



Effect of Flame Retardants and 1% Stabilizer on Burning, Flammability Behaviour, and Thermal Decomposition Properties Via Polypropylene Material Treatment

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Abstract: This study aimed to understand the mechanism of combining the action of different types of flame retardants on thermal stability and flammability of Polypropylene polymer (PP). PP Polymer was chosen to be blended in a twin screw extruder with the flame retardants (FR) and an additive, which is a 1% Stabilizer, to investigate Polypropylene's burning moderation and reduce it by studying its burning behavior and thermal decomposition properties. Flammability behaviour tests which is known as LOI were applied in this study. It was found that halogenated flame retardants have a little effect on reducing the rate of gas escape from polymer melt which affects the viscosity, as it was found that APP and FR245 in PP Polymer help in some leftovers of the polymer. All samples with flame retardants and no clay were burnt completely, and the flame spread was reduced and samples were self-extinguished except for the one containing the fire retardants only. All these results were investigated by XRD, Scanning Electron Microscopic (SEM), and Digital images of the charred samples of polymers.

Keywords: Materials treatment, Physical Sciences, Polymer science, Flammability behaviour, Polymers burning moderates and reduces.

INTRODUCTION

The present study is a part of a larger project exploring the production of a synthetic nano/micro fiber-composite fire retardants. This work concentrated on Polypropylene or polypropene (PP), which is a useful commodity polymer mainly used in clothing, furniture, floor coverings, medical, geotextiles, and automotive applications due to its low cost, lightweight, good mechanical properties, and low reactivity towards other chemicals. Polypropylene (PP) had higher values for tensile strength at break, the Polypropylene polymer degradation is occurring at high temperatures and the Polypropylene polymer (PP) Melting temperature is 174° C if pp is 100% isotactic and the temperature of glass transition of pp polymer is -17°C. The main

advantage is that PP is an addition polymer made from the monomer propylene, causing it to be unusually resistant to many chemical solvents, acids and bases. However, being wholly aliphatic hydrocarbon structure, it burns very rapidly with a relatively smoke-free flame and without leaving any char residue (Zhu *et.al*, 2001). Lack of polar groups in the structure makes it difficult to react with reactive flame retardants. Additive flame retardants if used, are required in large amounts (> 20% w/w) to provide the required fire protection to products (Zhang *et.al*, 2005), this flame retardancy effect increases with increasing irradiation and vanishes with decreasing irradiation (Qin *et.al*, 2005). However, such high levels of additives cause polymer processing problems, in particular for their extrusion into thin films or fibers. The

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flame retardancy is sensitive to modification of the flame retardant, the use of synergists/adjuvants, and changes to the polymeric material. A detailed understanding facilitates the launch of tailored and targeted development (Morgan and Wilkie 2007). Flammability tests still require some amount of conventional flame retardants. It must be noted, however, that with this approach of using flame retardants as additives, the polymer content in the formulation is reduced compared to the unmodified polymer. In our earlier publications, we have demonstrated that nanoclays can be nanodispersed in polypropylene with a proper choice of compatibilizer, and the compounded polymer can be extruded into fibers (Gilman, 2007- Qin *et.al*, 2005). Nanoclays, although increasing the thermal stability of polypropylene and helping in char formation (Xie *et.al*, 2001), they do not reduce the flammability of PP fibers to a large extent (Gilman, 2007). Clay, nanoclay, and a small amount of flame retardant (5%) when added together to PP containing certain compatibilizers, the extruded fibers could be self-extinguished. In our previous work, we have only used ammonium polyphosphate (Qin *et.al*, 2005) whereas in this study, we use different phosphorus. The main aim of this work is to understand the mechanism of combining the action of different types of flame retardants on thermal stability and flammability of PP. A number of polypropylene samples containing compatibilizer, clay, stabilizer, and different flame retardants have been compounded in a twin screw extruder.

MATERIALS AND METHODS

The following materials were obtained from commercial sources: the seven different thermoplastic Polypropylene polymers (PP). Samples are tested after blended with UV-Stabilizer (Nor) and Flame Retardants.

Polymer Preparation: The 7 polypropylene samples composition (wt %) and additives

were blended with 1% Stabilizer (Nor 116), and 5% FR as shown in Table 1.

For LOI and burning tests, coarse monofilaments (strands) were blended to the PP wt %, stabilizer 1 wt %, and FR 5 wt % (Table 1). However, the nanoclays which could be used (Cloisite 20A, and Southern Clay Products, USA) are montmorillonite clay modified with dimethyl, and dihydrogenated tallow quaternary ammonium chloride. This modified clay was chosen because of its nonpolar alkyl substituents. A Thermoelectron Prism Eurolab 16 twin screw extruder with a temperature profile over six heating zones between 179–190°C was used for compounding. The polymer samples (diameter 1.8 ± 0.2 mm) were collected before pelletising.

Table (1): Mass percentages of various components in the formulations where Stabilizer 1% is NOR 116.

	Sample	pp %	Graft 1%	FR 5(%)
1	PP-Nor116	100	---	---
2	PP-APP 107	96	Polybond (pb)	---
3	PP-NOR-NH	91	Polybond	APP
4	PP FR 107	91	Polybond	¹ FR245
5	PP Amgard 107	91	Polybond	Amgrad NH
6	PP 3OB	96	Polybond	---
7	PP APP 3OB	92	---	APP

Note: ¹FR = APP, NH, FR245, also PP-NOR-NH is PP 107,FR372 or FR245

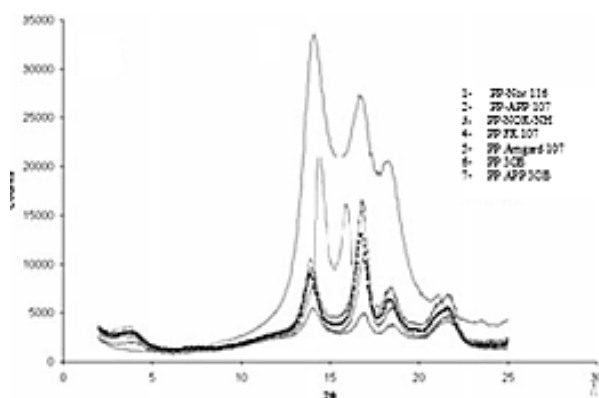


Fig. (1): The XRD curves for compounded clay-containing polymer samples showing the effect of clay and flame retardants on dispersion, where FR is APP and FR245

Characterisation and Testing: Limiting oxygen index (LOI) (Table 2) tests were conducted using a standard procedure (Morgan and Wilkie 2007). The burning behavior of each sample was observed and noted.

Table (2): LOI and flame spread results of compounded PP polymer samples.

PP sample	LOI (%)	Burning time (sec)	Burning behaviour
1	18.4 - 8.5	2.23 -5.07	Very small flame-black ash and fast Drips.
2	17.8 - 17.9	1.46 -2.7	Very small flame, black ash.
3	17.9	4.3	Very small flame, drips, ash, and then the flame became bigger.
4	1-18.8	17.44	Very small flame, slow drips, black ash
5	17.4 - 17.5	3.73- 4.16	Very small flame.
6	18.2	35.13	Small flame, drips and then the flame became bigger
7	18.3 - 18.4	7.1- 8.3	Very small flame-black ash.

RESULTS AND DISCUSSION

The chars were examined for PP as obtained in Fig. 2 and 3, and surface characteristics and morphology by Scanning Electron Microscopy (SEM) using a Cambridge Stereoscan 200 SEM. A Nicolet, Magna-IR Spectrometer 550 was used to study any structural changes in the chars, using KB discs containing 2% (w/w) char (Xie *et. al*, 2001, Morgan and Wilkie 2007).

PP-NOR-FR245



PP-NOR-APP



Figure (2): Digital images of charred samples of heating polymers .



Fig (3): clay in polypropylene–clay prepared by melt compounding polypropylene, A small fraction been included.

Although the XRD study was carried out in the range $2\theta = 2 - 600$, only the regions between $2\theta = 2 - 80$ were analyzed in detail. XRD curves for compounded clay-containing polymer samples showing the effect of clay and flame retardants on dispersion are presented in Figure 1. Also, the XRD and thermal analytical results of compounded polymers for the clay 1% value was 2.53nm. For sample PP-NOR, no peak could be observed, which could indicate to an exfoliation of the clay. In all flame retardant containing samples, the clay peak could be observed but at a slightly lower 2θ angle (Figure 1). Hence, higher d- spacings, and FR245 containing sample have a greater d-spacing (3.46 nm), followed by NH and Amgrad NH (sample PP Amgard 107) as recorded in Table1) (3.32, 3.31 nm), (Hu *et al*, 2007-B. Scharrel *et. al*, 2006) APP (3.23nm) and FR245 (3.20nm).

The differences are due to the effect of different flame retardants on dispersion of the clay (Xie *et.al*, 2001, Morgan and Wilkie 2007) as seen by the microscopic studies e.g. PP- NOR-107 (Fig. 3).The transmission electron micrographs of different samples in Figure 2 showed the effect of two types of flame retardants on clay dispersion. In Figure 2a, larger particles are appeared to be the flame retardant (APP) whereas the smaller and more structured particles appeared to be clay platelets that have started to delaminate and separate, thereby indicating that delamination is taking place. This delamination is also apparent in higher resolution electron micro-

scopic images of this sample in Figure 3. The dispersion appears to be much better for the sample PP-FR107-FR372 and PP-NOR107 (Figure 4), indicating that the flame retardant FR245 is much better dispersed compared to the nanoclay (Morgan and Wilkie 2007). In general, it can be concluded that although structures observed here are not obviously intercalated or exfoliated micro composites, a dispersion is indeed at the Nano level (Morgan and Wilkie 2007), i.e. particle size $< 1\mu\text{m}$. The clay particle widths appear to be $< 0.1\mu\text{m}$ with lengths up to $0.5\mu\text{m}$.



Figure (4): SEM image of charred PP-NOR-107 heated sample.

Thermal analysis: As a result, the addition of clay together with conventional flame retardants enhances both the overall thermal stability forming PP polymer. The compatibilizer helps in improving dispersion of the clay in the polymer (Morgan and Wilkie 2007), it also reduces the rate of gas escape from polymer melt affecting the viscosity. Also as can be seen from Figure 2, APP and FR245 in PP help in some char formation.

Characterization of the char residue: Selected samples are shown in Figure 2, it shows the presence of maleic-anhydride-grafted polypropylene, APP and clay in PP sample 3 (PP-NOR-NH)) has encouraged char formation (Figure 2b) whereas no char could be seen for the control sample. PP-NOR, which is still a molten polymer, has no char therefore could be observed for samples containing clays only (Fig 2b). Also as seen as in Fig. 3, the clay in polypropylene-clay was prepared by melt compounding polypropylene in a twin screw extruder. A small fraction (1–3% w/w) of modified grafted poly-

propylene (Morgan and Wilkie 2007) had also been included to improve dispersion of the clay (Morgan and Wilkie 2007). Scanning electron microscopic (SEM) images (Fig. 3 and 4) of these heated samples of polymers are shown in Figure (2b) and confirmed the analyses of images in Figure 2a. For example, the PP control sample in Figure (2b) showed the absence of any charred structure. The clay presence (Figure 3) (Figure 2 and 3) changed the morphology of *PP-NOR-107* polymer sample where it is seen to be more textured. Obvious char formation is not apparent until both clay and flame retardant are present together (Figure 2b), and respective char structures appear to differ albeit in an unclear way as seen in images of charred samples of polymer (Fig. 2a).

Limiting oxygen index (LOI): Limiting oxygen index (LOI) values for various samples are listed in Table 1 where it can be seen that clay and additives presence reduce them compared to either control or respective flame retardant containing samples. This behavior is not unexpected as clay presence changes the burning behavior of polymer by reducing its thermoplasticity (Beyler and Hirschler, 2002). In the presence of clay, the polymer neither melts nor lose energy via melt dripping. The polymer thus burns more easily and consistently as it was also evident from burning test results given in Table 6.

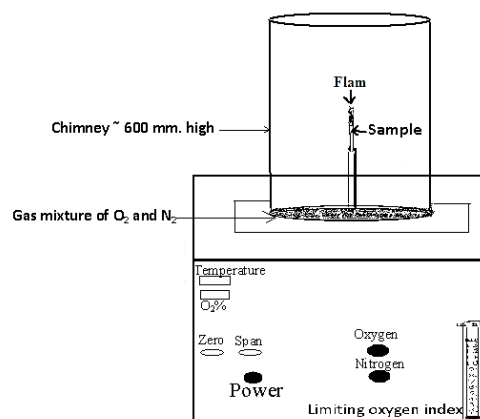


Fig. (a), The schematic of the (LOI) tests

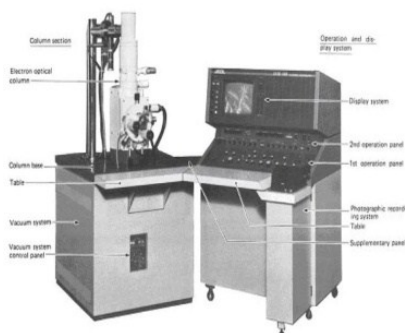


Fig. (b), Scanning electron microscopic (SEM)



Fig. (c), The XRD technique

CONCLUSION

The dispersion of nanoclay can be improved by compounding polymer-clay samples (Morgan and Wilkie 2007), and by adding a compatibilizer. LOI values are not changed significantly following the addition of clay and even in the presence of other flame retardants. However, the presence of nanoclay alone changes the thermal stability and burning behavior of the polypropylene. With additional flame retardant presence, the polymer can show self-extinguishing properties.

The effect of different flame retardant types on the thermal stability, flammability, and char formation tendency of Figure 3 optical micrographs of tape samples showed an effect of Polybond (pb) on clay dispersion. Polypropylene (PP) was studied. PP, compatibilizer, Clay, stabilizer, and different flame retardants have been compounded in a twin screw extruder to produce polymers with im-

proved thermal and flame retardant properties. Thermal analysis has been used to study the thermal properties and LOI. All flame retardants acting in the condensed phase (phosphorus- and nitrogen- containing) (Xie *et.al*, 2001) lowered the rate of decomposition, whereas halogenated flame retardants had a little effect. Addition of 1% compatibilizer with 3% clay in sample 3 has caused microdispersion of the clay particles. However, by increasing level of compatibilizer to 3%, the dispersion at the micro level has improved as observed by the absence of clay layer. The samples compatibilizer and clay have been previously masterbatched prior to dilution and blending. Flame retardants increased the thermal stability of all samples and helped in char formation (Morgan and Wilkie 2007). Flammability behavior testes and LOI are carried out to measure flammability properties and have been examined with digital images. The decomposition significantly reduces the molecular weight, followed by an easy flowing of polymer melts. The melting wax can flow over surfaces of the specimen and drip. Thus, it is expected that the small-size dripping is independent on the cross-sectional area of the specimen, that is the first dripping time or the mass of the first drop has a little to do with the thickness of the specimen.

Outcome and future work

Up to this period, this research completed the recent developments in the area of polymer – nanocomposites science, and has suggested that the addition of just a small quantity (< 5%) of organically modified layered-silicate nanoclay (montmorillonite) (Morgan and Wilkie 2007) to a PP polymer matrix could enhance many of the properties of that polymer, including the fire performance (Beyler and Hirschler, 2002). In polypropylene (PP), the lack of polar groups in the polymer chain makes the direct intercalation or exfoliation of the nanoclays almost impossible (Beyler and Hirschler, 2002) without the use of a compatibilizer (Gilman 2007, Morgan and

Wilkie 2007). Maleic anhydride-grafted polypropylene (PP-g-MA) can be used as a compatibilizer, which enhances the interaction between the clay and polymer with a strong hydrogen bonding between -OH or -COOH and the oxygen groups of clay (Xie *et.al*, 2001- Morgan and Wilkie 2007).

We expect that the research of Polymers science is one of the many sides and applications of material science and for the development of the Polymers and material treatments for a bright forthcoming future, for example we watched the effects of flame retardancy, FR and additives on the Polymers by assessing its burning behaviours, its chemical and physical properties, and its dripping when used to stop a fire which is now used for health and safety in real life and fire conditions.

Therefore it's very important to collect and record all the results related to these aims and more, (i.e. the flame retardancy effect increases with increasing treatment and disappears with decreasing treatment) (Schartel *et.al*, 2006), until now they found that the structures at the polycrystalline level. However, in most publications, the terms nanodispersion and nanocomposite (Morgan and Wilkie 2007) (the Nanoclay is Cloisite 20A, Southern Clay Products, USA, is a montmorillonite clay modified with dimethyl, dehydrogenated tallow-quaternary ammonium chloride (Morgan and Wilkie 2007), and this modified clay was chosen because of its non-polar alkyl substituents) are taken as mean conditions fulfilling (Morgan and Wilkie 2007).

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تأثير مثبطات اللهب و 1% مثبت، على الاحتراق وسلوك اللهب وخصائص التحلل الحراري من خلال معالجة مادة البولي بروبيلين

مستورة افحيمة

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المستخلص: تهدف هذه الدراسة الى فهم آلية توحيد تفاعل أنواع مختلفة من مثبطات اللهب الملهجنة على استمرار التحلل الحراري من 7 عينات مختلفة من البوليمر البولي بروبيلين (PP). تم اختيار البوليمر PP لمزجه في جهاز twin screw extruder مع مثبطات اللهب (FR) والمادة المضافة وهي 1% مثبت للتحقق واختبار التحكم في احتراق البولي بروبيلين وتقليله من خلال دراسة سلوك الاحتراق وخصائص التحلل الحراري. وتم إجراء اختبارات سلوك الاشتعال والمعروفة باختبار LOI في هذه الدراسة. كما وجد أن مثبطات اللهب الملهجنة لها تأثير ضئيل على خفض معدل ضياع وخروج الغاز الناتج عن ذوبان البوليمر والذي يؤثر على اللزوجة، كما وجد أن مثبطات اللهب APP وFR245 في بوليمر البولي بروبيلين (PP) يساعد في تشكيل بعض بقايا البوليمر. جميع العينات مع مثبطات اللهب وبدون المثبت Clay احترقت بالكامل، حجم اللهب قلَّ والعينات انطفت تلقائياً، ماعدا العينة التي تحتوي على مثبطات اللهب فقط. كل هذه النتائج فحصت باستعمال تقنية XRD و SEM وصور دقيقة (Digital images) العينات البوليمر المحترقة.

الكلمات المفتاحية: معالجة المواد، العلوم الفيزيائية، علم البوليمر، سلوك الاحتراق، التحكم وتقليل احتراق البوليمر.