FLAMMABILITY AND THERMAL PROPERTIES OF POLYPROPYLENE/ SILICON-BASED PRECERAMIC POLYMER COMPOSITES

Damla Eroglu and Goknur Bayram

Department of Chemical Engineering, Middle East Technical University, Ankara 06531, Turkey.

Introduction

Polypropylene (PP) is one of the most commonly used thermoplastic owing to its easy processing and good mechanical strength. However due to its wholly aliphatic structure, PP is highly flammable [1, 2]. In literature, many different kinds of flame retardants (FRs) are added to PP in order to decrease its flammability [1-3].

Environment-friendly FRs, meaning halogen-free FRs have received much attention since the degradation products of these FRs are less toxic, less corrosive and they do not contain halogen gases [1]. Silicon-based FRs are widely studied in literature since they provide effective flame retardancy without releasing harmful products to environment [1-3]. These FRs are also effective in the improvement of the thermal properties of PP due to their high thermal stabilities [1]. Silicon-based preceramic polymers that are converted to silicon carbide upon pyrolysis are also used in literature as FRs in PP. Addition of these preceramic polymers to PP provides flame retardancy by the ceramic char formation which acts as a heat and diffusion barrier and protects the unburned polymer [3-5].

The aim of this study was to investigate the effect of silicon-based preceramic polymers on the flammability and thermal properties of PP-based composites.

Experimental

Materials

PP (PETOPLEN MH418) was purchased from PETKIM with a melt index (ASTM D-1238) of 4.0-6.0 g/10min. Two different preceramic polymers were used to prepare the composites: poly(methylsilyne), (PMS) that was electrochemically synthesized in our laboratory [6], and allylhydridopolycarbosilane (SMP-10) purchased from Starfire Systems. In order to obtain synergism with the silicon containing polymers in PP, triphenylphosphate (TPP) (ACROS Organics) and a metal complex, M (Smokebloc AZ-12/BFR-4) (Great Lakes Chemical Corporation) which is a blend of antimony trioxide, zinc/magnesium oxide complex and a proprietary mineral silicate were used.

Composite Preparation and Characterization Tests

PP was ground to powder form by Wiley mill intermediate model grinder before blend preparation in order to achieve better mixing with the preceramic polymers. PMS and SMP-10 were dry mixed with PP before they were fed and melt blended with PP in a co-rotating twin-screw extruder (Thermoprism TSE 16 TC) with a screw speed of 100 rpm and a temperature profile of 180-185-195-205-215^{0}C from hopper to die. The polymer blends were pelletized after extrusion and then dried at 100^{0}C for 4 h before they were molded in injection molding (DSM Xplore Micro 10 cc Injection Molding Machine). The compositions of the blends prepared in the extruder can be seen in Table 1.

Table 1. Compositions of the composites

MATERIALS	PP %	SMP-10/ PMS %	TPP %	M %
PP/1SMP	99	1	-	-
PP/10SMP/10TPP	80	10	10	-
PP/10SMP/5TPP/5M	80	10	5	5
PP/1PMS	99	1	-	-
PP/10PMS/10TPP	80	10	10	-
PP/10PMS/5TPP/5M	80	10	5	5

LOI test was carried out according to the ASTM D2863 standards in the Dynisco Polymer Test LOI machine. TGA was performed by using a SHIMADZU 60H-DTG machine in the temperature range from room temperature to 800^{0}C by the heating rate of 20^{0}C/min.

Results and Discussion

Flammability Properties

The LOI values which are used to evaluate the flame retardancy of the composites are tabulated in Table 2.

Table 2. LOI values of the composites

	LOI (%)
PP	17.5
PP/1SMP	17.5
PP/10SMP/10TPP	20.5
PP/10SMP/5TPP/5M	23.5
PP/1PMS	18.0
PP/10PMS/10TPP	21.0
PP/10PMS/5TPP/5M	21.0
PP/10TPP/10M	19.5

LOI values of pure PP and PP/10TPP/10M containing only TPP and the metal complex are also given in order to make comparison. SMP-10 and

PMS are not effective flame retardants in small concentrations.

The most significant improvement in the flame retardancy is obtained in PP/10SMP/5TPP/5M set where SMP-10, TPP and the metal complex are used together in PP since the LOI value is increased to 23.5% from 17.5%. When this result is compared with the LOI value of PP/10TPP/10M blend, it can be concluded that TPP and the metal complex provide a synergy with SMP-10 since although both blends contain totally 20 wt% of flame retardant, PP/10TPP/10M has a much lower LOI value. PMS is more effective than SMP-10 in PP when it is used alone or with TPP. However, it does not provide a synergy with the metal complex like SMP-10. The synergy obtained in silicon and phosphorus-based compounds are mainly due to the increase in the amount and thermal stability of the char formed during burning. Both silicon and phosphorus containing flame retardants act in condensed phase by char promotion. When they are used together, a synergistic effect is seen due to the thermal stability of the char coming from the silicon-based compounds and increase in the char formation due to the phosphorus-based compounds [1]. The addition of the metal complex clearly provides a synergy with silicon and phosphorus-containing compounds most probably by increasing the thermal stability of the polymer by char promotion [7, 8].

Thermal Properties

TGA is performed in order to investigate the thermal stability of the composites and to complete the evaluation of flame retardancy, since char yield calculated by TGA gives important information about the flame retardancy mechanisms. TGA curves of the composites and the char yield % and average decomposition temperatures calculated from these curves are presented in Figure 1 and Table 3, respectively.

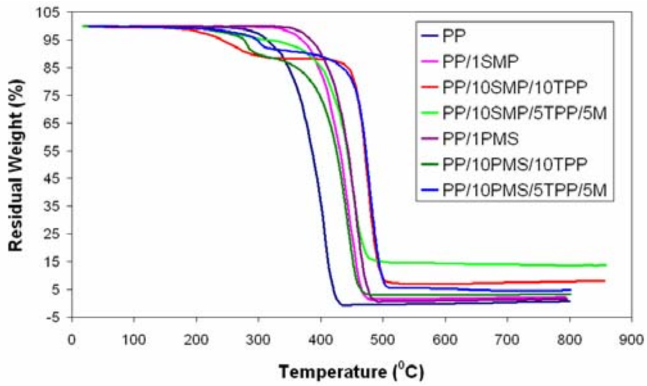

Figure 1. TGA curves of the composites in N_2

The addition of SMP-10 and PMS results in a significant increase in the average decomposition temperatures. This can also be seen from the shift of the curves to the right with the addition of FRs. PP/10SMP/5TPP/5M sample with the highest LOI value has the highest char yield of 13.74% proving that char promotion is the main flame retardancy mechanism for this synergy. On the other hand, the increase in the char yield with the addition of PMS is not as high as SMP-10, however the increase in the decomposition temperatures is very high. Therefore, increasing the thermal stability of the polymer composite is more significant than char promotion in the flame retardancy mechanism of PMS.

Table 3. Char yield % at 800^0C and average decomposition temperature of the composites

MATERIALS	Char Yield (%)	Ave. Decomp. Temp. (^{0}C)
PP	0.83	406
PP/1SMP	2.21	448
PP/10SMP/10TPP	7.92	478
PP/10SMP/5TPP/5M	13.74	453
PP/1PMS	1.62	457
PP/10PMS/10TPP	3.40	446
PP/10PMS/5TPP/5M	4.69	480

Conclusions

The effect of silicon-based preceramic polymers on the flammability and thermal properties of PP was investigated. With the addition of SMP-10, PMS, TPP and the metal complex, the flame retardancy and thermal properties were improved. A synergy was obtained when SMP-10, TPP and the metal complex were used together in PP. The LOI value increased to 23.5 from 17.5%, the char yield increased to 13.74 from 0.83% and average decomposition temperature increased to 453 from 406^0C. The main flame retardancy mechanism in this synergy was explained by char promotion.

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