

Improvement of Thermal and Fire Properties of Polypropylene

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ABSTRACT: In the present research, the thermal stability and fire properties of polypropylene (PP) have been improved through direct melt intercalation of PP, organically modified montmorillonite (OMMT), calcium carbonate (CaCO_3) nanoparticles, and conventional flame retardants, i.e., decabromodiphenyl oxide (DB) and antimony trioxide (AO). The morphology of the compound was characterized by means of X-ray diffractometry and transmission electron microscopy. Thermogravimetry analysis (TGA), cone-calorimetry, limiting oxygen index, UL-94, and tensile tests were also employed to investigate thermal and mechanical properties as well as the flammability of the compounds. Data, obtained from TGA, indicated that simultaneous incorporation of both OMMT and

CaCO_3 nanoparticles forms a synergistic effect to improve both the thermal and thermo-oxidative stability. The kinetic analysis of polymer degradation showed that the presence of nanoparticles hindered the thermal degradation of PP. The combination of OMMT and CaCO_3 was more effective to improve fire properties than OMMT and DB/AO. The experimental results indicated that the incorporation of OMMT and CaCO_3 improved both the tensile (i.e., the increase of yield strength, tensile strength, and Young's modulus) and thermal properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2971–2979, 2008

Key words: flame retardance; nanocomposites; mechanical properties; thermal properties

INTRODUCTION

Because of the chemical structure and weak bonding among the molecules, synthetic polymers degrade easily when they are exposed to the high temperatures. This problem significantly limits their industrial applications, so many research works have been carried on to improve thermal and fire properties of these materials.^{1–4} Additives and reactive flame retardants such as chlorinated paraffin, brominated polystyrene, poly vinyl chloride, and ammonium phosphate have been used to protect polymeric materials against fire in the recent years. Those additives are usually added to the polymer during the compounding process and to some extent solve the problem.^{2,3} However, using these additives causes two major problems; first, the migration of the additives from the bulk to the surface of the polymer forms a nonuniform compound after a while. Second, because of the weak interaction between the additives and the polymer matrix, weak points are formed in the matrix which decrease the mechanical strength of the specimens.^{1–3} The reactive flame retardants, such as tetrachlorophthalic and tetrabro-

mophthalic, are also used to increase flame resistance of the polymers. They are used as comonomers and placed into the polymer chain during the polymerization process.^{2,3} Although introducing flame retardant comonomers into polymer chemical structure is an effective way to increase flame resistance of the polymer, the high cost of the material as well as difficulties with the polymerization process and also the environmental concerns limit the use of this method. It is cited that the reactive flame retardants do not affect the physical and mechanical properties of the polymers.^{1–6} In 1950, the theory of nanoparticles was presented by Richard Feynman. Several years later, the first nanocomposite was made in the TOYOTA Co. labs. This was the beginning of the employment of nanoparticles into polymeric matrices. Many researchers started to use nanoparticles to improve polymers fire resistance rather than the conventional methods.^{7–11} The use of nanoparticles not only reduces the peak heat release rate (HRR) of polymers but also improved their physical and mechanical properties.^{12–14} Nanoparticles with different structures and natures have been used to reinforce polymers against fire. One nanoparticle which is extensively used is clay. According to the previous researches, clay retards the degradation process of the polymer matrix; two investigations on degradation kinetics of polyamide 6 (PA6)/clay¹⁵ and polystyrene (PS)/clay¹⁶ show that the activation energy

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of degradation is increased when clay is added to the polymer. This is attributed to the two dimensional structure of clay layers that prohibit the heat transfer from the exterior layer to the interior and also stop the mass transfer from the solid to the gas phase.¹⁷⁻¹⁹

Wilkie and coworkers investigated the role of the ions, existing in the structure of clay, in capturing the radicals resulted from the degradation of macromolecule chains. They deduced that the clay caused the radicals to recombine, so that it decreased the rate of weight loss in this manner.²⁰

Other types of nanoparticles as well as a mixture of them also have been used to reinforce polymers against thermal degradation or fire. Kashiwagi and coworkers used multiwalled carbon nanotubes to decrease the flammability of polypropylene (PP).²¹ Laachachi et al. utilized titanium oxide (TiO₂), ferric oxide (Fe₂O₃), and organically modified montmorillonite (OMMT) nanoparticles to increase resistance to flammability of poly(methyl methacrylate) (PMMA). The synergetic effect was observed when a mixture of TiO₂, a nanometallic oxide, and OMMT was added to PMMA matrix. They significantly improved the heat resistance of the polymer by decreasing the HRR.²² Zaharescu et al. employed CaCO₃ nanoparticles to improve the oxidative degradation of PP.²³ Longzhen et al. added magnesium hydroxide (Mg(OH)₂) nanoparticles to poly(ethylene-co-vinyl acetate) (EVA) to increase the resistance to flammability of the polymer.²⁴ Avell et al. used CaCO₃ nanoparticles modified with fatty acids to investigate the thermal properties of PA6. They observed that the same additives have a negative effect on the thermal and thermo-oxidative stability of PP.²⁵ Other than conventional systems and nanoparticles, intumescent flame retardants (IFR) are also used to thermally stabilize the polymers. Yang et al. used IFR and MMT system to increase thermal stability of PP.²⁶ Meifang et al. utilized a new system based on melamine phosphate and pentaerythritol/polyurethane composite that formed an intumescent system in which char forming phenomenon improved the thermal stability of PP.²⁷

In this research, the influence of two types of conventional reactive flame retardants decabromodiphenyl oxide (DB) and antimony trioxide (AO), and two types of nanomaterials i.e., nanoclay and nano-CaCO₃ and their mixtures, are investigated on PP. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) analyses are carried on to study the morphology of the nanocomposites. The effects of these systems on the thermal and thermo-oxidative degradation and the flammability of PP are probed using thermogravimetry analysis (TGA), Cone Calorimetry, limiting oxygen index (LOI) and UL-94 tests. Finally, using tensile test, the mechani-

cal properties of the samples are studied to determine any changes caused by those additives.

EXPERIMENTAL

Materials

PP granules, grade PI0800, with a MFI index equal to 8 g/10 min were obtained from Bandar Emam Petrochemical Co. Maleated polypropylene (PP-g-MA) with a commercial name called Fusabond, with MFI equal to 420 g/10 min was also obtained from Dupont Co. MMT (CEC = 97 mequiv/100 g, average particle size of 20 μm) was provided by KeYan (Heifei, China). Hexadecyltrimethylammonium bromide (C16) as the organo-modifier of OMMT was provided from Shanghai Chemistry Company (China). The surface modified CaCO₃ nanoparticles by titanate coupling agent were from KeYan (China). The flame retardants i.e., decabromodiphenyl oxide (DR-83R) and AO (Trimonox) were from Great Lakes Co.

Sample preparation

The PP nanocomposites were prepared by melt mixing in an internal mixer (300 cc, Haake Mixer-Sys 90). The mixing temperature was 180°C and the rotation speed was 60 rpm.^{28,29} Before mixing, PP, PP-g-MA, OMMT, and CaCO₃ were placed in an oven, where the temperature was set at 100°C, for 2 h. The sequence of feeding was as follows: PP and PP-g-MA were mixed until the torque remained unchanged.²⁸ Then the nanoparticles were added and the mixing continued until a steady torque was attained again. Finally, DB/AO mixture was added to the compound and enough time was given to reach the constant torque. The total time of mixing to reach a constant torque varied from 8 to 15 min depending on the nanocomposite inclusions. The final product then was hot pressed at 180°C and 20 MPa to make sheets with 3 mm thickness. Table I shows the samples including various inclusions.^{30,31}

Characterization

The OMMT dispersion state in PP matrix was evaluated by XRD (XRD, BRUKER-XS X-ray diffraction-meter, 30 kV, 10 mA, Cu K_α) and bright field TEM. The TEM study was done by use of PHILIPS CM200 with an acceleration voltage of 200 kV microtomed with Reichert U3 ultra microtome. TGA as well as differential thermogravimetry (DTG) of the samples was done by use of a DuPont TGA V5.1A thermogravimetric analyzer with temperature range of 10–600°C while heating rate was 20°K/min under both air and nitrogen atmospheres with flow rate of 40 mL/min. Cone-Calorimetry tests were carried out

TABLE I
Composition of the Samples

| Sample code | PP (%) | PP-g-MA (%) | DB (%) | AO (%) | OMMT (%) | CaCO ₃ (%) |
|-------------|--------|-------------|--------|--------|----------|-----------------------|
| PP | 92 | 8 | – | – | – | – |
| PPDA | 78.2 | 6.8 | 11.25 | 3.75 | – | – |
| PPO5 | 87.4 | 7.6 | – | – | 5 | – |
| PPC5 | 87.4 | 7.6 | – | – | – | 5 |
| PPDAO1 | 77 | 6.7 | 11.25 | 3.75 | 1 | – |
| PPDAO3 | 74.4 | 6.56 | 11.25 | 3.75 | 3 | – |
| PPDAO5 | 73.6 | 6.4 | 11.25 | 3.75 | 5 | – |
| PPO5C5 | 82.8 | 7.2 | – | – | 5 | 5 |

with heat flux of 50 kW/m². It was on accordance with ASTM E 1354.³² The LOI experiment was done according to ASTM D2863.³³ Dimension of test specimen bar was 20 cm × 15 mm × 3 mm. The flammability of the samples was probed in a mixture of nitrogen and oxygen for 3 min. Figure 1 shows the schematic representation of the LOI test. UL-94V test was done based on ASTM D3801,³⁴ which qualitatively classified the samples. The leakage and time of flammability of 12.7 × 127 × 3 mm³ specimens were measured. Considering these factors, the samples were categorized in V-0 to V-2 showing the level of resistance to flammability. Mechanical properties were investigated using tensile test (ASTM D638,³⁵ Instron model, strain rate of 50 mm/min). Young's Modulus, yield strength, and elongation at break were reported.

RESULTS AND DISCUSSION

Morphology of the samples

Figure 2 shows XRD patterns of MMT, OMMT, PPO5, PPDAO5, and PPO5C5 samples. MMT shows a peak at $2\theta = 5.9^\circ$ that corresponds $d_{001} = 1.49$ nm.

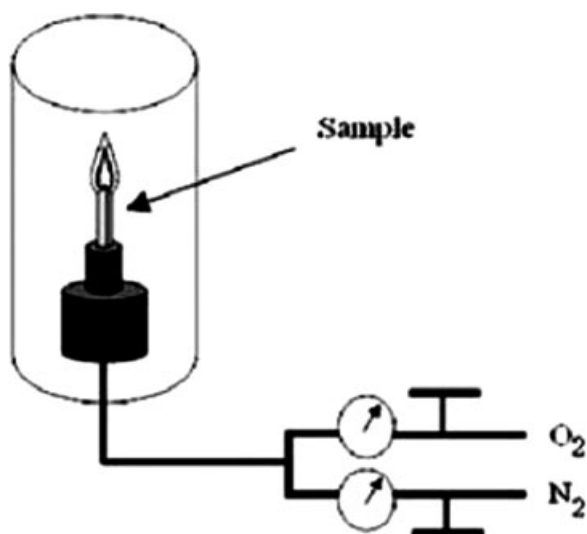


Figure 1 LOI instrument.

Such gallery spacing shows that PP, as the matrix, is not able to intercalate into the MMT layers.³⁶ OMMT shows three major peaks at $2\theta = 2.7^\circ$, $2\theta = 4.7^\circ$, and $2\theta = 7.2^\circ$, corresponding to interlayer spacing of 3.52, 1.87, and 1.19 nm, respectively. The peaks represent crystal aspects of d_{001} , d_{002} , and d_{003} , respectively. Shifting of the d_{001} peak to lower degrees indicates that the organo-modifier increases gallery spacing. The increase of gallery spacing, in turn, reduces the Van der Waals forces among the platelets so that the PP macromolecule chains intercalate into the layers more easily and the delamination process of the clay layers will be accomplished more effectively. The PPO5 mixture shows a less intensive peak at $2\theta = 4.5^\circ$, indicating a nearly exfoliated state, which is created by interdiffusion of PP matrix or PP-g-MA chains as the coupling agent of OMMT layers and PP matrix. Tang and Kawasumi have been reported that PP chains are not able to enter the interlayer spacing in absence of PP-g-MA.^{37,38} In PPDAO5 and PPO5C5 mixtures, the absence of any peaks confirms the exfoliated structure of the related nanocomposites. In the former case, the exfoliation

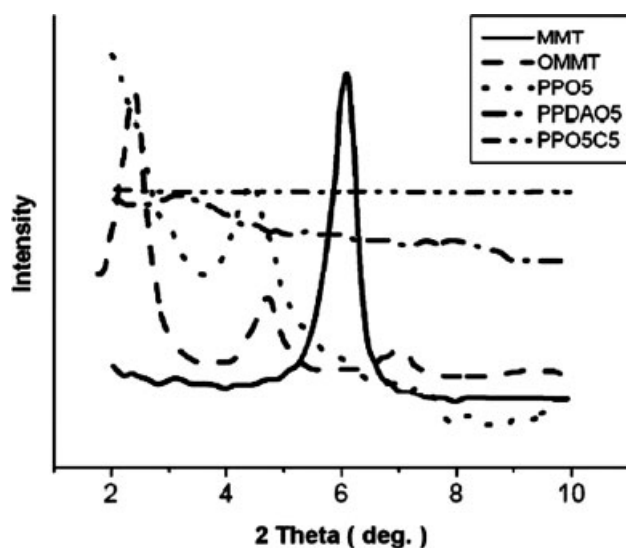


Figure 2 XRD graphs of MMT, OMMT, PPDA, PPO5, PPC5, PPDAO5, and PPO5C5 samples.

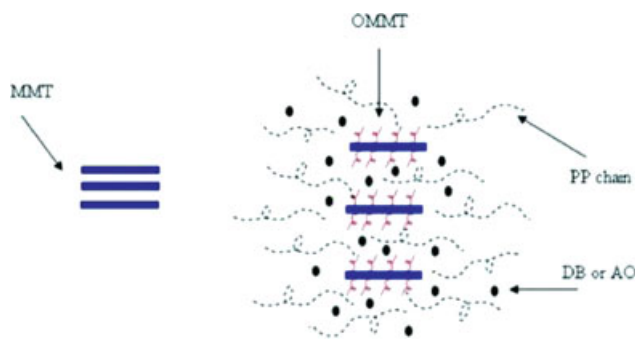


Figure 3 Schematic representation of clay platelets in presence of DB/AO particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of clay platelets is contributed to the polar structure of DB/AO. Wang et al. showed that the increase of DB/AO in the compound improved the dispersion of clay in acrylonitrile butadiene styrene (ABS) matrix.³⁹ Figure 3 schematically shows how DB and AO work together to delaminate clay platelets. In the case of PPO5C5, the uniform distribution of CaCO₃ nanoparticles facilitates the separation of clay platelets. A similar phenomenon was reported by Hu et al.⁴⁰ Figure 4 illustrates the TEM images of PPO5, PPC5, PPDAO5, and PPO5C5 samples. The dark regions point up the clay layers and CaCO₃ nanoparticles whereas the light regions indicate the PP matrix. In the TEM graph of PPO5 sample, patterns are observed that prove the existence of intercalated and exfoliated structure of OMMT as well as some of OMMT aggregates. In the PPDAO5 and PPO5C5 samples fully exfoliated structures are observed which is in good agreement with XRD analysis.

Thermal properties

Figure 5(A) shows the TGA and DTG curves of PP, PPDA, PPO5, and PPC5 under air atmosphere. Table II reports the temperatures at 10% weight loss ($T_{0.1}$),

temperatures at 50% weight loss ($T_{0.5}$), and weight residue at 400 and 600°C. As indicated in the table, DB/AO and CaCO₃ increase both $T_{0.1}$ and $T_{0.5}$ whereas OMMT decreases those parameters of PP. The $T_{0.1}$ and $T_{0.5}$ records show that OMMT has a negative effect on thermo-oxidative stability of PP. This is attributed to the early degradation of organic groups attached to the surface of OMMT.

This is correlated to the PPC5 ability of dispersion in the PP matrix as it is evidenced by TEM morphological studies. In the PPO5 specimen, despite the onset of degradation in lower temperatures compared with pristine PP, the rate of weight loss is lower in a temperature range of 300–400°C. This is associated to layer structure of OMMT. The OMMT layers acting as insulators decrease the heat transfer flux and reduce oxygen diffusion into the polymer and consequently decrease the thermo-oxidative degradation rate. Also the mass transfer rate from the solid to gas phase decreases so that the rate of degradation decreases.^{41,42}

Figure 5(B) shows the TGA and DTG curves of PPDAO1, PPDAO3, PPDAO5, and PPO5C5 under air atmosphere. In comparison with PP, $T_{0.1}$ increased 15, 14.4, 13.6, and 23.6%, respectively. Also, $T_{0.5}$ increased 14.9, 19.4, 20.6, and 23.6%, respectively. Thus, the simultaneous incorporation of DB/AO and OMMT into the PP matrix was more effective than that of any of them alone. This synergistic effect is attributed to the contribution of DB/AO to improve the degree of exfoliation of OMMT in the PP matrix, as evidenced by TEM analysis. Interestingly, incorporation of both OMMT and CaCO₃ to the PP matrix dramatically enhanced the thermal stability. This is because the dispersion of OMMT is enhanced in the presence of CaCO₃ nanoparticles as indicated by the morphological analysis. The DTG curves of PP, PPDA, and PPC5 appear very similar. In all cases DTG has detected only one single peak for each sample that indicates degradation has happened in one-stage and it is controlled by one single mechanism. On the other hand, DTG

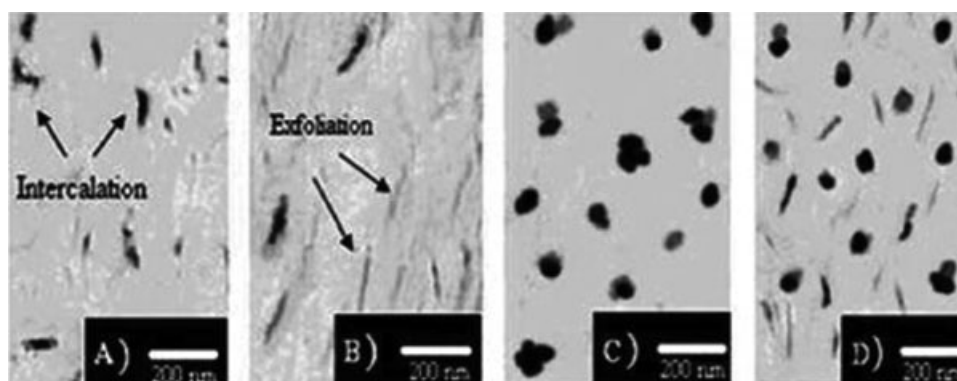


Figure 4 TEM images of A: PPO5, B: PPDAO 5, C: PPC5, and D: PPO5C5 samples.

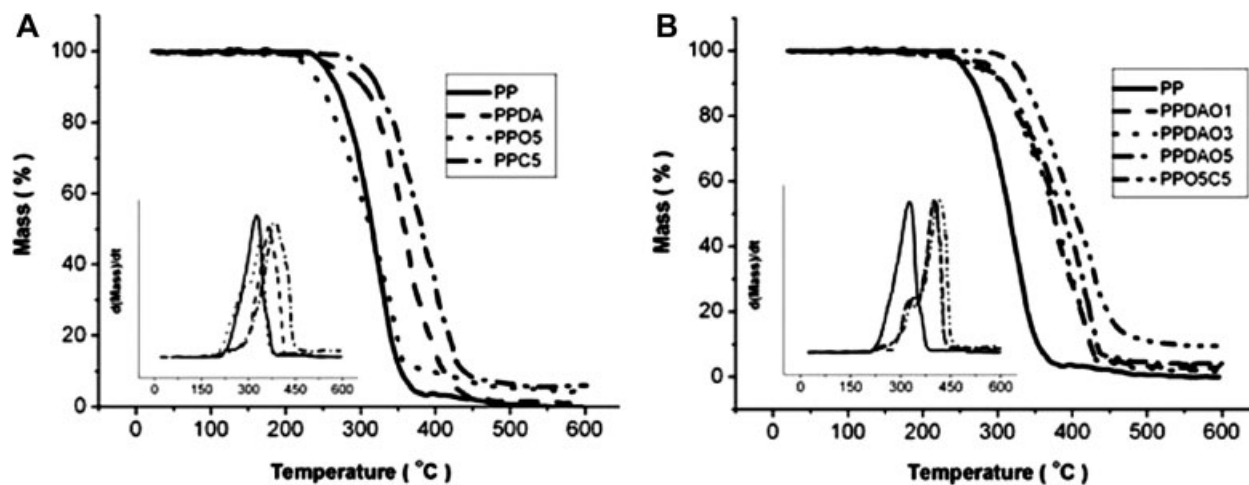


Figure 5 TGA and DTG thermograms of A: PP, PPDA, PPO5, PPC5 and B: PP, PPDAO1, PPDAO3, PPDAO5, and PPO5C5 samples conducted in air atmosphere.

curve for PPO5 shows two peaks that demonstrate a two-stage degradation mechanism where first stage is related to the degradation of organo-modifier tethered to the surface of the OMMT layers and the second one is due to degradation of PP macromolecule chains.

Kinetic analysis of thermal properties

TGA and DTG analysis was performed for all the samples under nitrogen atmosphere as shown in Figure 6 to analyze the kinetic of degradation. There exist different methods to investigate the kinetic of degradation such as Kissinger,⁴³ Coats-Redfern,⁴⁴ and Freeman-Carroll methods.⁴⁵ Eq. (1) is the starting point for all those methods

$$r = \frac{d\alpha}{dt} = Ae^{(-E/RT)}(1 - \alpha)^n \quad (1)$$

where r is the reaction rate, α the weight loss, t time, T temperature, A prefactor, R the gas constant, E

TABLE II
TGA Data of the Samples

| Sample | $T_{0.1}$ (°C) | $T_{0.5}$ (°C) | Mass in 400°C | Mass in 600°C |
|--------|----------------|----------------|---------------|---------------|
| PP | 271 | 325 | 96.5 | 0.092 |
| PPDA | 305 | 358 | 86.7 | 1.52 |
| PPO5 | 251 | 322 | 90.3 | 4.2 |
| PPC5 | 322 | 389 | 62.6 | 4.8 |
| PPDAO1 | 309 | 382 | 76.16 | 1.76 |
| PPDAO3 | 311 | 388 | 65.02 | 2.58 |
| PPDAO5 | 315 | 392 | 53.64 | 5.35 |
| PPO5C5 | 335 | 410 | 48.2 | 9.1 |

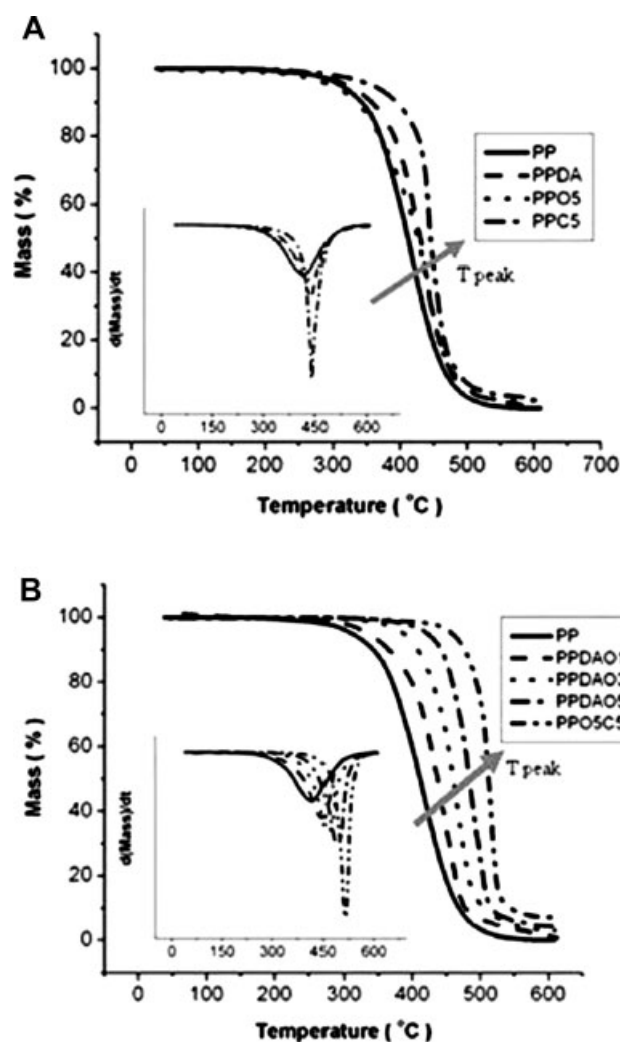


Figure 6 TGA and DTG thermograms of A: PP, PPDA, PPO5, PPC5 and B: PP, PPDAO1, PPDAO3, PPDAO5 and PPO5C5 samples conducted in nitrogen atmosphere.

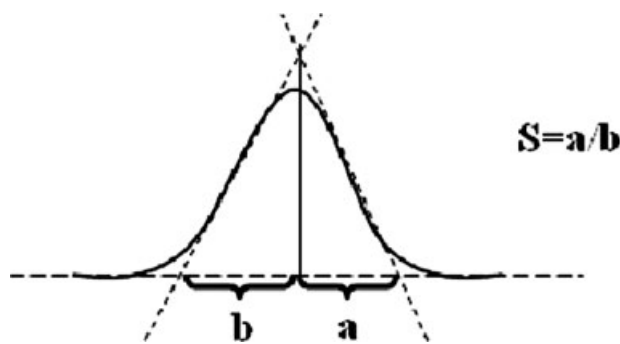


Figure 7 Determination of shape factor, s , used in Kissinger's method.

activation energy, and n reaction order. Using Kissinger's method, the reaction order is calculated as

$$n = 1.26\sqrt{s} \quad (2)$$

where s represents the shape factor of DTG thermograms that is calculated as shown in Figure 8.

Investigation on the degradation kinetics of the samples is based on Coats-Redfern's method

$$\log \frac{g(\alpha)}{T^2} = \log \left\{ \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] \right\} - \frac{E}{2.3RT} \quad (3)$$

$$g(\alpha) = -\ln(1 - \alpha) \quad (4)$$

$$g(\alpha) = (1 - (1 - \alpha)^{(1-n)}) / (1 - n) \quad (5)$$

where $g(\alpha)$ is a function of weight loss and β differentiation of temperature respect to time (dT/dt). If n , the reaction order, equals 1, then $g(\alpha)$ in eq. (3) can be replaced by eq. (4), otherwise $g(\alpha)$ is replaced by eq. (5). The reaction order (n), is calculated using

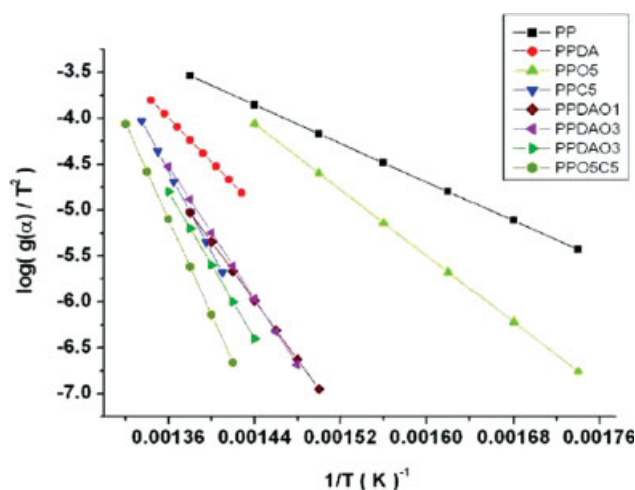


Figure 8 Kinetic of degradation curves calculated using Coats-Redfern's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Kinetic Parameters Obtained from Kissinger and Coats-Redfern Methods

| Sample | Kissinger Method | | Coats-Redfern Method | | |
|--------|------------------|------|----------------------|--------|--------|
| | s | n | n | E | R |
| PP | 0.52 | 0.91 | 0.91 | 100.32 | 0.9997 |
| PPDA | 0.28 | 0.66 | 0.66 | 229.4 | 0.9996 |
| PPO5 | 0.50 | 0.89 | 0.89 | 172 | 0.9993 |
| PPC5 | 1.06 | 0.78 | 0.78 | 420 | 0.9988 |
| PPDAO1 | 0 | 0 | 0 | 305.9 | 0.9972 |
| PPDAO3 | 0 | 0 | 0 | 344.19 | 0.9983 |
| PPDAO5 | 0 | 0 | 0 | 382.44 | 0.9992 |
| PPO5C5 | 0 | 0 | 0 | 497.1 | 0.9995 |

Kissinger's method in Figure 7. Then in the next step, n values are applied into the Coats-Redfern's equation to calculate E , the activation energy. Figure 8 shows the curves obtained using Coats-Redfern's method. Table III shows the acquired data including the activation energy of degradation and the correlation coefficients of the curves. If the correlation coefficient is in the range of 0.996–0.998 then the reaction orders, calculated from Kissinger's method, are accurate and reliable. The reaction order for PP is determined and found to be 0.91 that is in good agreement with the value of 1 which is already reported by the other investigators.^{46–48} The reaction orders for degradation of PPDA, PPO5, and PPC5 are measured and found to be 0.66, 0.79, and 0.88, respectively. On the other hand, the reaction order for degradation of PPDAO with 1, 3, and 5% of OMMT and also PPO5C5 are found to be zero. The different values for reaction order, tell us the mechanism of degradation reaction is different for each compound. Qin et al.¹⁹ showed that under the nitrogen atmosphere the order of degradation reaction for PPO5 is zero.

As the experimental results indicate, the amount of OMMT between 1 and 5% has no effect on the degradation reaction order of PP; neither does the replacement of DB/AO with CaCO_3 .

When reviewing the activation energy of degradation, PPO5 nanocomposite demonstrates the lowest value. It is due to the degradation of the organic molecules with low thermal stability used for surface modification of MMT. However, the activation energy of degradation of PPO5 is higher than that of PP, showing the effect of OMMT layers to increase the thermal stability. The synergetic effect of OMMT and CaCO_3 nanoparticles results in a remarkable increase in the activation energy of PPO5C5 samples.

Fire properties

Figure 9 illustrates the HRR curves for PP, PPDA, PPO5, PPC5, PPDAO5, and PPO5C5 nanocomposites

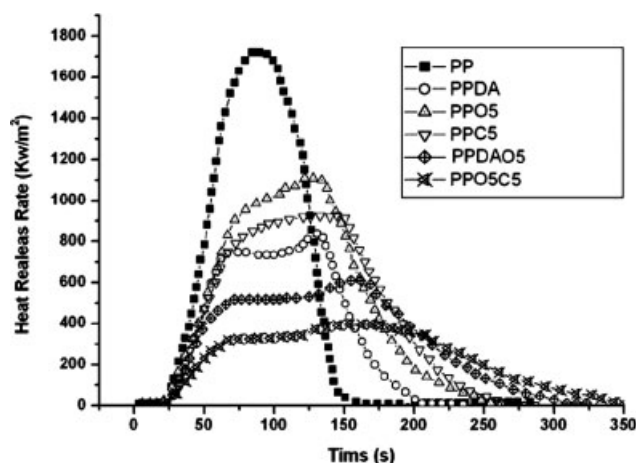
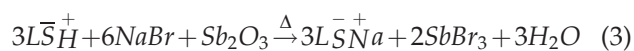
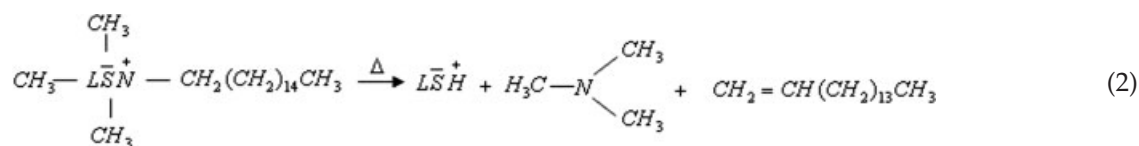


Figure 9 HRR curves of the studied samples.

provided by cone-calorimeter. The HRR peak of PPDA, PPO5, and PPC5 appear 53, 36, and 59% lower than that of PP, respectively. This is explained by the reaction of AO with the halogenated compound that is DB in this case (see reaction 1).⁴⁹ CaCO₃ decreases the flammability more than what OMMT does. This is attributed to the superior dispersion of CaCO₃ in the compound and the presence of fewer agglomerates.

Comparing HRR data obtained for PPDAO5 and PPO5C5 samples to that of PP, demonstrates 70 and 81% decrease, respectively. The more efficient synergism of the OMMT and CaCO₃ compound in comparison with OMMT and DB/AO compound to decrease the HRR of PP is explained by more effective exfoliation of OMMT layers by CaCO₃ nanoparticles. This is already observed in TEM photographs.

Furthermore, two peaks are observed in the range of 50–100s for all samples. The first peak is formed as the carbonaceous char at the surface of the condensed phase is developed.^{50,51} The second peak at 100s is attributed to the degradation of the carbonaceous char layer. The total time to complete the destruction process of the protective layer depends on the composition of the compounds. Incorporation of OMMT in the PPDA blend stabilizes the char structure and decreases the HRR peak; however, it does not increase the time to collapse. The dispersed clay enhances the formation of the char, which acts as an excellent insulator so that more barriers to mass transfer is created and the rate of heat release decreases. When OMMT and DB/AO are both present in the compound, reactions among those substances are discovered (see reactions (1), (2) and (3)).^{52,53} The thermal decomposition of the OMMT takes place at 200°C. It proceeds in accordance to the Hofmann degradation mechanism.¹⁸ The initial step is the formation of an olefinic molecule as well as an amine molecule. An acidic proton detached from these obtained products is exchanged with quaternary ammonium cation placed between layered silicates (*LSN*⁺) and yields *LSH* (reaction 2). The reaction between AO and sodium bromide, as an impurity due to the ion exchange reaction, yields antimony tribromide, which is an effective flame retardant gas (reaction 3). Reactions 1, 2, and 3 cause the destruction of the char yield to happen at a slower pace, so that the flammability of PPDAO5 increases.



Flame resistance

Table IV indicates the values of limited oxygen indices. In this test, the minimum amount of required oxygen to stabilize the flame of the samples is reported; the higher the LOI value is, the higher the resistance to flammability will be. The LOI value is obtained based on eq. (6)

$$LOI\% = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} \quad (6)$$

The LOI value of PP is 17.4% that indicates relatively high flammability. Incorporation of OMMT into PP increases LOI value to 22.7%.¹⁸ Since the LOI value is higher than 22%, the PPO5 sample is classified as a material with average flammability. The LOI of PPDA reaches to 24.3%. DB and AO reduce the activity of free radicals and make them inactive. Thus, a higher amount of oxygen will be needed to stabilize the flame. Where OMMT included samples are exposed to the flame, the organo-modifier molecules will degrade fast as evidenced by TGA analysis. Consequently, a reinforced charred silicate structure forms. The produced

TABLE IV
Flame Characteristics and Mechanical Properties Indicators for the Samples

| Samples | LOI (%) | UL-94V | Yang's Modulus (MPa) | Tensile Strength (MPa) | Elongation at break (%) |
|---------|---------|---------|----------------------|------------------------|-------------------------|
| PP | 17.4 | burning | 1960 | 40 | 16 |
| PPDA | 24.3 | V-2 | 1887 | 28.81 | 10 |
| PPO5 | 22.7 | burning | 3652 | 43.5 | 8 |
| PPC5 | 23.6 | V-0 | 3721 | 46.32 | 6.50 |
| PPDAO1 | 24.9 | V-2 | 2128 | 32.6 | 8.60 |
| PPDAO3 | 26.3 | V-1 | 2632 | 38.1 | 8.20 |
| PPDAO5 | 28.5 | V-0 | 3448 | 41.5 | 7.30 |
| PPO5C5 | 29.2 | V-0 | 4365 | 55.21 | 4.50 |

structure acts as an insulator and both the heat transfer flux to the underneath layers and volatilization of gaseous products into the gas phase reduce. The LOI value of PPDAO5 is 28.3% which categorizes it in the materials with low flammability. To obtain such a LOI value, 27 wt % of halogenated flame retardants is needed in the PP matrix which is in accordance to the previous work done by Jelle et al.⁵⁴ Using 27 wt % of flame retardants in PP not only deteriorates the mechanical properties of the polymer but also causes environmental problems. The LOI values increase as the clay content increases up to 5 wt %. For higher inclusions, the LOI index decreases due to the poor dispersion and agglomeration of OMMT platelets in the PP matrix. Poor dispersion and agglomeration of OMMT prevents the clay to reach a layered structure and consequently the flammability and mechanical properties do not improve as expected.^{28,29}

Table IV presents the observations from test UL94-V. PP and PPO5 samples failed in the test because of being burnt. PPDA and PPDAO1 are categorized in V-2 class. In these samples, the stability of flame is

low but the leakage problem, that spreads the flame, remains. PPDAO3 shows poor flammability property categorized in V-1 class. PPC5, PPDAO5, and PPO5C5 are classified in V-0 category that means the stability of the flame decreases dramatically and the flame is extinguished in less than 10 s and the flammability to spread is reduced remarkably.

Mechanical properties

Figure 10 depicts the stress–strain behavior of the samples. The obtained results are shown in Table IV. According to the reported data, incorporation of DB/AO to the PP matrix decreases the Young's Modulus and yield strength 3.7 and 28%, respectively, compared with PP. To justify the reduction of the mechanical properties, it must be noted that DB and AO have polar molecules so that they are not able to establish a strong interaction with nonpolar PP molecules.⁵⁴ In PPO5 samples, due to an exfoliated/intercalated structure of OMMT layers, the Young's Modulus and yield strength increase 86 and 8%, respectively, compared with PP. In PPC5 sample, the Young's modulus and yield strength increase 89 and 15.8%, respectively, compared to PP. In PPDAO5 sample, Young's Modulus and yield strength increase and elongation at break decreases. The incorporation of DB/AO facilitates the exfoliation of OMMT layers that results in more effective stress transfer between OMMT and PP matrix. The PPO5C5 sample shows the highest level of improvement in mechanical properties. This is because the highest degree of exfoliation of OMMT occurs in presence of CaCO₃ nanoparticles as evidenced by XRD and TEM analyses.

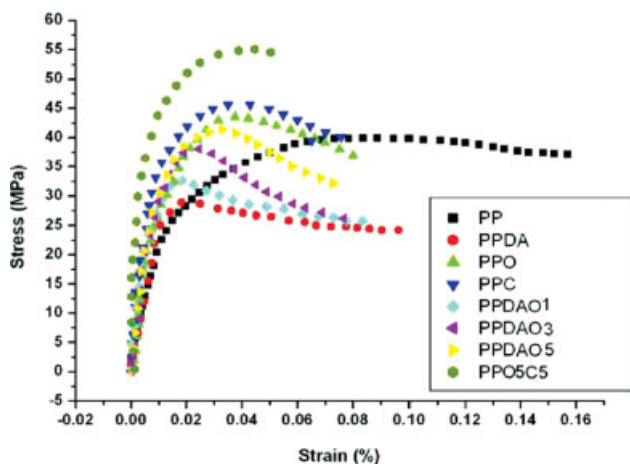


Figure 10 Stress–strain curves of the studied samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

In this study, PP is blended with classical flame retardants i.e., DB and AO, and nano size fillers i.e., OMMT and CaCO₃. The morphological analysis is accomplished using XRD and TEM. It is shown that in PPDAO5 and PPO5C5 samples, adding DB/AO

and CaCO₃ nanoparticles to the PP matrix helps OMMT layers to exfoliate more. TGA analysis shows that simultaneous incorporation of DB/AO and OMMT into the PP matrix improves the thermal stability more effectively compared to when they are added separately. Also, it is observed that the synergistic effect between OMMT and CaCO₃ is more efficient than that between DB/AO and OMMT to improve the mechanical properties and the flammability. Investigation of kinetic of degradation using Coats-Redfern model shows that simultaneous incorporation of OMMT and CaCO₃ nanocomposites significantly enhances the activation energy of degradation. Cone-calorimetry data indicates that PPO5C5 sample has the lowest HRR among the samples. LOI test shows that the flammability properties of PPO5C5 are improved the most compared to the other samples. UL-94 test demonstrates that the PPDAO5 and PPO5C5 samples are categorized in V-0 class. The tensile tests reveal that the PPO5C5 compound provides the highest yield strength and young modulus among the samples. Finally, it is concluded that adding only 10 wt % nanoparticles i.e., OMMT/CaCO₃ to PP improves both the thermal and mechanical properties more comparing when 21% wt of DB/AO is added to PP.

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