Effect on thermal behaviour of polyamide 66/clay nanocomposites with inorganic flame retardant additives

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Polyamide 66 (PA66)/clay nanocomposites have been prepared with inorganic additives by melt blending method using an extruder. Inorganic additives such as potassium nitrate, zinc borate and magnesium hydroxide along with organic phosphinate have been used to study their effect on thermal behaviour of PA66/clay nanocomposites. The nanocomposites have been characterized by XRD which confirms the formation of intercalated and/or exfoliated nanocomposites. The thermal degradation behaviour of nanocomposites has been studied by TG, DTA, DSC and FTIR. PA66/30B nanocomposite is thermally stable in the higher temperature range beyond 450 °C with increase in char yield due to formation of nanocomposite and hindered diffusion of volatile products. DSC curve of PA66/30B shows an endothermic peak at 452 °C with higher heat of absorption (378 J/g) during the decomposition stage due to intercalation of PA66 between the 30B interlayers. The presence of a band in the FTIR spectrum in the range 2224−2245 cm\(^{-1}\) in all PA66 nanocomposites char residue samples at 400 °C indicates the presence of nitrile group in the degradation products of PA66. The addition of zinc borate along with organic phosphinate induces a change in path of decomposition of polymer, leading to higher char formation which may protect the polymer from burning.

Keywords: Organoclays, Composites, Nanocomposites, Clay composites, Polyamide 66, Thermal stability, Flame retardants

Polymers have an important role in modern life as their use is rapidly increasing in all spheres of human actively. However, when polymers, particularly thermoplastics, are heated they lose strength, melt and drip. On further heating they are ignited and start burning vigorously with a flame and often produce smoke and toxic gases during combustion without leaving any char. The use of durable and environment friendly flame retardant additives is of growing importance in several industries including textiles and plastics in view of the increasing health concerns in the society. Therefore, to extend their use for wider applications, search for alternatives to toxic halogen-based flame retardants to improve the thermal stability and fire retardant behaviour of polymers is a major challenge. Thermal degradation studies of polymers are also important in understanding their thermal stability for application and thermal cycling.

Polymer nanocomposites based on layered silicates have gained attention due to their ability to improve mechanical, thermal, barrier to mass and heat transfer and fire retardant properties of polymers compared to pure polymers\(^{1,2}\) and are considered to be environment friendly alternatives to most traditional flame retardants. The unique properties of polymer layered silicate nanocomposites are attributed to their nanometer size features and the extraordinarily high surface area of the dispersed clay\(^{3}\). Nanocomposites can be synthesized via melt intercalation, in situ polymerization and solution polymerization. Melt intercalation is considered an industrially, economically and environmentally sound method\(^{4,5}\) since no solvent is involved in the process and it can be performed through conventional processing techniques.

Polyamide (PA66) contains a mixture of chains that have only amines or only acid groups, or a combination of two at their ends. PA66 is a versatile engineering plastic and is characterized by its excellent physical and mechanical properties\(^{6}\) and good processability. Therefore, it is widely used in engineering applications. Also, it has a polar and polymorphic structure\(^{7}\), and therefore, is expected to have more interaction with organoclay having functional groups. However, the flammability of virgin PA66 seriously limits its applications. PA66/clay nanocomposites were reported by Kojima et al.\(^{8}\) and Kohan\(^{9}\). Goettler et al.\(^{10,11}\) have analyzed the effect of compounding method, molecular weight, amine/carboxyl end group ratio on the properties of
nanocomposites of PA66. All these properties make these nanocomposites interesting for a wide variety of applications, e.g., automotive, electric and electronics, packaging, cable, and others.

Herein, we have studied the effects of inorganic additives such as potassium nitrate, zinc borate and magnesium hydroxide at low loading with halogen-free organic phosphinate and organoclay on PA66 in terms of thermal behaviour, synergy and their influence on charring of PA66. The use of zinc borate in combination with other halogen-free flame retardants is advantageous and it has been demonstrated that it acts as smoke suppressant, afterglow suppressant, corrosion inhibitor and synergistic agent\(^{12,18}\). The magnesium hydroxide used as flame retardant functions through dehydration to magnesium oxide with absorption of heat\(^{19,20}\). Different combinations were investigated for PA66 composites with organoclay and inorganic additives using thermal techniques such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR).

Materials and Methods

PA66 was purchased from Sigma Aldrich. Cloisite 30B abbreviated as 30B (sodium montmorillonite modified with methyl tallow bis-(2-hydroxyethyl) quaternary ammonium cation) was supplied by Southern Clay Products Inc., US. Organic phosphinate (OP), (Exolit OP 1230, \([C_4H_{10}PO_2]_3\)Al) was obtained from Clariant Inc., Germany. The inorganic additives such as potassium nitrate (KN), zinc borate (ZB) and magnesium hydroxide (MH) were purchased from Himedia Chemicals Co., India. All these materials were used as received without further purification. For Cloisite 30B, the cation exchange capacity was about 90 meq per 100 g clay and % weight loss on ignition was 30 %. The composition of the samples is given in Table 1.

Preparation and characterisation of nanocomposites

PA66 pellets were oven dried at 85 °C for 10 h and ground. The desired proportions of the materials (Table 1) were mixed and the samples were processed by using melt blending method in a single screw extruder (Maxwell mixing extruder, 3/4 inch dia.) at a throughput (material extruded per unit time) of 200 g/h. Extrusion was performed within the temperature range 240–250 °C at a screw speed of 30 rpm. The extrudate in the form of strands was air cooled. Granules were formed using the pinch rolls of the Take up (CS–194T) and chopper (CS–194C). The granules were again oven dried at 80 °C for 10 h and ground to obtain coarse material.

X-ray diffraction (XRD) measurements were performed with Bruker D8 Advance equipped with Cu–K\(\alpha\) radiation (\(\lambda = 0.1542 \text{ nm}, 40 \text{ kV}, 40 \text{ mA}\)) with 20 scan range of 3–30° at room temperature. XRD allows the determination of the spaces between structural layers of the silicate utilizing Bragg’s law: \(\sin \theta = n\lambda/2d\). The changes in the interlayer spacing of the organoclays were calculated in order to determine the extent of exfoliation or intercalation in the nanocomposites.

Thermal analysis

Thermal analysis (TG/DTA) was performed at a heating rate of 10 °C/min from ambient temperature to 700 °C in air atmosphere (flow rate = 100 mL/min) using TA instrument (SDT 2960). DSC analysis was carried out using a TA instrument differential scanning calorimeter thermal analyzer (DSC Q–10). The samples (4–8 mg) were weighed in the aluminum pan and placed in the DSC cell, and heated from 40 to 500 °C at a heating rate of 10 °C/min under constant nitrogen flow (50 mL/min).

Fourier transform infrared spectroscopy

Infrared spectra of PA66 and its composites were recorded before heating in the range 4000–400 cm\(^{-1}\) using Shimadzu IR affinity–I 8000 FTIR spectrometer at a resolution of 4 cm\(^{-1}\). The samples were heated in a muffle furnace at 400 °C for 10 minutes and then FTIR spectra of the char residues obtained was taken.

Results and Discussion

Polymer/clay nanocomposites were formed by insertion of polymer chains between the clay layers resulting in increase in the gallery space and forcing the clay layers to separate. A shift in the clay peak in XRD spectrum is associated with the formation of an intercalated structure, while disappearance of \(d_{001}\) peak is indicative of an exfoliated structure in nanocomposites\(^{21}\). Reduction in intensity of the clay peak results from the decrease in the amount of intercalated clay suggesting the breakdown of platelet agglomerates or partial exfoliation. Figure 1 shows the XRD pattern of 30B, OP and its composites with pure PA66. The basal spacing of 30B was found at 1.746 nm corresponding to \(2\theta = 5.05^\circ\). For PA66/30B nanocomposite, the diffraction peak at \(2\theta = 5.05^\circ\) shifts to even lower angles in this study, indicating intercalation of PA66 into 30B, whereas in the case of PA66/30B/OP, the
characteristic peak of 30B is absent up to the lowest measurable angle of 3° indicating exfoliation of clay. This phenomenon can be attributed to two different situations. The first is that the 30B content in the sample is so small that the diffracted intensity is too weak to show a diffraction peak. The second is that layers of clay have been exfoliated into a matrix, and hence the $2\theta$ value of the diffraction peak is not seen on the curve. According to Vaia and Gianelis\textsuperscript{22}, the absence of the characteristic $d_{001}$ diffraction peak of clay (either because of much too large spacing between the layers or because the nanocomposites do not present ordering anymore) is strong evidence of the formation of exfoliated or disordered nanocomposites. The quantitative measurement of nanocomposites formation is a challenge. Often intermediate state of nanocomposites with mixed

| Table 1—DTA and DSC data of PA66/clay nanocomposites |
|---|---|---|---|---|---|---|
| Sample | Comp. (%) | DTA | Nature of peaks | DSC\textsuperscript{a} | Heat flow (J/g) |
| PA66 | 100 | Initial temp. (°C) | Max. temp. (°C) | Initial temp. (°C) | Max. temp. (°C) |
| | | 239 | 265 | Exo | 247 | 261 | 82 |
| | | 392 | 415 | Exo | 404 | 406 | 90 |
| | | 437 | 440 | Endo | 428 | 445 | 194 |
| | | 448 | 452.464 | Exo | 452 | 464 | 495 | 530 |
| | | 478 | 495.530 | Exo | 495 | 530 | |
| PA66/30B | 95/5 | 245 | 264 | Endo | 252 | 262 | 73 |
| | | 337 | 357 | Endo | 413 | 452 | 378 |
| | | 383 | 394 | Exo | | | |
| | | 405 | 419 | Endo | | | |
| | | 445 | 474 | Exo | | | |
| | | 502 | 545 | Exo | | | |
| PA66/OP | 80/20 | 249 | 263 | Endo | 251 | 262 | 68 |
| | | 300 | 338 | Exo | 335 | 348 | 3 |
| | | 363 | 385 | Exo | 375 | 411 | 272 |
| | | — | 418 | Endo | 444 | 449 | 5 |
| | | — | 467 | Exo | | | |
| | | 485 | 496,560 | Exo | | | |
| PA66/30B/OP | 80/5/15 | 250 | 263 | Endo | 251 | 262 | 65 |
| | | 305 | 335 | Exo | 335 | 361 | 2 |
| | | 357 | 384 | Exo | 381 | 416 | 231 |
| | | 397 | 417 | Endo | 448 | 461 | 8 |
| | | 456 | 496,593 | Exo | | | |
| PA66/30B/OP/KN | 80/5/10/5 | 248 | 258 | Endo | 245 | 256 | 72 |
| | | 297 | 332 | Exo | 387 | 398 | 109 |
| | | 361 | 403 | Endo | | | |
| | | 451 | 471 | Exo | | | |
| | | 484 | 492 | — | | | |
| | | 492 | 505,583 | Exo | | | |
| PA66/30B/OP/ZB | 80/5/10/5 | 248 | 263 | Endo | 253 | 261 | 64 |
| | | 303 | 341 | Exo | 371 | 408 | 326 |
| | | 366 | 381 | Exo | 450 | 461 | 18 |
| | | 396 | 411 | Endo | | | |
| | | 447 | 457,625 | Exo | | | |
| PA66/30B/OP/MH | 80/5/10/5 | 250 | 263 | Endo | 252 | 260 | 48 |
| | | 316 | 352 | Exo | 374 | 381 | 480 |
| | | — | 370 | Endo | 438 | 449 | 4 |
| | | 523 | 558 | Exo | | | |

\textsuperscript{a}Under nitrogen; all peaks are endo.

Fig. 1—XRD patterns of (1) OP, (2) 30B, (3) PA66, (4) PA66/30B, and (5) PA66/30B/OP nanocomposites.
morphologies is formed with regions of different concentration of exfoliated and intercalated silicate layers along with tactoids (microcomposites).

The TG curves of samples indicate the number of stages of thermal degradation, weight loss in each stage, decomposition temperature and also provide information about the nature and extent of degradation of the material. TG data of PA66 and its nanocomposites with 30B and OP are shown in Fig. 2(a–d) and Table 2. The TG curve (Fig. 2a) of PA66 shows that PA66 degrades almost completely and only 0.3 % char residue remains at 650 °C. PA66 shows two stages of thermal degradation having different weight loss with DTG maxima observed at 454 and 550 °C. The first stage of degradation of PA66 is the main degradation step up to 485 °C with a weight loss of 82.5 %. The second stage of thermal degradation was observed in the range 485–700 °C with a weight loss of about 16 %. The highest rate of degradation of PA66 occurred in the first degradation stage around 455 °C. Levchik et al.\textsuperscript{23,24} and others\textsuperscript{25-28} have discussed the thermal degradation process of PA66 in detail and have shown that the major degradation products during radical scission degradation of PA66 are cyclopentanone, unreacted monomer (hexamethylene diamine), light volatile oligomers, ammonia, amides, amines, water and CO\textsubscript{2}. The onset temperature of degradation, $T_{10\text{wt} \%}$ (the temperature at which 10 % wt. loss takes place) of PA66 is 402 °C and $T_{50\text{wt} \%}$ (the temperature at which 50 % wt. loss takes place) is 448 °C.

DTA curve of PA66 in air (Fig. 2a) shows three major peaks corresponding to the first stage of thermal degradation in the temperature range 100–485 °C with a weight loss of about 82.5 %. The first endothermic peak at 265 °C represents the melting of the polymer and the second peak, which is exothermic with maximum at 415 °C, may be due to initial decomposition of polymer. The third peak is endothermic with a maximum at 440 °C, which represents the major decomposition due to radical scission of the PA66 in air near the temperature of maximum weight loss rate at 454 °C during the first stage of degradation. Further, the last exothermic peak, a double transition with maxima at 495 and 530 °C, corresponds to the second stage of thermal degradation in the temperature range 485–700 °C, which may be due to oxidation of released volatile products and residue left behind till the complete volatilization.

Effect of organoclay (30B)

The TG curve of PA66/30B (Fig. 2b) containing 5 wt % of 30B shows that $T_{10\text{wt} \%}$ decreases by 8 °C
while no significant increase is observed in $T_{50w\%}$. The decrease in onset temperature may be due to the presence of degradable organic moiety present in 30B. From TG curves, it can be seen that the thermal degradation behaviour of PA66/30B is almost similar to that of pure PA66 up to 450 °C. However above 450 °C, PA66/30B nanocomposite has stabilized as indicated by the DTG peak at 560 °C, which is 10 °C higher than that of pure PA66. This increase of thermal stability is attributed to formation of nanocomposite and hindered diffusion of volatile decomposition products within the nanocomposites. The char yield of PA66/30B is increased by 4.2 % as compared to pure PA66, probably due to the barrier effect of clay which prevents escape of decomposed volatile products from PA66. In the initial stage of degradation of polymer, the carbonaceous residue is not formed enough to form a cohesive layer with clay and hence catalytic effect of clay is dominant. However, at the later stage of thermal degradation enough carbonaceous residue is formed and effective concentration of clay is increased due to loss of polymer moiety. Therefore, after major decomposition of polymer at higher temperature, the combination of carbonaceous residue of polymer and clay itself forms a cohesive protective layer at the surface of substrate and acts as an effective barrier to both mass and heat transfer.

DTA response of PA66/30B in air shows three major peaks corresponding to the first stage of thermal degradation in temperature range 100−495 °C with a weight loss of 82.4 %. The first endothermic peak at 264 °C represents melting of the polymer composite while the second peak which is exothermic with a maximum at 394 °C is due to initial decomposition of the polymer. The third peak at 419 °C is endothermic and represents the major decomposition of the PA66 in air due to radical scission near the temperature of maximum weight loss rate at 460 °C during the first stage of degradation. These two peaks, exothermic at 394 and endothermic at 419 °C, occur at lower temperature in comparison of pure PA66 due to presence of organic moiety in clay and catalytic activity of clay because of its large surface area. Two more exothermic peaks with maxima at 474 and 545 °C are observed, which may be due to oxidation of released volatile products and residue left, respectively. The last DTA exothermic peak at 545 °C is at higher temperature by 15 °C, which is attributed to presence of dispersed clay layers in the composite which prevents the volatile products from escaping.

**Effect of organic phosphinate (OP)**

On incorporation of OP (20 wt%) into PA66, two stages of thermal degradation are observed. The thermal degradation of PA66/OP starts at lower temperature due to the catalyzing effect of OP on degradation of PA66. Therefore, a decrease in $T_{10w\%}$ and $T_{50w\%}$ by about 50 and 10 °C, respectively is observed as compared to pure PA66. Phosphonic, phosphinic and phosphoric acids (P−acids) are released by OP which catalyze the degradation of PA66 as supported by the lowered DTG peak at 340 °C in the case of PA66/OP. Subsequently, polyphosphoric acid and their metal salts are formed which further interact with PA66 and tend to increase the carbonaceous residue. In this sample, the last DTG peak is found to be increased by 25 °C in comparison to PA66 and thus this sample is seen to be stabilized after 450 °C. The weight loss of PA66/OP composite is less in comparison to that of pure PA66 due to lesser formation of volatile products which indicates that OP changes the decomposition behaviour of PA66 favourably for stabilization of PA66/OP composite. The increased stability of solid residue of PA66/OP after 450 °C is seen from the TG curve where $T_{75w\%}$ (502 °C) is higher by 40 °C as compared to that of pure PA66 (463 °C).

DTA curve of PA66/OP composite shows an additional exothermic peak at 338 °C, which may be due to formation of P−acids from OP. Table 1 and Fig. 2c reveal that the number and nature of DTA peaks of PA66/OP sample are similar to that of pure PA66, except that the peaks are observed at significantly lower temperatures (except the last exotherm at 560 °C) due to catalyzing effect of released P−acids from OP. The last exotherm at 560 °C is found at a higher temperature than that of pure PA66 (530 °C) which may be due to stabilization of the polymer composite residue probably due to the presence of metal phosphates and formation of compact and protective char layer. Horold also reported that polyphosphoric acid reacts with polyamide and/or its degradation product to yield a compact and protective char layer. Costa and Camino also reported that due to synergistic effect of P/N, organic phosphorus reacts with nitrogen containing compounds derived from PA66 and forms macromolecular substances such as (PNO) or (PN), with high thermal stability. These macromolecular substances further consolidate as a char protective layer.
In the case of PA66/30B/OP composite, on replacing 5 wt% OP out of the total 20 wt% OP with 5 wt% 30B, the onset degradation temperature of PA66/30B/OP is observed at a temperature 8 °C higher than that of PA66/OP. The DTG maximum (605 °C) of this composite is increased further by 30 °C, indicating the synergy of 30B and OP in stabilizing the polymer at the higher temperature range. This synergy is also seen from the last DTA exothermic peak at 593 °C (Fig. 2d) at a higher temperature than the PA66/OP composite. In the PA66/30B/OP sample, the char yield is lower than that of PA66/OP.

**Effect of inorganic additives in combination with 30B and OP**

TG curve (Fig. 3a) of PA66/30B/OP/KN composite with a total 20 % loading of additives (5 wt% of 30B, 10 wt% of OP and 5 wt% of KN) shows that addition of KN accelerates degradation of the sample in the initial stage. \( T_{10\text{wt\%}} \) of PA66/30B/OP/KN is observed at 343 °C, which is much lower than that of PA66/30B/OP. DTA curve shows that addition of KN to PA66/30B/OP sample (i) decreases the melting point by 5 °C, (ii) merges the two exotherms into one at 332 °C, (iii) shifts the endotherm at 403 °C due to chain scission to much lower temperature, and, (iv) increases the last exotherm at 583 °C due to oxidation in air. These observed effects may be due to the strong oxidizing behaviour of KN. Levchik et al. reported that KN as a strong oxidizer interacts with the polymer in condensed phase and increases the char yield since oxidation in the condensed phase promotes charring. KN decomposes to potassium oxides which may form potassium carbonates on interaction with CO\(_2\) with evolution of water on oxidation of the polymer. However, in our study, synergy of KN is not observed with 30B and OP as far as increase in thermal stability and production of char yield is concerned.

In the case of PA66/30B/OP/ZB where 5 wt% KN in PA66/30B/OP/KN is replaced by 5 wt% ZB, it is observed from the TG curve (Fig. 3b) of the studied additives, ZB stabilizes PA66/30B/OP/ZB composite the most. This is supported by the DTG maximum at a high temperature (630 °C). ZB has been studied along with metal hydroxide and not much is known about behaviour of ZB in combination with organic phosphinate and clay. ZB gives rise to higher char yield of about 14 % in the PA66/30B/OP/ZB sample. TG indicates that ZB stabilizes the nanocomposite in the higher temperature region which may be attributed to the carbonizing and cross-linking processes. Thus, addition of ZB induces a change in path of thermal decomposition of polymer leading to higher char formation. It has been demonstrated that reaction of ZB with phosphorus compounds and acids leads to the formation of zinc phosphates and borophosphates. ZB contributes to the enhanced char formation at the surface of the polymer, which protects the polymer from burning.

DTA curve of PA66/30B/OP/ZB is almost similar to that of PA66/30B/OP, except that the last exothermic peak at 625 °C is shifted to higher temperature which may be because of delay in effect of oxidation of polymer substrate due to presence of boron oxide.

The mass loss behaviour of PA66/30B/OP/MH during thermal degradation is different due to

![Fig. 3—TG and DTA curves of (a) PA66/30B/OP/KN, (b) PA66/30B/OP/ZB, (c) PA66/30B/OP/MH, and, (d) Mg(OH)\(_2\) samples.](image-url)
presence of MH. The TG curve (Fig. 3c) of this sample clearly shows three stages of thermal degradation in comparison to two stages of PA66. These three stages are in the temperature ranges 100–390, 390–525 and 535–700 °C with 48.5 %, 25.7 % and 12.7 % weight losses respectively supported by DTG peaks at 370, 458 and 570 °C, respectively. The DTA curve of MH (Fig. 3d) shows that it decomposes with the endothermic peak at 390 °C due to release of water. Once MH itself decomposes, it changes the degradation behaviour of PA66/30B/OP/MH. The onset degradation temperature of PA66/30B/OP/MH is 26 °C lower than that of PA66/30B/OP with lowering of the decomposition temperature of the polymer.

DTA curve of PA66/30B/OP/MH shows two major peaks; one endothermic peak at 370 °C which represents the major decomposition of the sample and the other exothermic peak at 558 °C due to oxidative degradation of the sample. DTA curve shows a plateau from 400-500 °C due to the endothermic decomposition of MH to form a thermally stable inorganic residue of MgO and water vapour. Many workers reported that MH serves as a typical inorganic flame retardant by endothermic decomposition, and, the release of water over 300 °C yields the oxide residue.

If we compare the thermal degradation behaviour of PA66 with and without additives, the first degradation step of PA66 composites occurs at a lower temperature as compared to pure PA66. However, during the later stage of degradation beyond 450 °C, the path of thermal degradation of PA66 composites containing FR additives changes significantly and polymer composites show higher thermal stability.

It is known that the ability of a polymer to form char is directly related to the flammability of a polymer. Therefore, higher the amount of residual char after combustion, lower is the amount of combustible material for perpetuating the flame and the greater is the degree of flame retardancy. In this study, increased flame retardancy is expected for PA66/30B/OP/ZB sample due to higher char yield of about 14 % in comparison to the other samples.

DSC studies

DSC thermograms of samples were obtained from ambient temperature to 500 °C in nitrogen atmosphere and are shown in Fig. 4. The initiation and maximum temperatures along with heat flow are given in Table 1. In the DSC curve of pure PA66, the endothermic peak at 261 °C corresponds to the melting point of PA66. There are two clear endothermic peaks at 406 and 445 °C with respective heat absorptions of 90 and 194 J/g, corresponding to the major thermal degradation of pure PA66. On addition of 30B to PA66, an endothermic peak is observed at 452 °C with higher heat of absorption (378 J/g) during decomposition. This may be due to difficulty in decomposing the thermally stable nanocomposite in nitrogen atmosphere due to intercalation of PA66 between 30B. The heat capacity and thermal conductivity of clay present in PA66 may also play a role in increasing the heat absorption in degradation of the polymer.

PA66/OP and PA66/30B/OP samples show major endotherms at 411 °C and 416 °C with 272 and 231 J/g heat absorption values, respectively, due to decomposition. Similar to DTA results, DSC curve of the sample with KN shows a decrease in the melting point by 5 °C. On addition of KN to PA66/30B/OP, the heat absorbed during decomposition decreases significantly. Therefore, KN being a strong oxidizer facilitates decomposition of the sample. During endothermic decomposition, respectively higher values of heat of absorption (326 and 480 J/g) are observed on addition of ZB and MH to PA66/30B/OP. The addition of MH makes the decomposition of sample highly endothermic due to dehydration of MH. MH shows a large endotherm at 411 °C with large heat of absorption (1218 J/g) due to decomposition of MH to MgO with release of water.

Char structures

PA66 and its nanocomposites were heated in a muffle furnace for 10 minutes at a temperature of

![Fig. 4—DSC curves of (1) PA66, (2) PA66/30B, (3) PA66/OP, (4) PA66/30B/OP, (5) PA66/30B/OP/KN, (6) PA66/30B/OP/ZB, and, (7) PA66/30B/OP/MH samples.](image-url)
400 °C to obtain their char residues. The visual observation of the residues showed a compact black char layer at the surface. The carbonaceous swelled char covers a larger surface area in the case of PA66/30B/OP with KN and ZB which prevents the contact of substrate with air atmosphere and volatile gases to escape. It appears that the hardness of the nanocomposites char is maintained up to 400 °C in all samples except PA66/30B/OP/KN and PA66/30B/OP/MH.

FTIR of PA66 and nanocomposites

The infrared spectra of PA66 samples are shown in Fig. 5. The IR spectrum of PA66/30B nanocomposite is similar to that of PA66 except for some additional Si–O bands of 30B. The relative intensity of out-of-plane Si–O stretching band (1041 cm\(^{-1}\)) of 30B is most sensitive to the degree of intercalation\(^{41}\) and this band is intense in PA66/30B and PA66/30B/OP, confirming the intercalation of PA66 chains in 30B interlayers. Si–O bending bands (526 and 463 cm\(^{-1}\)) of 30B in PA66/30B and PA66/30B/OP show the dispersion of 30B in the polymer matrix\(^{42}\). These bands indicate that there is a strong interaction between the clay layers and polyamide chain segments due to H–bond formation between Si–O and Si–OH group of 30B with C=O and N–H groups of PA66. In PA66/OP and PA66/30B/OP samples, highly intense peaks at 1076 (P–O stretching) and 1151 cm\(^{-1}\) (P=O stretching) are observed which are the characteristic peaks of phosphinates. In the case of PA66/30B/OP/KN, an additional peak at 1389 cm\(^{-1}\) shows the presence of NO\(_3\) ion along with the peaks of PA66, 30B and OP. An intense peak at 3692 cm\(^{-1}\) in PA66/30B/OP/MH shows the presence of OH group of MH.

FTIR of PA66 after heating at 400 °C shows that the H-bonded N–H band at 3317 cm\(^{-1}\) in pure PA66 sample is shifted to 3331 cm\(^{-1}\) in the char residue and becomes wider indicating the weakening of H–bonding in PA66 and disorderness of the polymer. The band for the free amide I group is shifted from 1666 cm\(^{-1}\) to 1690 cm\(^{-1}\) with decreased intensity whereas the band for the amide II group is shifted from 1583 cm\(^{-1}\) to 1518 cm\(^{-1}\) with decreased intensity on heating PA66 at 400 °C. In the char residue of PA66, the presence of CH\(_2\) stretching (2953 and 2872 cm\(^{-1}\)) and bending bands (1452 cm\(^{-1}\)) at 400 °C indicates significant retention of the hydrocarbon structure, while decreased intensity of N–H stretching (3076 cm\(^{-1}\)) at 400 °C shows decomposition of the polyamide structure. The presence of amide V (687 cm\(^{-1}\)) and amide VI (582 cm\(^{-1}\)) bands in the char indicates that PA66 retains its crystal structure even at higher temperature.

FTIR spectrum of PA66/30B residue obtained at 400 °C shows shifting of the free N–H stretching from 3314 to 3321 cm\(^{-1}\) and shifting of the amide I band from 1663 to 1676 cm\(^{-1}\). In the case of samples with OP, the presence of phosphinate bands with reduced intensity indicates that part of OP is still present in PA66 even at 400 °C. It is significant that band in the range 2224–2245 cm\(^{-1}\) is present in the char residues of all PA66 nanocomposites at 400 °C, which indicates the presence of nitrile group in the degradation products of PA66.

Conclusions

PA66/clay nanocomposites have been prepared by melt blending method. The PA66/30B nanocomposite is found to be thermally stable at temperatures higher than 450 °C with increase in char yield due to formation of nanocomposite and hindered diffusion of volatile decomposition products. The thermal degradation of PA66/OP starts at lower temperature due to P-acids released by OP which catalyze the degradation of PA66. Amongst the additives used, zinc borate stabilizes PA66/30B/OP/ZB composite the most as shown by the DTG maximum appearing at temperatures higher than 630 °C. Thus, zinc borate induces a change in path of thermal decomposition of polymer leading to higher char formation attributed to the carbonizing and cross-linking processes which may protect the polymer from burning. The intense bands of out-of-plane Si–O stretching (1041 cm\(^{-1}\)) and Si–O bending (526 and 463 cm\(^{-1}\)) of 30B in

![Fig. 5—FTIR spectra of (1) PA66, (2) PA66/30B, (3) PA66/OP, (4) PA66/30B/OP/KN, and, (5) PA66/30B/OP/MH samples.](image-url)
PA66/30B and PA66/30B/OP composites predict that there is a strong interaction between clay layers and polyamide chain segments due to H–bond formation between Si–O and Si–OH group of 30B with C=O and N–H groups of PA66.

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