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Effect of Clay Network Formation on Flame Retardancy of Polyethylene terephthalate/montmorillonite Nanocomposites

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Abstract

Considering the importance of determining potential hazards and factors that can cause an unexpected fire and due to the important role of nanotechnology to achieve more effective properties, this paper presents our experiments on preparing nanocomposites based on Poly(ethylene terephthalate)(PET) and montmorillonite (MMT) as organoclay via melt blending with different clay loadings to investigate their combustion behavior. The main objective of this work was employing cone calorimeter as a perfect device to investigate all combustion parameters such as time to ignition (TTI), heat release rate (HRR), mass loss rate(MLR), CO and CO_2 release and peak of heat release rate (pHRR). Thermogravimetric analysis (TGA), Cone calorimeter, limiting oxygen index (LOI) were employed to measure thermal stability and flammability of nanocomposite samples. Morphology and rheology of clay /PET nanocomposites also were investigated using X-ray diffraction (XRD) and Transmission electron microscopy (TEM).The relationship between decrease of intrinsic viscosity and thermal behavior of sample also was studied. Results indicate that clay network was formed in nanocomposites samples which strongly affected flammability of burning samples and resulted more residue during combustion which leads to decrease in dripping of PET during melting.

Keywords: *Poly(ethylene terephthalate), Nanocomposite, Morphology, Montmorrillonite.*

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Introduction

Polymer–layered silicate nanocomposites (PLSN) has attracted great interest because of possibilities of concurrent improvements in the mechanical, thermal , barrier , absorbency and flammability properties. PLSNs are known as materials in which one dimension of a dispersed phase is in the nanometer range (typically 1-20 nm)[1-3]. Compared PLSN with conventional filled polymers ;it is concluded that the property enhancements of PLSN are granted via the addition of small amounts of clay [4,5].Furthermore, significant improvements in flammability of polymer are reported with PLSNs. The improvements in flammability of polymer achieved with PLSNs are truly impressive since could become a "green" alternative to conventional ones such as halogen, phosphorous and intumescent flame retardants. Halogen-based flame retardants pose threats due to their emission of toxic gases such as HBr and HCl during combustion, which are harmful to human respiratory system, their risks by emission of dioxins and furans (carcinogens) during incarnation, and also their corrosivity [6-8]. Recent researches about PLSNs flame retardant properties mainly demonstrate a significant decrease in the peak heat release rate (PHRR), a change in char structure and a decrease in the rate of mass loss during combustion in a cone calorimeter [5,7].However introducing exact mechanism and clay polymer behavior during combustion is a great subject to be investigated [9,10]. The modified clays used in composite preparation include natural clays such a montmorillonite, hectorite , sepiolite, bentonite, and kaolinite , as well as synthetic clays including various layered double hydroxides, synthetic montmorillonite, etc [11].

Poly (ethylene terephthalate) (PET) finds wide variety of applications, both as fiber and non-fiber because it combines low cost with acceptable chemical resistance and in significant spinnability [12,13]. PET fibers have the biggest production amount and widest usage among all the synthetic fibers which can be used in transport system, protective garment, military, furniture upholstery, bed linen, mattresses, night wear and curtains [13].However, their combustibility and serious dripping during combustion, greatly limit their application. Therefore, the flame retardancy and the dripping resistance of PET have become a very important subject to deal with. Especially, when PET as fabric is used in public location such as restaurants and cinemas, flame resistancy could be a great matter to be considered [14-17].

In this article, PET based nanocomposites were prepared in the melt state with different clay loading levels. PET which was used in this experiment was fiber grade. The clay contents were 0, 3 and 5%. The morphology was characterized by X-ray diffraction (XRD), TEM. Also, dynamic rheological properties of PET/clay nanocomposites were investigated.

Thermal stability was conducted on samples by TGA. The flammability behavior and dripping resistant of nanocomposites were evaluated by LOI and cone calorimeter. It was tried to correlate the network structure with the fire performance and disclose the flame retarding mechanism of polymer/clay nanocomposites.

Experimental

Materials

Poly (ethylene Terephthalate)(PET) ,fiber grade(intrinsic viscosity 0.64 dl/g) and in the form of pellets, was purchased from Tondgooian Petrochemical Complex. Organo- MMT was obtained from Zhejiang Fenghong Clay Corp. with the commercial name DK2.

PET/MMT blending

PET was dried at 110°C under vacuum for 24hr. Organo-MMT (DK2) was dried at 80°C for 8 hr. The PET/MMT composites, with different contents of MMT(1,3and5 %), were obtained via melting process in a co-rotating twin screw extruder (Brabender ZSK25,l/d=25) with a screw speed of 250rpm. The residence time was in the range of 45-60s and the thermal profile was 250-250-260-260-270-270°C. PET was extruded in the same conditions without clay. The ratios of PET and organo-MMT are listed in Table 1.

Table1. Mass ratio of PET/MMT composites.

Sample	PET	MMT(DK2)
PET	100	0
PET1C	99	1
PET3C	97	3
PET5C	95	5

Characterization

X-ray diffraction (XRD)

XRD analyses were performed at room temperature using a Philips X-ray diffractometer from 2θ(2° -10°),using CuKα with wavelength of 1.54Å .

Transmission electron microscopy (TEM)

TEM micrographs were carried out using EM208 Philips transmission electron microscope (Mag=200,000). Ultrathin sections of about 30-60nm thick were cut with UMU3-C Reichert ultramicrotome equipped with a diamond knife and placed on a 400-meshed copper grid.

Rheological properties

Rheological measurements were performed using an MCR300 mechanical rheometer Physica Anton Paar) with a parallel plates geometry .Dynamic frequency sweep tests were executed in the frequency range of 1% and temperature 270°C.

Thermal and flame testing

Thermogravimetric analysis (TGA)

To perform thermogravimetric analysis, Dimond TGA/DTG system was used. Samples were heated at 10°C/min from 30°C to 600°C in a nitrogen atmosphere.

Limiting Oxygen Index (LOI)

LOI was measured using a Toyoseiki instrument on samples ($100\times6\times3mm^3$) according to standard ASTM D2863.

Cone calorimeter

A Fire Test Technology (FTT) cone calorimeter was used to carry out measurements on samples ($100\times100\times8mm^3$)following the procedure defined in International Standard ISO 5660.A heat flux of $50kW/m^2$ was used for running the experiments .

Results and discussion

Characterization

The XRD patterns of organo-clay (DK2), PET1C, PET3C and PET5C are shown in Figure 1. As it can be seen , the d001 peak of modified nanoclay has decreased from 2Ө=4.17 to 2.6nm(in accordance to Bragg`s Equation) for all samples indicating that interlayer distances has increased from 2.12 nm for DK2 to 3.31nm,3.33nm and 3.24nm for nanocomposite with organo-MMT content of 1, 3 and 5. Thus, the polymer molecules have entered into the silicate layers of organo-MMT and formed intercalated nanocomposite rather than exfoliated one, due to existence of sharp diffraction peaks. TEM micrograph shows (Fig.2) the interlayer distance of dispersed clay is about 3nm which confirms that polymer molecules have intercalated into the silicate layer galleries.

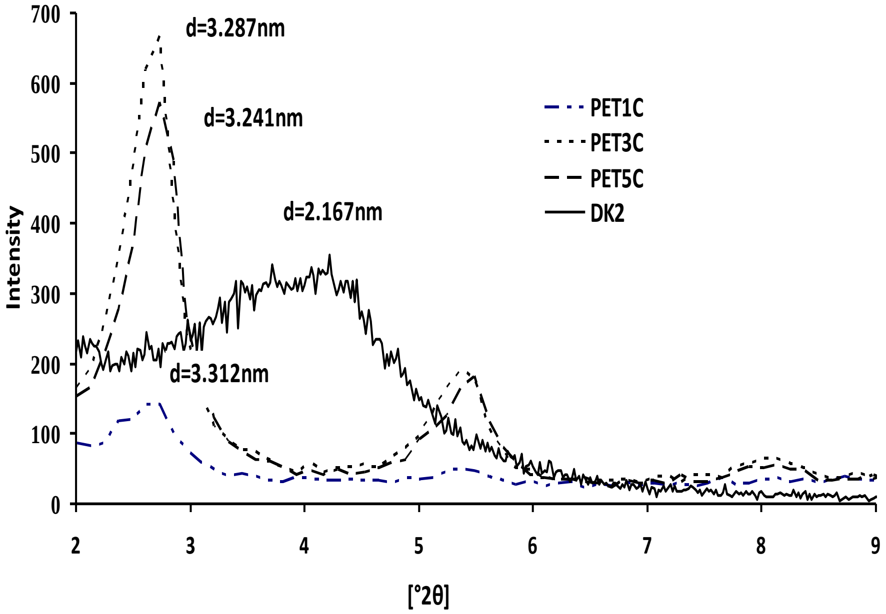
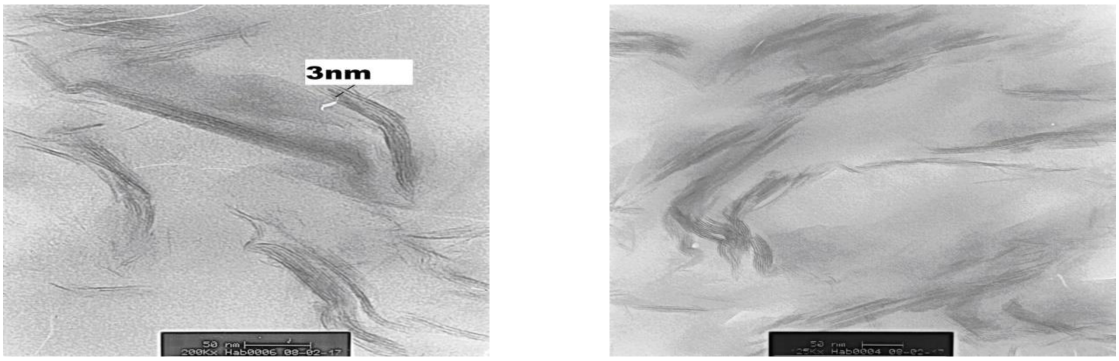


Figure 1. XRD curve of DK2, ,PET3C and PET5C.

Figures 2((a),(b)) show TEM micrographs for PET3C and PET5C,respectively.These results demonstrate that the interlayer distance of dispersed clay is about 3nm and confirm that polymer molecules have intercalated into the silicate layer galleries.



(a) (b)

Figure 2.TEM micrographs ofa)PET3C and (b) PET5C.

Intrinsic Viscosity

As it can be observed in Table 2 and Table 3, the extrusion of PET resulted in high reduction of intrinsic viscosity(η) , which is 33% for extruded PET(PET.ext) compared to virgin PET. During extrusion, the following processes may occur simultaneously: hydrolysis and condensation (the predominating process depends on water content); trans-esterification, cycle formation; thermal degradation by decomposition of weak points (diethylene glycol); chain resulting of oxidation at high oxygen concentration and cross linking resulting of oxidation at low oxygen concentration. All materials were dried in vacuum oven before melt compounding. It must be noted that the moisture and oxygen during process had notbeen removed [12-15]. The nanocmposite samples experienced much more degradation as the content of clay increased from 1% to 5% because the hydroxyl groups acted as Brønsted acidic sites to accelerate polymer degradation. Thus the nanocomposite with larger amount of organo-clay experienced much more degradation compared to virgin PET, depending upon acidic sites produced by Hofmann elimination reaction of ammonium. [13]

Table 2.Intrinsic Viscosity of virgin, extruded and nanocomposite samples.

Samples	Intrinsic Viscosity(dL/g)
PET	0.64
PET.ext	0.43
PET1C	0.57
PET3C	0.44
PET5C	0.41

Table 3.Percentage Reduction of IV of Nanocomposite and extruded samples with respect to virgin PET.

Samples	Percentage variations (%)
PET.ext	33
PET1C	10.94
PET3C	31. 2
PET5C	36

Viscoelastic Properties

Figure 3 shows effect of organoclay on storage modulus G´ of nanocomposite samples. Due to small reduction of molecular weight of PET during melt extrusion confirmed by intrinsic viscosity (η),similar reduction of G´ observed for PET -clay nanocomposites. The storage modulus indicates stiffness and frequency dependence characterizes where the material is a liquid-like or solid like state. As the content of clay increases to 5%, G´ becomes nearly constant at low frequencies .This indicates a transition from liquid state to solid state, which accompanies the formation of a mechanically stable network structure .The presence of the network structure becomes critical for effective flame retardancy at higher temperatures.

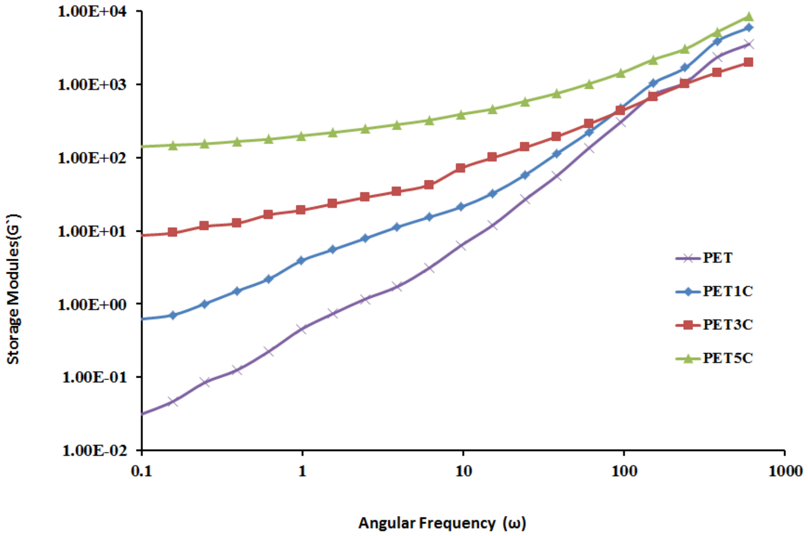


Figure 3. Storage modulus (G´) of pristine PET and clay/PET nanocomposites versus frequency (ω).

The frequency dependence of G'' showed a similar trend. From the result in figure 4, it can be seen that the increase of storage modulus of all samples was greater than the increase of the loss modulus. Therefore, the structure of nanocomposites is more sensitively reflected on storage modulus than on the loss modulus.

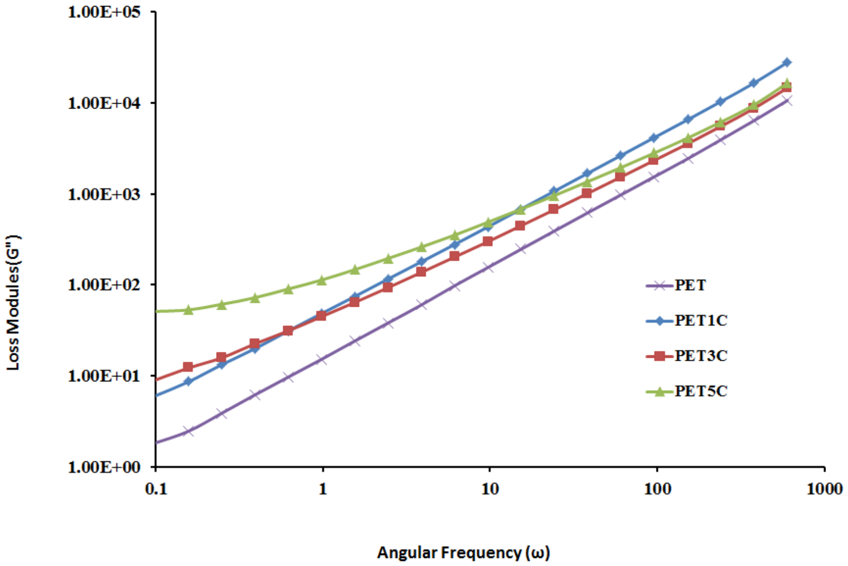


Figure 4. Loss modulus (G'') of pristine PET and clay/PET nanocomposites versus frequency (ω).

Thermal stability

The TGA thermo grams of PET and PET nanocomposites are presented in Figure 5. The onset decomposition temperature of nanocomposites is 3°C for PET1C, 4°C for PET3C and 11.5°C lower than that of pristine PET .It is because of catalytic effect of clay to accelerating decomposition PET matrix. According to some research have done on thermal degradation of polymer/clay nanocomposites, it can be due to (a) volatizing out of absorbed or bounded water in MMT;(b) Catalytic effect of hydroxyl groups which acts as acidic active centers of sorption .The bigger loss of onset decomposition of PET5C compared with other samples, could be caused by the thermal degradation of organic treatment of the clay.

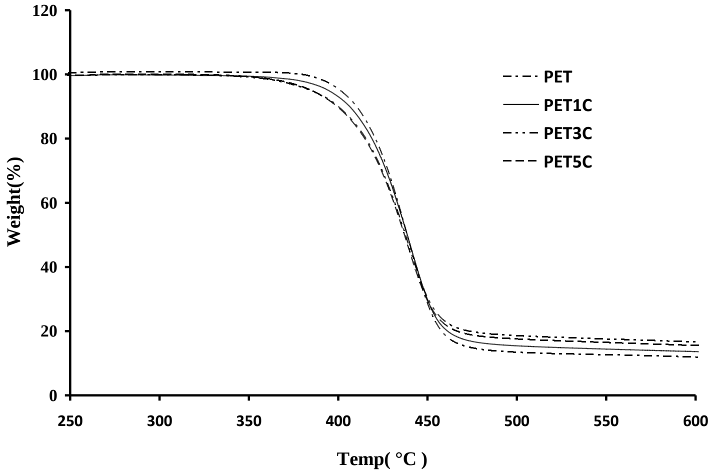


Figure 5. TGA curves of pristine PET,PET1C,PET3Cand PET5C in N_2 atmosphere(TGA heating rate : 10°C/min).

Flammability

Limiting oxygen index (LOI) values of samples are given in table 5. LOI increases as the content of organo-clay increases. However, the decrease is not very significant and it seems that nanocomposites samples do not perform better than pristine PET.

Table 5. The LOI values of PET/MMT.

Sample	LOI	Drip
PET	21.5	heavy
PEY1C	22	Almost heavy
PET3C	23	scarce
PET5C	24.2	no

The effect of varying organo-MMT loading in the heat release rate of nanocomposite samples is demonstrated in Figure 6.

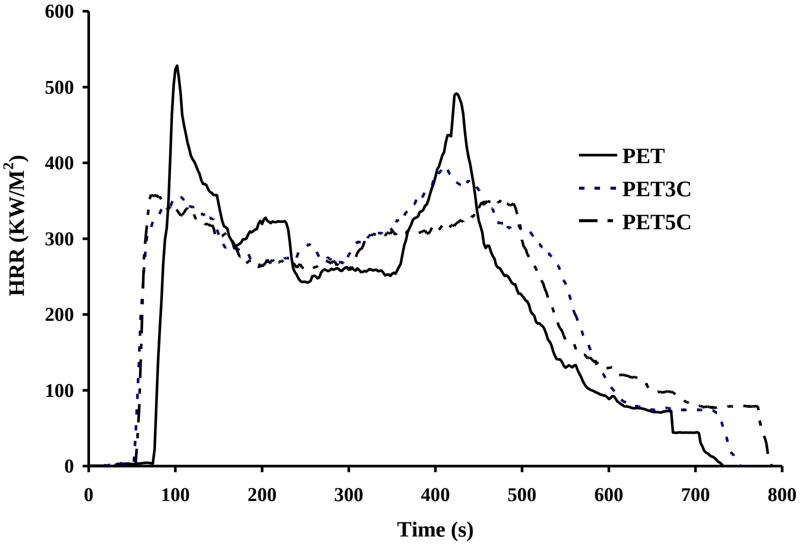


Figure 6. Heat release rate (HRR)dataforPET, PET3C and PET5C.

The results indicate that addition of MMT has decreased the HRR of PET matrix. The greater the organo-MMT content, the lower the heat release rate. The peak of HRR values of PET3C and PET5C are reduced, respectively, about 25% and 32% in comparison with pristine PET. The lower peak of HRR is due to barrier effect of clay in nanocomposite. According to previous studies [14-15], formation of carbonaceous char in the condensed phase leads to decrease in flammability of polymer/clay nanocomposites. The carbonaceous-silicate char acts as a barrier and insulates the underlayed polymer matrix. Thus, it slows down heat and mass transfer between the gaseous and condensed phases. Considering Fig. 5, the addition of MMT accelerate the ignition of the PET. Catalytic decomposition effect of MMT on polymer causes acceleration of the PET ignition which can be confirmed by TGA result. Fig.7. shows the mass loss rate results during the cone calorimetric experiments. The MLR curves are almost identical to the HRR curves.Due to these observations, it can be clearly concluded that the formation of coat-like carbonaceous char is responsible for the improvement in flammability properties.

Some cone calorimetric data of pristine PET and its nanocomposites are listed in Table.3. As it can be seen, there is a small decrease in THR obtained. CO production during the combustion of PET3C and PET5C was significantly lowered compared to pristine PET whereas no significant differences in theCO_2 release were evolved. Addition of clay greatly improved the amount of char residue from $W/W_0=0.11$ in case of pristine PET to 0.15 and 0.43 for PET3C and PET5C, respectively.

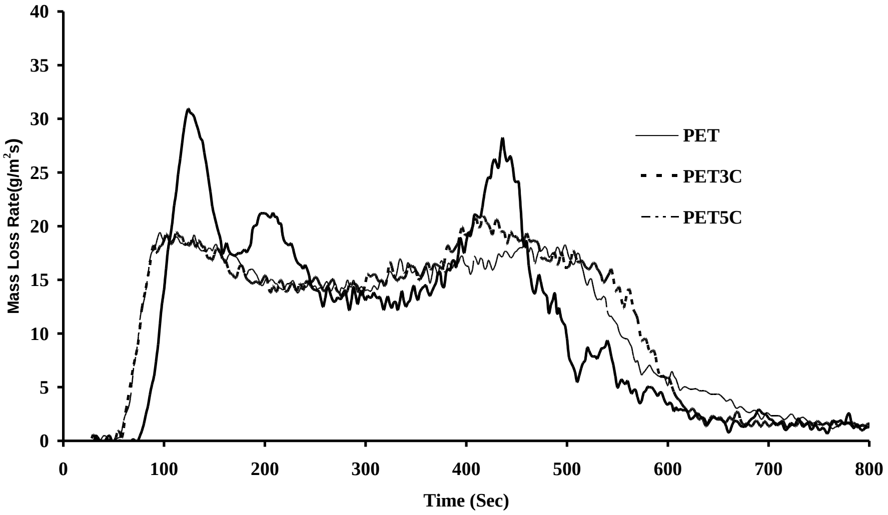


Figure 7. Mass loss rate(MLR) data for PET,PET3C and PET5C.

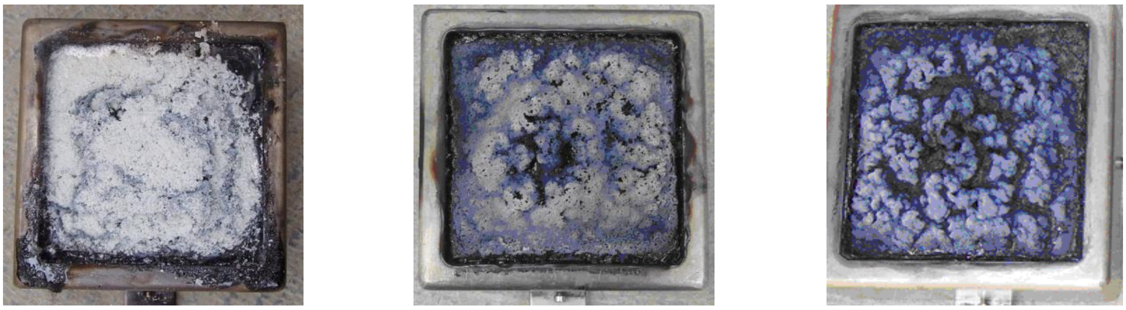
The EHC (effective heat of combustion) results of nanocomposites are similar to those of pristine PET.

Table 6. Cone calorimetry measured properties for pristine PET and its nanocomposites.

Sample	PET	PET3C	PET5C
Peak HRR(kW/m^2)	598.29	396.57	357.97
Total Heat ReleaseRate (THR) (MJ/m^2)	188.7	171.7	169.1
Average EHC(MJ/kg)	18.12	17.45	17.41
Average SEA(m2/kg)	269.53	287.25	304.68
Average CO yield (kg/kg)	0.0683	0.0346	0.0337
Average CO_2 yield(kg/kg)	1.94	1.79	1.77
Char residue (W/W_0)	0.11	0.15	0.43
Ignition time (s)	76	56	59

Note: HRR, heat released rate; EHC, effective heat of combustion; SEA, specific extinction area.

Observation of the combustion phenomenon during the cone calorimetric measurements revealed that pristine PET sample melted and had a boiling surface followed by some large bubbles. At the end of combustion pristine PET left almost no residue as shown in Fig.7.The nanocomposite with 3% clay melted but it was more viscous than PET and small carbonaceouschar formed on the surface without covering it. The PET5C appeared more viscous and it did not melt .Addition of 5% nano-clay inhibited bubbling process and formed a continuous solid coat-like carbonaceous char as it can be seen in Fig.8. Thus, the protective carbonaceous char acts as a barrier and covers the surface. Hence, the exposure of the molten polymer to heat and oxygen and volatilization of nanocomposites will be reduced. Formation of network-structured protective layer during the burning was confirmed RMS results Figure3and 4.PET burns with heavy dripping while, PET3C hasscarce dripping and PET5C shows dripping resistance. The residues of nanocomposites at the end of test is char like and for pristine PET is melt materials.



PET PET3C PET5C

Figure 8. Residue images at the end of cone calorimetric test.

Conclusion

In this research, PET/MMT nanocomposites with different contents of clay were prepared by melt blending. The intercalated morphology was confirmed by XRD and TEM. The catalytic decomposition effect of MMT is presented in TGA and viscometeryresults. Cone calorimeter experiments and LOI tests presented that flame retardant property of PET/MMT nanocomposite improves as the content of clay increase. A nanocomposite containing 5% clay shows insignificantly flame retardancy and dripping resistance. Flammability of clay PET nanocomposite are strongly affected by the clay network. The clay network restrains mobility of the polymer chains during combustion which leads to significant improvement of flame retardancy for nanocomposites. Hence presence of montmorillonite slowed down burning and improved char enhancement which is the main objective of PET flame retardancy treatment. All mentioned results along with eco-friendly behavior of organoclay, makes it a greatcandidate for conventional, harmful and toxic halogen-based flame retardants.

References

[1]T. Kashiwagi,M.Mu, K.Winey, B.Cipriano, S.R. Raghavan,S. Pack, M.Rafailovich, Y. Yang, E. Grulke, J. Shields,R.Harris, J.Douglas,*Polym. J.*, 49, 4358 (2008).

[2] S.S. Ray, M.Okamoto, *Prog. Polym.Sci*.,28, 1539 (2003).

[3] M. Ahmadi, S. Sedaghat, L. Khalaf, *J. Appl. Chem. Res*., 9, 117 (2015).

[4]S. Habibi, A.Rashidi, M.Shahvaziyan and S. Bazgir, *Asian J.Chem*., 22,7087(2010).

[5] K. Apaydin, A. Laachachi, V. Ball, M.Jimenez, S.Bourbigot, V. Toniazzo, D.Ruch, *Polym. Degrad. Stab*.,98, 627(2013).

[6]A.B. Morgan, R.H. Harri., T.Kashiwagi, L.J.Chyall.,C. Gilman, *J. Fire Mater*., 26, 247(2002).

[7] M. H.Yun, S. Ping, F.Zheng, *Sci. China Chem*.,92,1439 (2011).

[8] P. Lerdkajornsuk , S.Charuchinda, *J.Met.Mater. & Miner.* , 20, 63 (2010).

[9] S. Habibi,A. Rashidi, S. Bazgir, A.A.Katbab, M. Montazer, *Asian J. Chem*.,21,4881(2009).

[10] Y. Li, J. Schulz, S. Mannen,C.Delhom, B.Condon, S.Chang,M. Zammarano,*Acsnano J*.,4, 3325 (2010).

[11] M. Kotal, A. Bhowmick, *Prog. Polym. Sci***.,** 51, 127 (2015).

[12]A.Liu, A. Walthert, O. Ikkala, L. Belova, L.A. Berglund, *Biomacromolecules*, 12, 633 (2011).

[13] U. Gurmendi, J.I. Eguiazabal, J. Nazabal, *Eur.Polym. J*., 44, 1686 (2008).

[14]A. Dasari, Z.ZhongYu,G.P. Cai,W.M. Yiu,*Prog.Polym. Sci***.,** 38, 1357 (2013).

[15]J. Tata, J. Alongi,F.Carosio and A. Frache.*Fire.Mater.* , 35, 397 (2010).

[16]G. Guo, C.Chun, D.Zhang, *Appl. Polym. Sci*., 95, 1443 (2005).

[17]H. Ma, L.Tong, Z.Xu, Zh. Fang, *Polym.Degrad.Stab*, 92, 1439(2007).