CARBON *letters*

Preparation of melamine-grafted graphene oxide and evaluation of its efficacy as a flame retardant additive for polypropylene

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Abstract

The present study aimed to prepare a novel efficient flame retardant additive for polypropylene. The new flame retardant was prepared by chemical grafting of melamine to graphene oxide with the aid of thionyl chloride. Fourier-transform infrared spectroscopy and thermogravimetric analysis proved that melamine had been successfully grafted to the graphene oxide. The modified graphene oxide was incorporated into polypropylene via solution mixing followed by anti-solvent precipitatio. Homogeneous distribution as well as exfoliation of the nanoplatelets in the polymer matrix was observed using transmission electron microscopy. Thermogravimetric analysis showed a significant improvement in the thermo-oxidative stability of the polymer after incorporating 2 wt% of the modified graphene oxide. The modified graphene oxide also enhanced the limiting oxygen index of the polymer. However, the amount of improvement was not enough for the polymer to be ranked as a self-extinguishing material. Cone calorimetry showed that incorporating 2 wt% of the modified graphene oxide lowered total heat release and the average production rate of carbon monoxide during burning of the polymer by as much as 40 and 35%, respectively. Hence, it was concluded that the new flame retardant can retard burning of the polymer efficiently and profoundly reduce suffocation risk of exposure to burning polymer byproducts.

Key words: carbon composites, combustion, infrared spectroscopy, stabilization, transmission electron microscopy

1. Introduction

Polypropylene (PP) is a versatile thermoplastic material, and is used in many commercial applications due to its relatively low price, excellent processability and favourable physical and mechanical properties [1]. However, it ignites easily in contact with a flame and burns sustainably with a glowing flame. In addition to combustibility, its melt dripping while burning is another major drawback of this commodity polymer [2]. Hence, over the past decades numerous research works have been devoted to devising strategies to hinder the flammability of PP. The most straightforward way to increase the fire resistance of the polymer is to incorporate so-called flame-retardants into the polymer [3]. However, high levels of commonly used flame retardants are required to achieve acceptable fire resistance in PP. These loading levels of flame retardants increase brittleness and impair the mechanical performance of the polymer.

Not surprisingly, it is usually challenging to modify the burning behavior of a polymer without sacrificing its other important properties. Nonetheless, it has been shown that some nano fillers, whose outstanding potential to enhance the mechanical and thermal properties of polymers have been proved, are able to improve the flame retardancy characteristics of macromolecular compounds even at low concentrations [4-6]. However, the quality of the nano fillers' dispersion in the polymer matrix is one of the key parameters affecting its ultimate flame retardancy. Moreover, despite the ability of nano fillers to enhance the fire resistance of polymers, it is hardly possible to achieve excellent fire
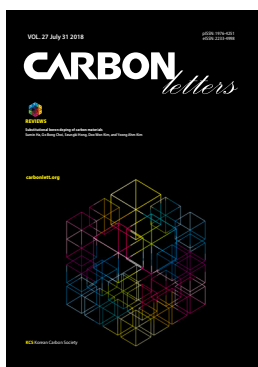
resistance, such as self-extinguishing properties, using nano fillers alone. Thus, nano fillers are often used together with other flame retardants [7].

Since 2004, following the discovery of graphene with its combination of extraordinary physical properties and ability to be dispersed in various polymer matrices, a new class of polymer nanocomposites have been developed [8-10]. Graphene is an atomically thick, two-dimensional sheet composed of sp² carbon atoms arranged in a honeycomb structure and can be produced using various methods, including micromechanical cleavage, epitaxial growth, chemical vapor deposition, exfoliation of graphite intercalation compounds and chemical oxidation-reduction methods [11-13]. It provides a variety of superior properties including high electrical and thermal conductivity as well as excellent mechanical properties, with a Young's modulus of about 1 TPa and tensile strength of about 130 GPa. Due to its high aspect ratio and two-dimensional nanostructure, graphene is expected to be a potential flame retardant for polymers. The incorporation of graphene and its derivatives into both charring and non-charring polymers has been shown to have a marked influence on the burning behavior of polymer/graphene nanocomposites. Ran et al. [14] reported the enhanced flame retardancy of polyethylene (PE) using graphene nanoplatelets and attributed it to the tortuous pathway effect, which leads to delay in the escape of volatile degradation products.

However, graphene needs some kind of surface modification in order to be efficiently dispersed in polymer matrices, because of strong van der Waals forces and π–π attraction between the nanosheets, which make their exfoliation difficult, especially in non-polar polymers [15]. Graphene oxide (GO), due to the presence of oxygen-containing functional groups on its nanosheets as well as larger interlayer spacing, is a suitable starting material for the preparation of polymer/graphene nanocomposites [16,17]. The surface modification of GO sheets is usually carried out by either covalent functionalization or non-covalent functionalization. The covalent modification not only plays an important role in controlling the exfoliation behavior of GO, but also provides various capabilities, in particular, antioxidant and flame retardation activities [18,19]. Hofmann et al. [20] showed that functionalized thermally reduced graphene oxide, in contrast to conventional nano- and micron-sized carbon fillers such as expanded graphite, nano-scaled carbon black and multi-walled carbon nanotubes, combined uniform dispersion with enhanced flame retardancy in PP.

Melamine is a nitrogen-based flame-retardant with low toxicity, and produces a low level of smoke during combustion. The main mechanism of flame retardation by graphene is to delay the escape of gaseous decomposition products, whose access to flame is essential for sustainable burning. Adding melamine and graphene to a polymer together is expected to result in a synergy between these two additives. This is because melamine, similar to other nitrogen-based fire-retardants, enhances the flame retardancy of polymers primarily by decreasing the concentration of oxygen in the gas phase. The combined additives should simultaneously diminish the concentration of both oxygen and gaseous fuel, which are the two necessary ingredients in the so-called fire triangle.

Recently, Yuan et al. [21] reported that GO was better dispersed in PP matrix after modification by melamine via non-covalent interactions, than that of virgin GO. They also showed that the incorporation of the modified GO into the PP matrix led to greater improvements in thermo-oxidative stability and flame retardancy than a GO/PP composite and neat PP. It seems that the covalent bonding of melamine to GO leads to additional enhancement in thermal stability and burning resistance in PP. This could be due to better dispersion in the polymer matrix, and also the replacement of labile oxygen-containing functional groups of GO by more stable chemical groups. To the best of our knowledge, this approach has not been applied so far. Hence, in this study, for the first time ever, we functionalized GO by melamine via a chemical reaction between amine groups of melamine and carboxylic acid moieties located on the edge of GO layers. Also, we studied the effects of incorporating the modified GO into PP, and its effects on the thermal stability and flame retardancy of the polymer.

2. Experimental

2.1. Materials

Polypropylene (Jampilen HP510M grade) with a melting point of 167°C, bulk density of 0.90 g cm⁻³ and melt flow index (MFI) of 9.0 g per 10 min was supplied by Jam Petrochemical Company, Iran. Research grade graphene oxide nanoplatelets as powder, with specifications shown in Table 1, were obtained from Nanosany Corporation, Iran. Melamine and all chemicals used for the grafting reaction, that is, thionyl chloride, dimethylformamide (DMF), pyridine, as well as methanol and toluene, which were used for the preparation of the nanocomposite samples, were supplied by Merck Company, Germany. The antioxidant, which was used for the preparation of the nanocomposite samples, was SONGNOX 1010 with a melting point of 118°C, and was obtained from Songwon Industrial Company, South Korea. All the mentioned raw materials were used as received.

2.2. Grafting of melamine on the graphene oxide nanoplatelets

Melamine was chemically grafted onto graphene oxide nanoplatelets through a two-step esterification reaction with the aid of thionyl chloride as follows [22]: Firstly, 1.0 g of graphene

Table 1. Specifications of the used graphene oxide nanoplatelets

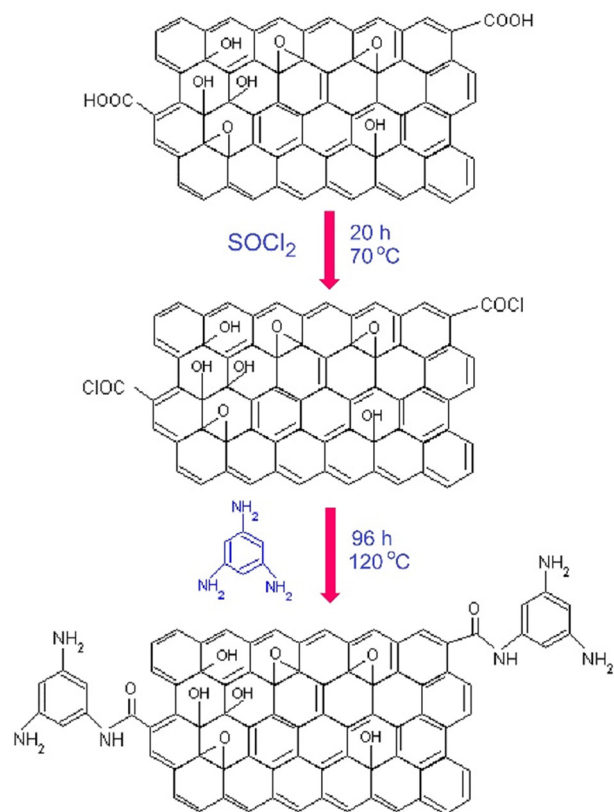| Properties	Facts
Purity (%)	99
Thickness of platelets (nm)	3.4–7
Diameter (μm)	10–50
Specific surface area (m² g⁻¹)	100–300
Carbon/oxygen content (%)	92.7 / ≤7.3

Fig. 1. A schematic representation of the adopted procedure for the functionalization of graphene oxide.

oxide was suspended in a mixture of 30 mL thionyl chloride (SOCl$_2$) and 0.5 mL of DMF. Then, the suspension was heated up to 70°C while being stirred, and then was maintained for 20 h under reflux. Afterward, the unreacted thionyl chloride was removed by reduced pressure distillation to yield the acyl chloride-functionalized graphene oxide, which was subsequently added to a solution of 1.5 g of melamine and 0.5 mL pyridine in 60 mL of DMF and the reaction mixture was stirred at 120°C for 96 h under reflux. Then, the mixture was cooled down to room temperature and centrifuged to separate the suspended nanoplatelets. Lastly, the separated grey solid powder was collected, washed several times with water and dried at 70°C for 1h under vacuum. The final powder is hereinafter called chemically modified graphene oxide (CMGO). The overall procedure of the chemical modification is schematically shown in Fig. 1.

2.3. Preparation of nanocomposite samples

Two PP/CMGO nanocomposite samples containing 1 and 2 wt% of CMGO, respectively, were similarly prepared by solution mixing followed by anti-solvent precipitation as follows: Firstly, a certain amount of PP powder was dissolved in 200 mL of toluene using mechanical stirring at 110°C for 4 h. In order to prevent thermal oxidation of the polymer during the dissolution, a certain amount of SONGNOX 1010 antioxidant, which was as much as 0.1% by weight of the polymer, was dissolved in toluene before the addition of the polymer. In parallel, the desired amount of CMGO was dispersed in 30 mL of toluene

Table 2. Sample designations

Sample designation	PP (wt%)	Melamine (wt%)	CMGO (wt%)
PP	100	-	-
PP/2ME	98	2	-
PP/1CMGO	99	-	1
PP/2CMGO	98	-	2

with the assistance of sonication for 20 min at room temperature. The prepared suspension was then warmed up to 110°C and then added to the PP/toluene solution. The final suspension was further homogenized by an extra 30 min stirring. Afterwards, the final suspension was gradually poured over 1 L of methanol as anti-solvent, which was already being intensely stirred. The resulting suspension was stirred for 1 h, and then the sediment was collected and dried in an oven at 40°C for 24 h.

Two extra PP samples, one containing 2 wt% of melamine alone and the other a blank (pure PP) sample, were prepared using a procedure similar to the one used for the preparation of the nanocomposite samples. The formulations of the prepared film samples are given in Table 2. The prepared samples were then converted into sheets with a thickness of 5 mm at 190°C and 100 bar within 8 min using a laboratory hot press.

2.4. Characterization

2.4.1. Investigation of occurrence of the grafting reaction

Fourier transform infrared (FT-IR) spectroscopy was performed using a Thermo Nicolet, Nexus 870 model spectrophotometer (USA) at a resolution of 4 cm^{-1} in the range of 4000–500 cm^{-1}. X-ray diffraction (XRD) patterns were obtained using a Seifert XRD 3003 PTS instrument (Germany) equipped with a Cu K$_\alpha$ radiation source (λ=0.1542 nm) at potential of 40 kV, beam intensity of 30 mA and imaging speed of 0.01 s^{-1} in the 2θ range of 2–15°. Peak position in the patterns and the Bragg equation, as can be seen in Eq. 1, were used to calculate the distances between the layers.

$$n\lambda = 2d\sin\theta \tag{1}$$

Thermogravimetric analysis (TGA) was carried out on a Linseis, STA PT1600 model thermal analyzer (Germany). Samples of about 5 mg weight were heated from 20 to 600°C at a constant heating rate of 10°C/min under a stream of nitrogen with a flow rate of 50 cm^3 min^{-1}.

2.4.2. Assessment of state of dispersion in the prepared nanocomposite samples

Transmission electron microscopy (TEM) was conducted to investigate the state of dispersion of the CMGO in the PP matrix. TEM images of the prepared nanocomposites were taken using a Philips EM 208 instrument (the Netherland). Samples for TEM were prepared by putting and drying a small drop of the dispersion, which had been previously prepared by microtomy, in distilled water on 100 mesh copper grid.

2.4.3. Evaluation of heat stability and flame resistance of the prepared samples

The thermo-oxidative stability of the nanocomposite samples was examined using the aforementioned TGA instrument. All samples for the analysis were heated from 20 to 600 °C at a heating rate of 10°C/min under an air stream with a flow rate of 50 cm^3 min^{-1}. Flammability of the nanocomposite samples was evaluated by measuring their Limiting Oxygen Index (LOI) according to ASTM D 2863 using a candle type model D Toyo Seiki flammability tester (Japan). Burning properties of the samples were evaluated according to ISO5660-1 using a Fire Testing Technology cone calorimeter (UK). Samples with dimensions of 100×100×5 mm^3 were burned under an external heat flux of 50 kW m^{-2}.

3. Results and Discussion

3.1. Investigation of occurrence of the grafting reaction

Melamine has six amine hydrogen atoms, which can react with carboxylic acid groups located at the edges of graphene oxide platelets. FT-IR spectra of the graphene oxide, melamine and CMGO, respectively, are presented in Fig. 2. In Fig. 2a, which illustrates the FT-IR spectrum of the GO, the stretching of carboxylic carbonyl groups (C=O) at 1715 cm^{-1}, bending of hydroxyl groups at 1414 cm^{-1}, stretching of epoxy groups (C–O–C) at 1218 cm^{-1} and stretching of carboxylic C-O group at 1043 cm^{-1} can be seen [23]. The absorption band at 1621 cm^{-1} can be assigned to either the stretching vibration of C=C bonds in the aromatic rings or physically absorbed water. Moreover, a broad absorption band in the range of 3500–2700 cm^{-1} with a peak at 3391 cm^{-1} is present in the spectra, which is typical of the stretching vibration of hydroxyl groups of carboxylic acid moieties.

In the FT-IR spectra of the melamine, Fig. 2b, the absorption peaks at 1534, 1429 and 812 cm^{-1} are attributed to 1, 3, 5-s-triazine rings [21]. Furthermore, three absorption bands at 3500–3300 cm^{-1} and an absorption band at 1719 cm^{-1} are associated with the stretching and bending vibrations of NH$_2$ groups, respectively. Also, the band at 1019 cm^{-1} corresponds to the stretching vibration of the C–N bond.

In Fig. 2c, which exhibits the FT-IR spectrum of CMGO, some characteristic absorption peaks of GO and melamine can be observed, for instance, 1428, 1217, 1019 and 812 cm^{-1}, as well as some new peaks. It can be seen that the characteristic broad absorption band of carboxylic OH groups in the GO at 3500–2700 cm^{-1} and the absorption peaks due to stretching of the NH$_2$ groups in melamine at 3500–3300 cm^{-1} have evolved into two weak broad bands at 3459 and 3390 cm^{-1}. The former absorption band can be ascribed to the stretching of NH$_2$ groups of the grafted melamine molecules and the latter is due to unreacted carboxylic OH groups and intact alcoholic groups on the surface of the graphene oxide.

In addition, a new peak at 1598 cm^{-1} has appeared, which can be attributed to the bending of NH in the newly formed amide groups. Moreover, instead of peaks due to bending vibrations of the NH$_2$ groups and the stretching of carboxylic carbonyl groups at 1719 and 1715 cm^{-1}, respectively, a new peak at 1700 cm^{-1} has appeared, which can be assigned to the stretching vibration of carbonyl groups present in the formed amide groups. Thus, it can be concluded that melamine was successfully grafted onto the graphene oxide according to the reactions illustrated in Fig. 1 [22].

TGA was also conducted in a nitrogen environment to further probe the occurrence of the grafting reaction. Fig. 3 shows TGA graphs of GO and CMGO, respectively. As seen in the figure, GO undergoes a weight loss of about 15% below 150°C, which is due to the evaporation of residual moisture [21]. The major stage of weight loss of the GO occurs within the temperature range of 150–320°C, and is attributed to the decomposition of
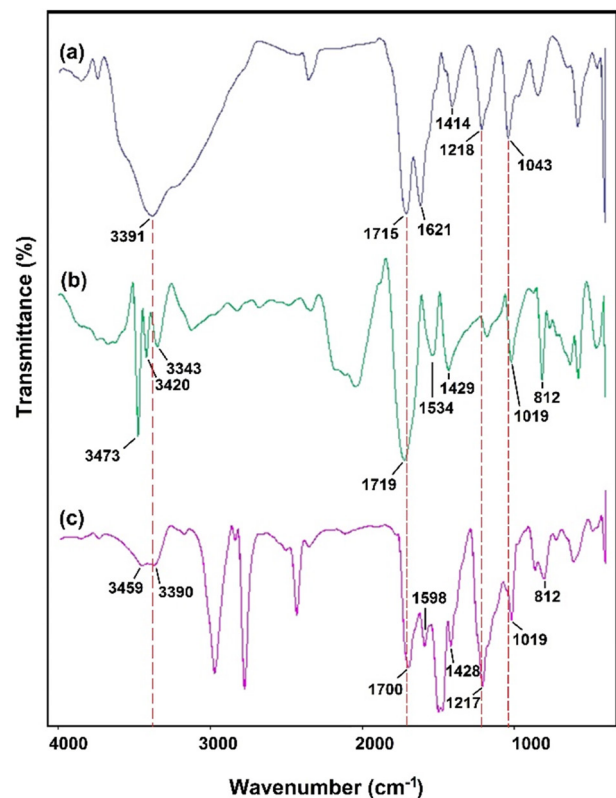

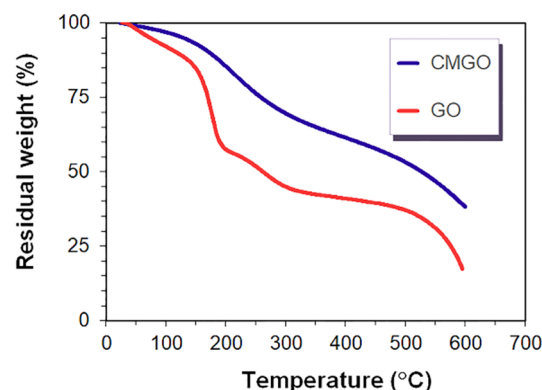**Fig. 2.** FT-IR spectra of GO (a), melamine (b), and CMGO (c).
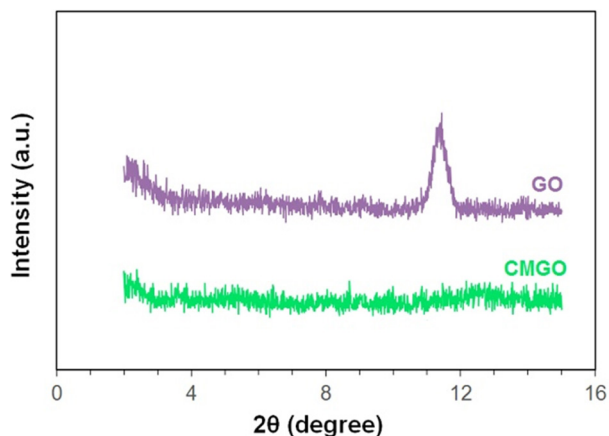

Fig. 3. TGA curves of GO and CMGO.

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Fig. 4. XRD patterns of GO and CMGO.

Fig. 5. TEM images of the PP/2CMGO sample with two different magnifications: (a) 32 kx and (b) 125 kx.

the labile oxygen-containing functional groups, such as hydroxyl and carboxyl groups. The gentle removal of the more stable functional groups leads to the gradual mass loss above 320°C. Moreover, it is obvious in the figure that upon heating up to 600°C, GO undergoes an overall weight loss of about 82%. For CMGO weight loss is about 62% up to the same temperature, indicating a pronounced improvement in thermal stability owing to the chemical modification, which transforms the labile carboxylic acid groups of the graphene oxide to more stable amide groups through the reaction with melamine.

XRD is a powerful tool for the structural analysis of layered materials such as GO. Hence, XRD patterns of GO and CMGO were prepared and are presented in Fig. 4. A diffraction peak at $2\Theta=11.4°$ is seen in the XRD pattern of the GO, which is typical for these nanoplatelets. According to the Bragg equation, the interlayer distance corresponding to the above diffraction peak is 0.776 nm. On the other hand, in the XRD pattern of CMGO, there is no significant diffraction peak, which should be due to the much greater interlayer distance in CMGO compared to that in GO.

Yuan et al. [21] reported a shift in the characteristic peak of the XRD pattern of GO from $2\Theta=11.4$ to 9.8°, upon the non-covalent interaction of GO with melamine. They interpreted the observed shift and the relevant enlargement of interlayer spacing based on the intercalation of melamine molecules. However, the disappearance of the characteristic GO peak in the XRD patterns of CMGO in the present work is a more pronounced phenomenon compared to that observed in the work of Yuan et al. [21]. Hence, it can be inferred that, compared to the intercalation of melamine molecules, the covalent bonding of these molecules on the edges of the GO nanoplatelets has a more significant effect on interlayer spacing [24].

3.2. Assessment of state of dispersion in the prepared nanocomposite samples

When layered nano-fillers are incorporated into a polymer matrix, two different types of morphologies can result: intercalated and exfoliated [25]. Intercalation occurs when polymer chains enter the interlayer region of the layered structure without creating changes in the ordered structure. On the other hand,
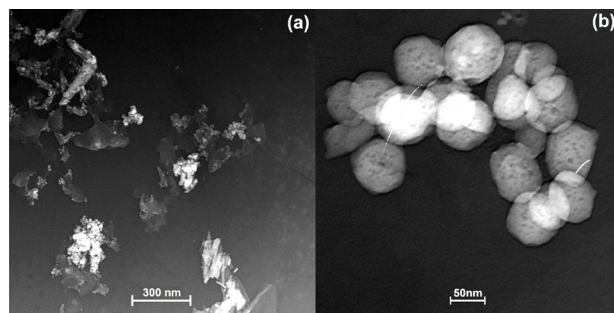
exfoliation involves penetration of the polymer chains into the layered structure and delamination of the layers, which entails the random dispersion of individual nanosheets in the matrix. Since the exfoliated structure exposes a larger surface area of the nanoplatelets, it generally results in the highest improvement in the properties of the resulting nanocomposites.

Accordingly, the state of CMGO dispersion in the polymer matrix was studied in the present work using TEM. Fig. 5 illustrates TEM images taken from the PP/2CMGO sample with two different magnifications. In Fig. 5a, some randomly distributed small clusters of CMGO are observed. With higher magnification, as shown in Fig. 5b, the clusters are found to be composed of a few partly exfoliated graphene layers. The level of CMGO dispersion can be attributed to the grafted melamine molecules, which induce a profound enlargement of interlayer spacing. This facilitates penetration of the polymer chain molecules into the interlayer region. In fact, the covalent bonding of melamine to GO platelets, in addition to its main expected role in enhancing the flame retardation effect in GO, resulted in better dispersion of the nanoplatelets in the polymer matrix. This in turn can lead to an additional improvement in the fire resistance of the polymer.

3.3. Evaluation of the heat stability and flame resistance of the prepared samples

The first stage in the process of burning a polymer material is decomposition of the polymer. Elevation of the thermal decomposition temperature of a polymer may assist in enhancing its fire resistance. Hence, when evaluating the efficiency of a new candidate flame retardant for a certain polymer, it is important to study its effect on the heat stability of the polymer. This can be accomplished by carrying out TGA experiments.

Moreover, since burning usually takes place in atmospheric air environment, from a practical application standpoint it is important to evaluate the thermal properties of materials in air or oxygen rather than in a nitrogen environment. The TGA and derivative thermogravimetric (DTG) curves obtained from the tests in air environment are shown in Fig. 6a and b, respectively. The figure shows that the weight loss of the PP/2CMGO sample and its maximum decomposition rate occurs at higher temperatures compared to the neat PP sample. This can be interpreted as a demonstration of the stabilization effect of CMGO on the polymer.

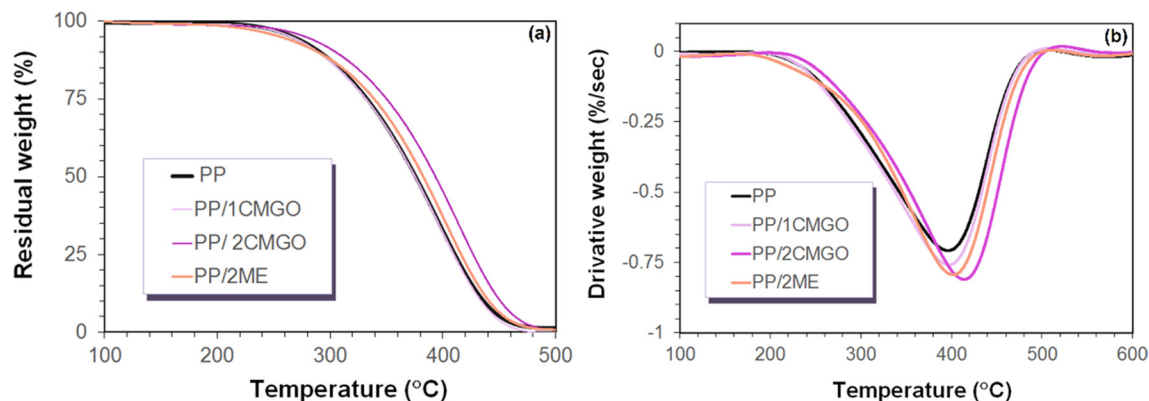However, in order to make a clearer comparison of the ther-

Fig. 6. (a) TGA and (b) DTG curves of the samples obtained under air atmosphere.

Table 3. TGA data and LOI value of the PP samples			
Sample designation	IDT (°C)	T_{max} (°C)	LOI (% O_2)
PP	267	398	17.2±0.2
PP/2ME	256	401	19.2±0.7
PP/1CMGO	266	397	18.2±0.2
PP/2CMGO	278	416	19.4±0.2

Value are presented as mean±SD.

mal stabilities of the samples, two important characteristics of the curves, that is, the initial decomposition temperature (IDT) and the temperature T_{max} were extracted from the TGA and DTG curves, respectively, and are presented in Table 3. In the TGA curve, the temperature at which the overall weight loss reaches 5 wt% is defined as IDT. Also, in the DTG curve, which is a plot of the derivative of the weight loss (TGA) curve or the decomposition rate, the temperature at which the decomposition rate reaches its maximum is defined as T_{max}. The table reveals that the IDT and T_{max} of the PP, PP/2ME and PP/1CMGO are similar. The only exception is the IDT of the PP/2ME sample, which is 11°C lower than that of the neat PP sample. Partial evaporation of melamine, which is a low molecular weight compound, in the PP/2ME sample can be the reason that the weight loss begins earlier in this sample relative to the PP sample. On the other hand, the PP/2CMGO sample shows higher thermo-oxidative stability than the PP sample, so that the IDT and T_{max} of the PP/2CMGO sample are 11 and 18°C higher than those of the PP sample, respectively. The observed delay in thermo-oxidative degradation of the polymer following the incorporation of 2 wt% of CMGO into PP is probably due to the physical protective barrier of the CMGO nanoplatelets, the so-called tortuous pathway effect [14].

LOI is a simple and effective method for appraising the flame retardancy of polymeric materials [24]. Tests to were performed on the prepared samples in order to evaluate the effect of CMGO on the flame retardancy of PP. The obtained LOI values are listed in Table 3. It is seen that PP has a relatively low value of LOI (17.2%), which indicates it has expected high flammability [19].

The addition of 2 wt% of melamine to the polymer, in the case of PP/2ME sample, elevated the LOI value as much as 2%.

The data presented in Table 3 also shows that incorporating CMGO into the polymer increases the LOI value, and the amount of the increase is proportional to the concentration of the nanoplatelets in the polymer. Similar improvements in the LOI value of PP have been reported by Huang et al. [26] and Nie et al. [19] after incorporating reduced GO and GO decorated N-containing zirconium organophosphate, respectively, into the polymer. The above observation is consistent with the results of TGA experiments and proves the potential capability of CMGO for enhancing the flame retardancy of the polymer. However, the amount of improvement is not high enough for the polymer to be a self-extinguish material, since the available concentration of oxygen in the air is 20%, which is more than the highest obtained LOI value (19.4%).

Cone calorimetry is widely used for a realistic assessment of the combustion behaviour of polymeric materials [21,26,27]. It provides valuable information on many important burning characteristics, such as, time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), and rates of production of CO and CO_2. Thus, this test was carried out on the prepared samples, and the obtained data are presented in Fig. 7. As can be seen in Fig. 7a and b, respectively, the maximum rate of heat release or PHRR and THR for the neat polymer are higher than the other samples. Also, the TTI for the neat polymer is larger than that of the other samples. This means the release of heat during burning of the polymer, which is a measure of the tendency to burn, is hampered by the addition of either melamine or CMGO to the polymer.

In order to show the exact amounts of improvement in these burning characteristics, the amounts of TTI, THR and PHRR of the samples are presented in Table 4. It can be seen that the samples containing CMGO ignite somewhat faster than the PP sample, which is a result of increased absorption of the irradiated heat of the cone heater by the nanocomposite samples due to the presence of the carbon nanomaterials [21]. Moreover, the amount of THR of the CMGO-containing samples is about 40% lower than that of the neat polymer sample. The observed amount of reduction of THR is more than that gained by the addition of melamine in the case of the PP/2ME sample, which is only 11%.
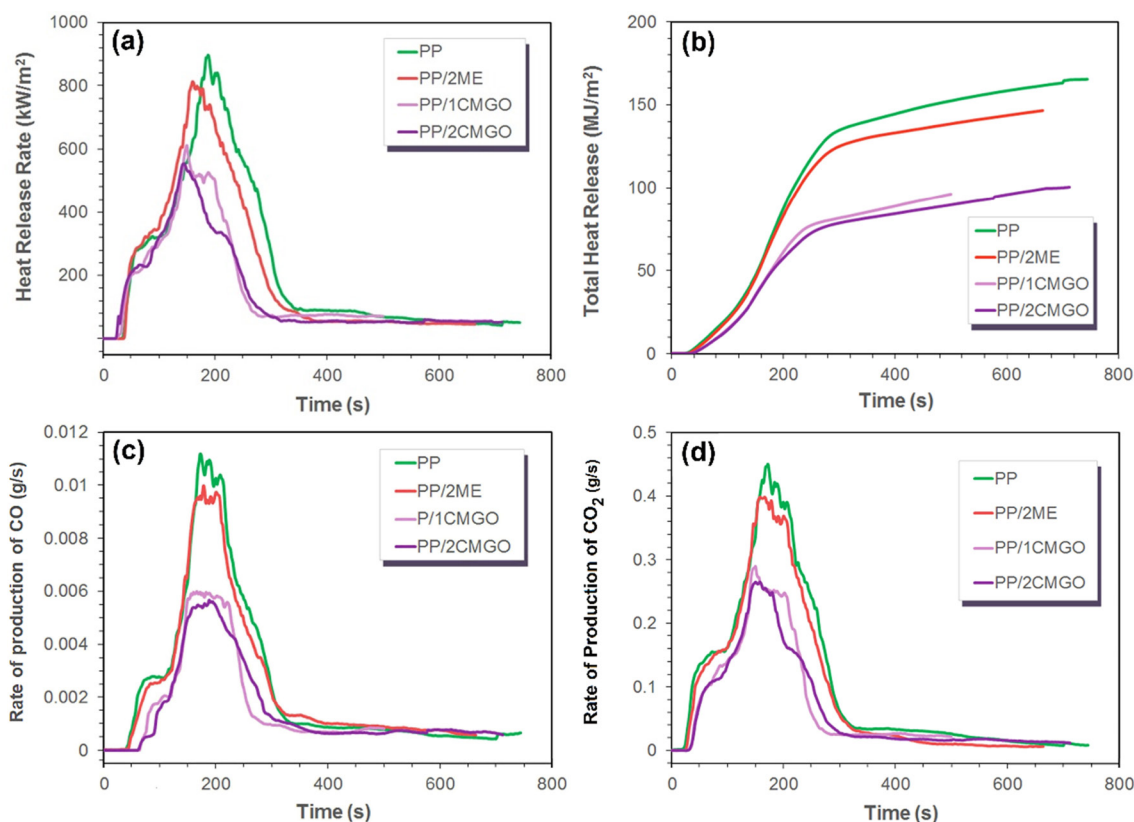
Fig. 7. Cone calorimetry results for the PP samples: curves of HRR (a), THR (b), rate of production of CO (c), and rate of production of CO_2 (d).

Table 4. Collected data of cone calorimetry for the PP samples

Sample designation	TTI (s)	THR (MJ m^{-2})	PHRR (kW m^{-2})	APRCO (g s^{-1})[a]	APRCO$_2$ (g s^{-1})[b]
PP	33	165.43	897.02	0.0023	0.1195
PP/2ME	38	146.61	812.72	0.0025	0.1162
PP/1CMGO	25	96.16	610.24	0.0019	0.1024
PP/2CMGO	24	100.51	551.87	0.0015	0.0818

[a] Average production rate of CO.
[b] Average production rate of CO_2

Furthermore, the outstanding modification of the THR of PP by the addition of CMGO is far more than that obtained by the addition of non-covalent melamine-modified graphene oxide, which was about 2% [21]. This difference can be attributed to the better dispersion of the modified graphene oxide in the polymer matrix. In addition, the results in Table 4 show that the amounts of reduction in the PHRR of PP were 32% and 38% in the cases of the PP/1CMGO and PP/2CMGO samples, respectively, which are higher than the reduction caused by the addition of melamine (9%). Yuan et al. [21] reported 20% and 29% reductions in the PHRR of PP with the addition of 1 wt% and 2 wt%, respectively, of non-covalent melamine-modified graphene oxide. These improvements are again less than those observed in our study following the addition of the same amounts of CMGO, respectively.

The rates of CO and CO_2 production during combustion of a polymer determine the potential danger of exposure to the burning polymer to human health. It is evident from the curves in Fig. 7c and d that the incorporation of CMGO reduces the rates of both CO and CO_2 production. In order to clarify the comparison, the average production rates of CO and CO_2, which are abbreviated as APRCO and APRCO$_2$, respectively, are presented in Table 4. It shows that the reduction in both APRCO and APRCO$_2$ is proportional to the concentration of CMGO, so that their maxima are 35% and 32%, respectively, for the PP/2CMGO sample.

On the other hand, the addition of melamine results in a slight increase in APRCO and a small decrease in the APRCO$_2$ of the polymer. To the best of our knowledge, such an outstanding modification in the production rates of CO and CO_2 after in-

corporating the same amount of other nanoparticles into PP has not yet been reported. The maximum improvement reported by other researches belongs to Nie et al. [19], who achieved a maximum decrease in the peak of CO production of as much as 29% by incorporating 2 wt% GO decorated N-containing zirconium organophosphate in PP. Hence, the CMGO not only hampers flammability of PP significantly but also, eminently reduces suffocation risk due to exposure to burning polymer byproducts.

4. Conclusions

In an attempt to synthesize a novel efficient flame retardant for PP, we grafted molecules of melamine, a nitrogen-containing flame retardant, onto the edge of GO nanoplatelets, as confirmed by FT-IR spectroscopy and TGA. XRD analysis showed that the grafted melamine molecules enhanced the interlayer distance in the GO nanoplatelets. TEM images showed random distribution as well as exfoliation of the nanoplatelets in the PP matrix, which is attributed to an increase in the interlayer distance in the CMGO. It was also shown that at a concentration of 2 wt% the CMGO improves the thermo-oxidative stability of the polymer. The modified graphene oxide also enhanced limiting oxygen index of the polymer but not to the extent the polymer can be considered a self-extinguishing material. Cone calorimetry results showed that at a concentration of 2 wt%, which is much lower than the normal loading level of commonly used flame retardants (about 20%), CMGO lowers PHRR, THR, APRCO and $APRCO_2$ when the polymer burns by more than 30%. On the whole, it can be concluded that the reported compound can act as an efficient flame retardant for PP even at low concentrations, can simultaneously hamper the flammability of the polymer effectively, and profoundly reduce the hazard of exposure to burning polymer byproducts.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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