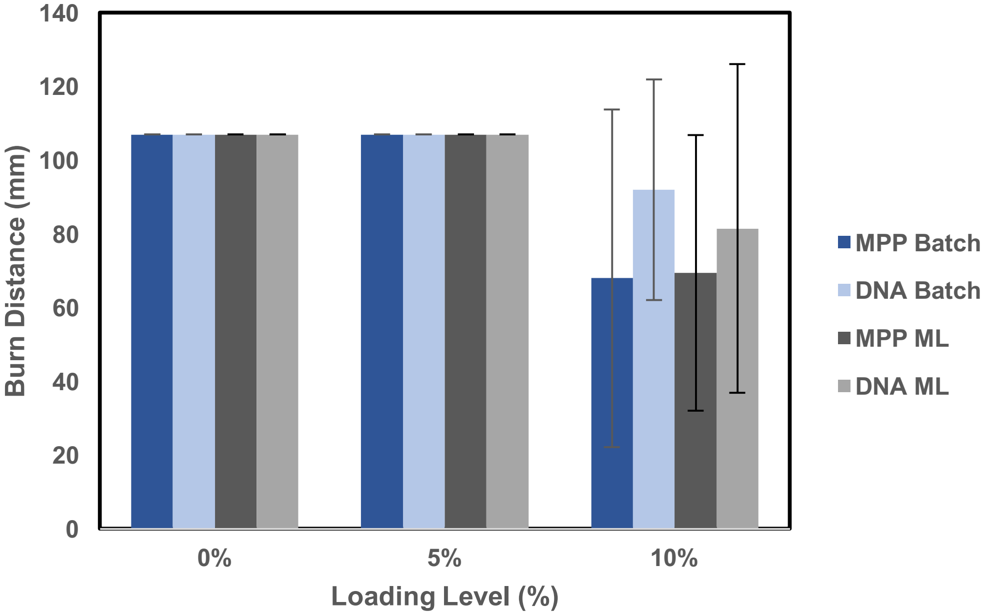

Figure 4.16. UL-94 HB test burn distances as a function of loading level for MPP and DNA in a batch mixed (Batch) and twin-screw compounded (ML) PS matrix.

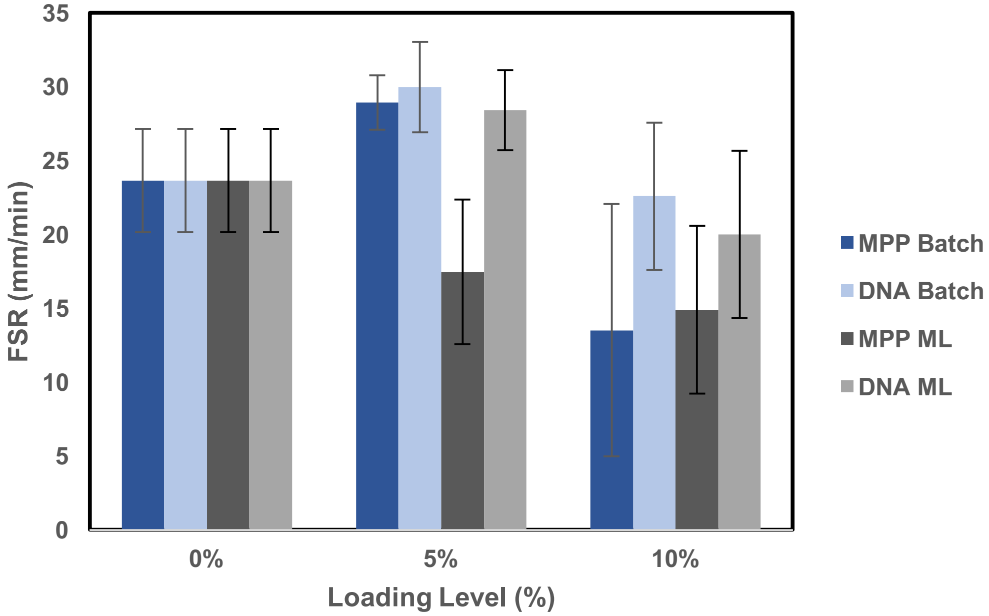

Figure 4.17. UL-94 HB test flame spread rate as a function of loading level for MPP and DNA in a batch mixed (Batch) and twin-screw compounded (ML) PS matrix.

the flame retardant properties of samples that underwent different processing techniques were compared.

Overall, the batch mixed samples performed similarly to their twin-screw compounded counterparts. The burn distances, shown in Figure 4.16, were all within error of each other. The 5% loaded samples did not self-extinguish for PS/MPP or PS/DNA as expected while 10% additive composition led to highly variable burn distances with only some samples extinguishing. The average burn distance of PS/DNA samples was higher than that of PS/MPP samples for both processing methods.

Flame spread rate also largely followed similar patterns irrespective of processing method, as seen in Figure 4.17. The largest discrepancy was seen in 5% loaded PS/MPP samples where the flame spread rate of the batch mixed version was 1.5 times larger than that of the twin-screw compounded samples. Based on this burn data, the secondary heat processing step required during batch mixing did not have a significant effect on the flame retardant properties of either additive. This indicates that larger scale tests involving additional processing can be implemented while still maintaining the flame retardant properties of the DNA.

CHAPTER 5

CONCLUSIONS

5.1 DNA as a Flame Retardant for Poly(ethylene)

DNA was investigated as a natural alternative to commercially used intumescent flame retardant MPP. Better incorporation into the LDPE substrate was seen with DNA leading to improved mechanical properties, such as higher tensile modulus and increased strain at break. Lower compounding torque was required to compound DNA with LDPE relative to MPP at the same loading levels. The early onset of DNA degradation better protected the LDPE from thermal degradation during burning, leading to plastic-like char formation and significant reduction of burn distance during horizontal burn testing at loading levels of 10% w/w and above. Substrate protection by DNA was confirmed by the retention of LDPE peaks in the FT-IR spectra of the char. In LDPE, DNA outperforms MPP, a commercially used flame retardant, at lower loading levels, giving it great potential for use in future applications.

5.2 DNA as a Flame Retardant for Poly(styrene)

In PS, DNA acts as an intumescent flame retardant with equivalent efficacy to the commonly used MPP. Loading levels above 10% w/w effectively decrease burn distance and flame spread rate during horizontal burn testing. PS/MPP and PS/DNA samples show similar increases in modulus and decreases in elongation at break as loading level increases. At all loading levels, samples with DNA show a decrease in compounding torque from neat PS while addition of MPP causes an increase in torque.

Larger scale batch mixing was also explored which necessitated a second thermal processing step. While this additional heating was seen to slightly alter the mechanical properties of the material by decreasing modulus and increasing elongation at break, little change in flame retardant effectiveness was noted. Therefore, DNA can be utilized as a flame retardant in commercial polymers on a larger scale even when material needs to be heat processed multiple times.

DNA provided good flame retardant properties in multiple commodity polymer substrates while minimizing compounding torque and decreasing the loss of mechanical properties. Overall, this research has shown that DNA can be employed on a large scale as a green flame retardant in commercial polymers.

REFERENCES

[1] Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, *Underwriters Laboratories,* 2013.

[2] Dasari, A., Yu, Z.-Z., Cai, G.-P., Mai, Y.-W. Recent Developments in the Fire Retardancy of Polymeric Materials. *Progress in Polymer Science* **2013**, *38*, 1357–1387.

[3] A.B. Morgan, C.A. Wilkie, The Non-halogenated Flame Retardant Handbook, John Wiley & Sons, 2014.

[4] Allen, J. G., Stapleton, H. M., Vallarino, J., McNeely, E., McClean, M. D., Harrad, S. J., Rauert, C. B., Spengler, J. D. Exposure to Flame Retardant Chemicals on Commercial Airplanes. *Environmental Health* **2013**, *12*, 17.

[5] L.S. Birnbaum, D.F. Staskal, Brominated flame retardants: cause for concern? *Environmental Health Perspective* **2004**, 112, 9-17.

[6] Gao, H., Hu, S., Han, H., Zhang, J. Effect of Different Metallic Hydroxides on Flame-Retardant Properties of Low Density Polyethylene/melamine Polyphosphate/starch Composites. *J. Appl. Polym. Sci.* **2011**, *122*, 3263–3269.

[7] P. Lv, Z. Wang, K. Hu, W. Fan, Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives, *Polymer Degradation and Stability* **2005**, 90, 523-534.

[8] Lu, S.-Y., Hamerton, I. Recent Developments in the Chemistry of Halogen-Free Flame Retardant Polymers. *Progress in Polymer Science* **2002**, *27*, 1661–1712.

[9] FDA, Interim Safety and Risk Assessment of Melamine and its Analogues in Food for Humans, U.S. Food and Drug Administration.

[10] Chen, H.-B.; Shen, P.; Chen, M.-J.; Zhao, H.-B.; Schiraldi, D. Highly Efficient Flame Retardant Polyurethane Foam with Alginate/Clay Aerogel Coating. *Applied Materials and Interfaces* **2016**, *8*, 32557–32564.

[11] Alongi, J., Carletto, R. A., Di Blasio, A., Carosio, F., Bosco, F., Malucelli, G. DNA: A Novel, Green, Natural Flame Retardant and Suppressant for Cotton. *Journal of Materials Chemistry A* **2013**, *1*, 4779–4785.

[12] Carosio, F., Di Blasio, A., Alongi, J., Malucelli, G. Green DNA-Based Flame

Retardant Coatings Assembled through Layer by Layer. *Polymer* **2014**, *54*, 5148–5153.

[13] Alongi, J., Cuttica, F., Di Blasio, A., Carosio, F., Malucelli, G. Intumescent Features of Nucleic Acids and Proteins. *Thermochinica Acta* **2014**, *591*, 31–39.

[14] Alongi, J., Cuttica, F., Bourbigot, S., Malucelli, G. Thermal and Flame Retardant Properties of Ethylene Vinyl Acetate Copolymers Containing Deoxyribose Nucleic Acid or Ammonium Phosphate. *Journal of Thermal Analysis and Calorimetry* **2015**.

[15] L. Wang, J. Yoshida, N. Ogata, S. Sasaki, T. Kajiyama, Self-assembled supramolecular films derived from marine deoxyribonucleic acid (DNA)cationic surfactant complexes: large-scale preparation and optical and thermal properties, *Chemistry of Materials* **2001**, 13, 1273-1281,

[16] Isarov, S., Lee, P., Towslee, J., Hoffman, K., Davis, R., Maia, J., Pokorski, J. DNA as a Flame Retardant Additive for Low-Density Polyethylene. *Polymer* **2016**, *97*, 504–514.