J Therm Anal Calorim (2010) 100:651–660
DOI 10.1007/s10973-009-0266-2

Thermal degradation studies on PMMA–HET acid based oligoesters blends

**Thangamani Rajkumar · Chinnaswamy Thangavel Vijayakumar ·
Palanichamy Sivasamy · Bojja Sreedhar ·
Charles A. Wilkie**

Received: 24 March 2009 / Accepted: 17 June 2009 / Published online: 25 July 2009

Abstract Imparting thermal stability to polymethyl methacrylate (PMMA) without affecting its optical clarity is attempted by incorporating HET acid based oligoesters. Pure PMMA and PMMA containing five and 20 wt% of four different oligoesters are separately prepared using bulk polymerization. The thermal properties of the materials studied using DSC, TG, TG–FTIR and Pyr–GC–MS are presented. The main volatile degradation products identified are CO, HCl, CO_2, H_2O, hexachlorocyclopentadiene, hexachloroendomethylene tetrahydrophthalic acid/anhydride and methyl methacrylate. A detailed mechanism for the influence of the degradation products of HET acid based oligoesters on the thermal degradation of PMMA is also presented.

Keywords Bulk polymerization · GC–MS · Mechanism · Oligoesters · PMMA · TG–FTIR · Thermal degradation

Introduction

Polymers are inherently flammable. In the presence of sufficient heat and oxygen, most organic polymers will burn [1]. The flammability of polymers depends on various factors such as their composition, structure, exposure time, nature of pyrolysis products, char yield, etc. Combustion cycle of polymer can be interrupted by selecting polymer system having strong bonds, polymer which forms a higher char yield or systems which can release non-flammable fuel diluents like carbon dioxide, carbon monoxide, water, hydrogen halides, etc.

Several authors achieved flame retardancy by developing new polymer systems with inherent flame resistance, copolymerizing with a flame retardant co-monomer, adding flame retardants to the polymer matrix or by applying flame retardant coating over the finished product [2]. The method of incorporating flame retardant in the polymer is more economical than other methods. A flame retardant is effective only when it interferes with at least any one of the stages of combustion process.

Flame retardants may be either reactive or additive [3, 4]. Reactive flame retardants are added during the polymerization process and become an integral part of the polymer. Additive flame retardants are incorporated into the polymer either prior to, during or more frequently following polymerization. They are used especially in thermoplastics. Additive flame retardants are only physically bonded to the polymer. An ideal flame retardant should not affect the properties and performance of the polymer which is flame retarded.

Optical clarity and excellent corrosion resistance properties of polymethyl methacrylate (PMMA) make it so popular and widely used in the building industry where the light transmission is required and finds extensive use in

---

T. Rajkumar · C. T. Vijayakumar (✉)
Department of Polymer Technology, Kamaraj College
of Engineering and Technology, SPGC Nagar,
K. Vellakulam Post 625701, India
e-mail: ctvijay22@yahoo.com

P. Sivasamy
Post-graduate Department of Chemistry, Ayya Nadar Janaki
Ammal College (Autonomous), Sivakasi 626124, India

B. Sreedhar
Inorganic and Physical Chemistry, Indian Institute of Chemical
Technology, Tarnaka, Hyderabad 500007, India

C. A. Wilkie
Department of Chemistry, Marquette University, P.O. Box 1881,
Milwaukee, WI 53201, USA

electrical fittings and insulations [5]. But it burns readily and therefore it is very important to protect it with flame retardants [6] without marring its special properties.

There is a wide range of flame retardant additives like halogenated paraffin, phosphate esters and inorganic fillers [7] are available. Also reactive organic flame retardants, such as HET anhydride/acid, tetrabromophthalic anhydride, etc. are used [2]. In the case of PMMA, products containing flame retardant additives must exhibit adequate flame resistance properties with out sacrificing optical clarity.

In the present investigation, attempts are made to impart thermal stability to PMMA by using hexachloroendomethylene tetraphthalic acid (HET) based oligoester additives, HET EG, HET 1,2-PD, HET 1,3-PD and HET 1,4-BD (obtained by condensing HET acid with diols, ethylene glycol, 1,2-propane diol, 1,3-propane diol and 1,4-butane diol) with out affecting its optical clarity. The thermal properties are investigated using DSC and TG. Detailed TG–FTIR studies of these materials are carried out to understand the effect of degradation products of HET acid based oligoesters on the degradation of PMMA. Off-line pyrolysis GC–MS studies are used to understand the degradation products distribution.

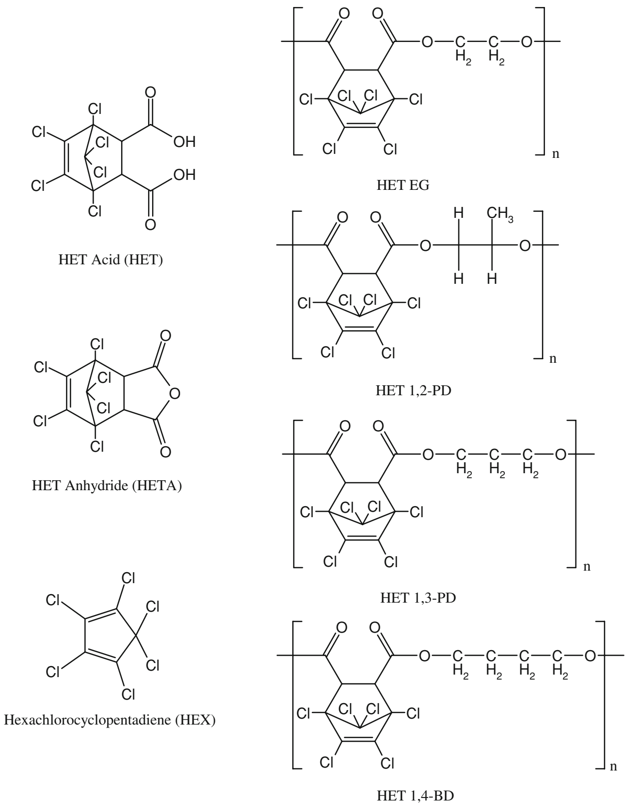
Experimental

Synthesis of halogenated oligoesters

Halogenated Oligoesters, HET EG, HET 1,2-PD, HET 1,3-PD and HET 1,4-BD (Scheme 1) were synthesized by condensing HET acid with four different diols, ethylene glycol, 1,2-propane diol, 1,3-propane diol and 1,4-butane diol in the presence of *p*-toluene sulphonic acid as a catalyst according to the procedure reported [8, 9].

Bulk polymerization of MMA and MMA containing oligoesters

Pure PMMA and PMMA containing HET acid based oligoesters were made using bulk polymerization technique. Methyl methacrylate (MMA) monomer and the requisite quantities of oligoesters were blended together and filtered. Azobisisobutyronitrile, AIBN (0.2%) was added as initiator. The materials were taken in test tubes and purged with oxygen free dry nitrogen. The test tubes were immersed in an oil bath maintained at 40 ± 1 °C for 72 h. Finally, the neat glass clear Pure PMMA and blends of PMMA containing five and 20 wt% of four different HET acid based oligoesters were carefully removed from the glass tube and post cured in a hot air oven for 6 h at 70 °C.



Scheme 1 Structures of monomers and oligoesters

Analysis

The optical clarity of pure PMMA and PMMA containing oligoesters was studied using SHIMADZU UV-1700 UV–Visible spectrophotometer. The analysis was performed for the samples of 1 cm thick with electromagnetic radiation of wavelength 200–800 nm.

Differential scanning calorimetry (DSC) facilitates the determination of relative heats of reaction. Mettler DSC 822^e Toledo instrument was used to record DSC curves. The samples were heated at a rate of 10 °C min^{-1} and about 5 mg of the sample was used for analysis. The measurements were made from room temperature to 650 °C in nitrogen atmosphere (30 mL min^{-1}).

TG–FTIR studies were performed under nitrogen flow (40 mL min^{-1}) on CAHN TG-131 instrument that was connected to Mattson Research grade FTIR. It provides information about the thermal stability, decomposition rate of materials and the effect of volatile degradation products as an alternative to ASTM methods for determining burning characteristics or rate [10]. The material was heated from ambient to 600 °C at a heating rate of 20 °C min^{-1}. The volatile degradation products were analyzed by in situ vapour phase FTIR. The sample size used to perform the analysis was 35–50 mg.

The off-line isothermal degradation of the material [11] was carried out in an all glass apparatus. About 100 mg of the material was degraded at 400 °C for 10 min under steady flow of nitrogen (40 mL min^{-1}). The degradation products trapped in the frozen matrix of acetone were allowed to thaw and transferred to a glass tube and stored at −40 °C for further analysis. The separation of the components of the volatile fraction was effected in a GC–MS having a computer work station. The identification was done using a HP5970 mass selective detector coupled to the GC using a jet-separator. The mass range scanned was 20–300 amu.

Calculation of energy of activation

The amount of energy required to activate the degradation was determined using Dharwadkar and Kharkhanavala equation [12, 13]. The equation is:

$$\ln\{\ln[1/(1-\alpha)]\} = \left(E_a/RT_i^2\right)[100\,\theta/(T_f - T_i)] + C$$

where α = Fraction reacted/degraded, E_a = Activation energy, R = Gas constant, T_i = Temperature of inflection of the reaction, T_f = Temperature of completion of the reaction, $\theta = (T - T_s)$, difference between T_s and temperature under consideration, T_s = Temperature at the point of inflection in TG curve and C = Constant. A plot of $\ln\{\ln[1/(1-\alpha)]\}$ against θ results in a straight line with a slope of $(E_a/RT_i^2)\,[100/(T_f - T_i)]$ from which E_a can be computed.

Results and discussion

Study on transparency

The ultraviolet–visible spectra of about 1 cm thick pure polymethyl methacrylate (PMMA) and PMMA containing 5 wt% of oligoesters are depicted in Fig. 1. Pure PMMA absorbs 79–71% of visible light radiation (800–400 nm) [14–16] and its transparency to ultraviolet radiation starts to drop at 400 nm and reaches zero at 300 nm. Transparency of pure PMMA to UV radiation in the range of 200–300 nm is almost zero. UV–Visible spectra of PMMA containing 5 wt% of four different oligoesters follow the same trend observed in the case of pure PMMA. A drop in the percentage of transmittance observed for PMMA containing 5 wt% of HET 1,4-BD in the range of 380–440 nm is attributed to its pale yellow colour. One can found that the transparency of pure PMMA to visible radiation is affected only to a very small extent of about 6% by incorporating 5 wt% of HET acid based oligoesters to impart thermal stability.

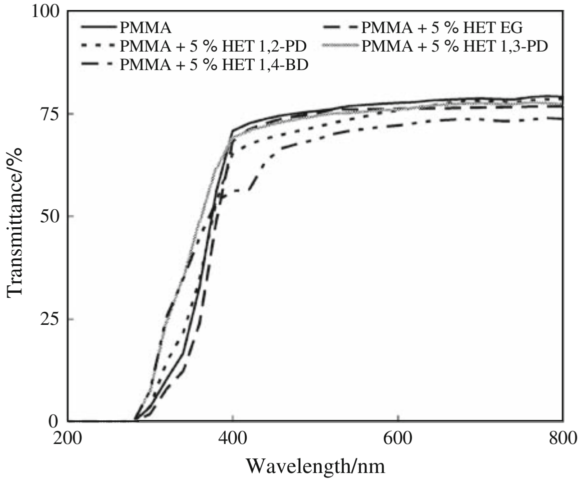


Fig. 1 UV–Visible spectra of pure PMMA and PMMA containing HET acid based oligoesters

Thermal degradation of PMMA and PMMA containing 5% of HET acid based oligoesters

DSC curves obtained during first heating (10 °C min^{-1}) of pure PMMA and PMMA containing 5 wt% of HET acid based oligoesters under inert nitrogen atmosphere are presented in Fig. 2. The degradation of the materials proceeds by an endothermic reaction over a wide temperature region. The relative heat of degradation computed from DSC results given in Table 1 is used to study the role of incorporated oligoesters on the thermal stability of PMMA. The onset, peak and endset temperatures of the degradation of

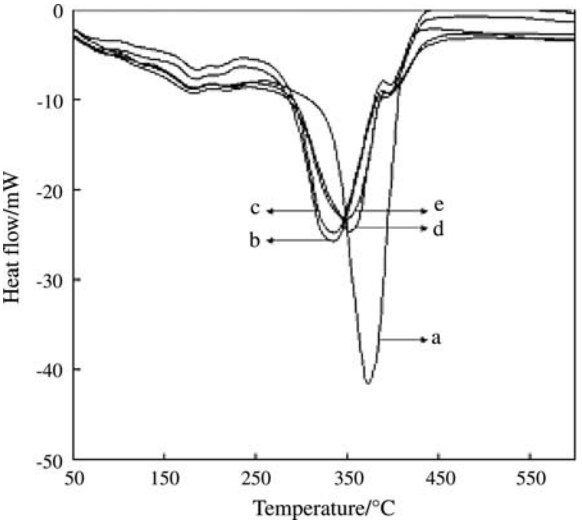


Fig. 2 DSC traces of PMMA and PMMA containing oligoesters obtained in nitrogen atmosphere (β: 20 °C min^{-1}): a—PMMA, b—PMMA + 5% HET EG, c—PMMA + 5% HET 1,2-PD, d—PMMA + 5% HET 1,3-PD and e—PMMA + 5% HET 1,4-BD

Table 1 DSC studies of PMMA and blends of PMMA with different HET acid based oligoesters: the available β-hydrogens and the total heat of decomposition

Material	Available β-hydrogens	Heat of decomposition*/J g^{-1}
PMMA	0	1234
PMMA + 5% of HET EG	4	523
PMMA + 5% of HET 1,2-PD	6	542
PMMA + 5% of HET 1,3-PD	2	611
PMMA + 5% of HET 1,4-BD	4	500

*Average of three values, average deviation approximately 4%

PMMA containing oligoesters are lower compared to pure PMMA. The lowering of onset degradation temperature indicates the interference of thermally degrading HET acid based oligoesters on the thermal degradation of PMMA. Oligoesters loaded in the PMMA decreases the heat of degradation by 50–60%. Based on the total amount of heat absorbed during the degradation in nitrogen atmosphere, the materials are arranged in the order: PMMA > PMMA + 5% of HET 1,3-PD > PMMA + 5% of HET 1,2-PD > PMMA + 5% of HET EG > PMMA + 5% of HET 1,4-BD. The above trend is explained with the help of the number of β-hydrogens present in the oligoesters incorporated in the PMMA matrix. The presence of more β-hydrogens (4 and above) in the oligoesters drastically reduces the total heat absorbed during the degradation in inert atmosphere. Hence, the incorporation of HET acid based oligoesters to PMMA may effectively interfere with the degradation of PMMA.

The thermal degradation of PMMA and PMMA containing 5 wt% of HET acid based oligoesters was followed by thermogravimetric technique in nitrogen atmosphere at a heating rate of 20 °C $\min^{-1}$. The mass loss against temperature variation and the rate of mass loss curves of pure PMMA and PMMA containing 5 wt% of oligoesters are presented in Figs. 3 and 4, respectively. The parameters derived from TG, the maximum degradation temperature ($T_{\max}$) of the major degradation process, energy of activation (E_a) of the degradation, mass loss at 350 °C and the char residue at 500 °C obtained during the degradation of pure PMMA and its blends are given in Table 2.

There is no significant change in the onset and endset temperatures of the degradation, which may be attributed to the faster heating rate employed for the TG studies. Although the loaded oligoesters do not have significant effect on the onset and endset temperatures of the degradation of PMMA, they affect the maximum degradation temperature.

The major degradation of pure PMMA shows a doublet [17–20] (Fig. 4) at a heating rate of 20 °C $\min^{-1}$. The loaded oligoesters show profound influence on the first degradation stage of PMMA and they reduce this $T_{\max}$ from 401 °C. The reduction in $T_{\max}$ for the first degradation is dependent on the structure of the diol unit of the HET acid based oligoesters blended with PMMA (Table 2). Further the second $T_{\max}$ noted in the case of PMMA (425 °C) is not much affected by the added HET acid based oligoesters. The well known unzipping is taking place during the thermal degradation of PMMA.

The energies of activation (E_a) calculated (Table 2) using Dharwadkar and Kharkhanavala method for the major degradations of PMMA [21] and its blends show that PMMA containing HET acid based oligoesters require higher amount of energy for the degradation than required for pure PMMA [22–28]. The order of activation energy for

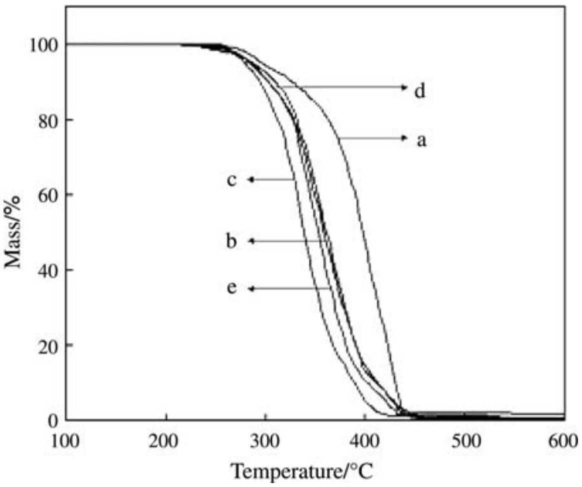


Fig. 3 TG traces of PMMA and PMMA containing oligoesters obtained in nitrogen atmosphere (β: 20 °C $\min^{-1}$): a—PMMA, b—PMMA + 5% HET EG, c—PMMA + 5% HET 1,2-PD, d—PMMA + 5% HET 1,3-PD and e—PMMA + 5% HET 1,4-BD

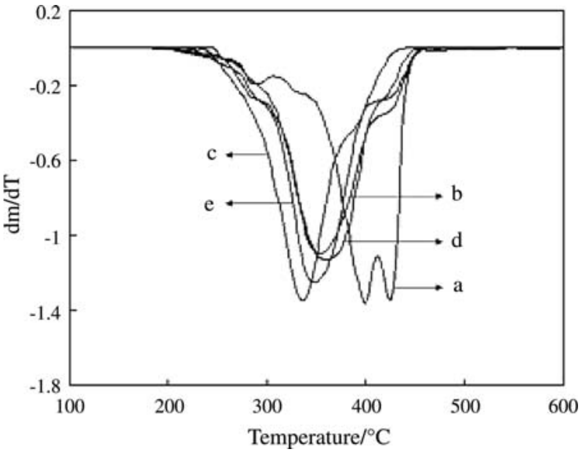


Fig. 4 DTG traces of PMMA and PMMA containing oligoesters obtained in nitrogen atmosphere (β: 20 °C $\min^{-1}$): a—PMMA, b—PMMA + 5% HET EG, c—PMMA + 5% HET 1,2-PD, d—PMMA + 5% HET 1,3-PD and e—PMMA + 5% HET 1,4-BD

Table 2 Parameters derived from the TG/DTG curves obtained for the degradation of PMMA and its blends with 5% loading of different oligoesters in nitrogen atmosphere (β: 20 °C min^{-1})

Materials	T_{max}/°C	E_a*/kJ mol^{-1}	Mass loss at 350 °C/%	Char at 500 °C/%
PMMA	401, 425	54	13	0.7
PMMA + 5% HET EG	356	86	39	0.6
PMMA + 5% HET 1,2-PD	335	70	60	1.2
PMMA + 5% HET 1,3-PD	350	68	42	1.9
PMMA + 5% HET 1,4-BD	340	76	43	0.8

*Average of three values, Average deviation <3%

degradation is PMMA + 5% HET EG > PMMA + 5% HET 1,4-BD > PMMA + 5% HET 1,2-PD > PMMA + 5% HET 1,3-PD > PMMA. E_a values computed from thermogravimetric analysis indicate that in situ polymerization of MMA with HET acid based oligoesters imparts sufficient thermal stability to the material.

The broadening of the DTG curves of blends than that of pure PMMA implies that the oligoesters loaded in the PMMA increases the temperature range of major degradation. The effect of blended oligoesters on the thermal degradation of PMMA matrix is evidenced from the mass loss measured at 350 °C. The mass loss order at 350 °C is PMMA + 5% HET 1,2-PD > PMMA + 5% HET 1,4-BD ~ PMMA + 5% HET 1,3-PD ~ PMMA + 5% HET EG > PMMA. A slight increase in the char formation is also noted in the case of blends compared to pure PMMA.

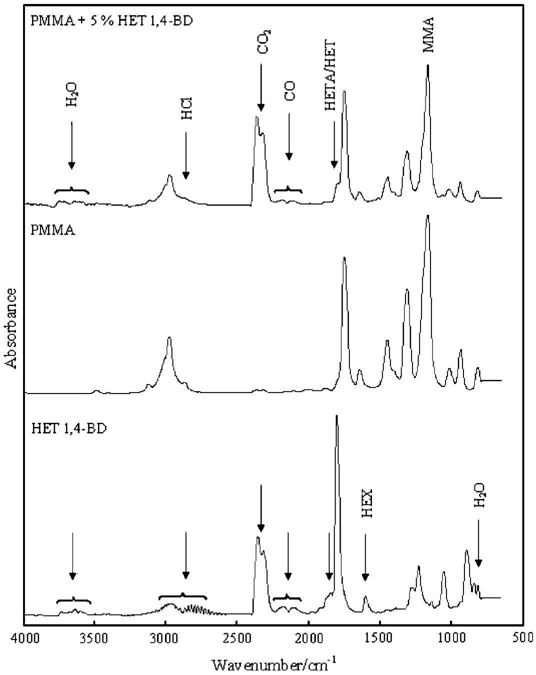


Fig. 5 FTIR spectra showing the degradation products correspond to their absorbance peak

Identification of the gases evolved during degradation of PMMA and PMMA containing oligoesters

The volatile degradation products identified are H_2O, CO, CO_2, HCl, hexachlorocyclopentadiene (HEX), hexachloroendomethylene tetraphthalic acid (HET)/anhydride (HETA) and MMA. The wave number/ranges considered for H_2O is 1500–1600 cm^{-1} and 3400–3800 cm^{-1}, for CO_2 is 600–700 cm^{-1} and 2300–2400 cm^{-1}, for CO is 2100–2300 cm^{-1}, for HET/HETA is 800–1300 cm^{-1} and 1750–1900 cm^{-1}, for HCl is 2700–2900 cm^{-1} [29], for HEX is 1600 cm^{-1} [30, 31] and for MMA is 1180 cm^{-1} (Fig. 5). The deformation vibrations are not considered because they may overlap with one another.

The nature of the volatile gases evolved during the degradation of PMMA and PMMA containing 5 wt% of oligoesters is analyzed using TG coupled with FTIR studies and the recorded FTIR spectra of the gases evolved are presented in Figs. 6 and 7.

The evolution profiles of the various gaseous degradation products identified during the thermal degradation [32, 33] of pure PMMA and PMMA containing 5 wt% of HET acid based oligoesters presented in Figs. 8 and 9 confirm the intervention of the degrading oligoesters on the thermal degradation of PMMA. The profiles of the MMA evolution from PMMA and blends show that MMA is formed in a broader temperature range with two peak maxima. The first maximum noted at 399 °C during the degradation of PMMA is shifted to still lower temperature when PMMA is loaded with oligoesters, whereas the second maximum noted at 429 °C is found to be unaffected by the loaded oligoesters. The maximum formation of all the gaseous degradation products identified occurs in the same temperature region for all the PMMA blends but the profile of evolution of the HEX varies depending on the nature of the HET acid based oligoesters loaded in the PMMA matrix. The non-flammable gaseous degradation products, HCl, CO, CO_2, H_2O, HETA and HEX evolved at the same degradation temperature significantly retard the burning process.

The non-flammable gases released during the decomposition of HET acid based oligoesters and the decomposition of PMMA to flammable MMA monomer are occurring nearly in the same temperature range. So, dilution of the flammable gases is possible in the gas phase.

Off-line pyrolysis of oligoesters and their blends with PMMA

The HET acid based oligoesters and materials of PMMA containing HET acid based oligoesters are thermally degraded under isothermal condition to study the degradation pattern and the mechanistic action of oligoesters on the thermal degradation of PMMA.

The total ion chromatograms of the volatile products of the oligoesters, HET EG, HET 1,2-PD, HET 1,3-PD and HET 1,4-BD are presented in Fig. 10 and the compounds identified on the basis of the mass spectra are listed in Table 3. The major volatile products identified in the degradation of oligoesters are HEX and pentachlorocyclopentadiene along with certain minor degradation products, carbon dioxide, acetone, vinyl chloride,

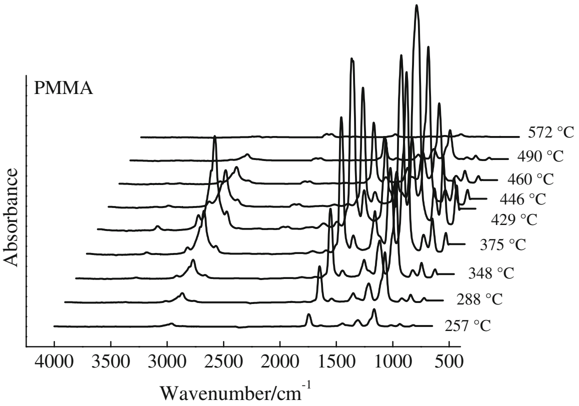


Fig. 6 FTIR spectra of the gases evolved during thermal degradation of pure PMMA

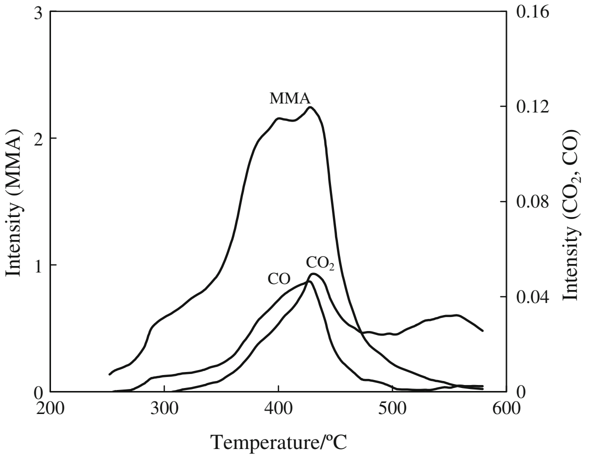


Fig. 8 The profile of the volatile gases evolved during the thermal degradation of PMMA

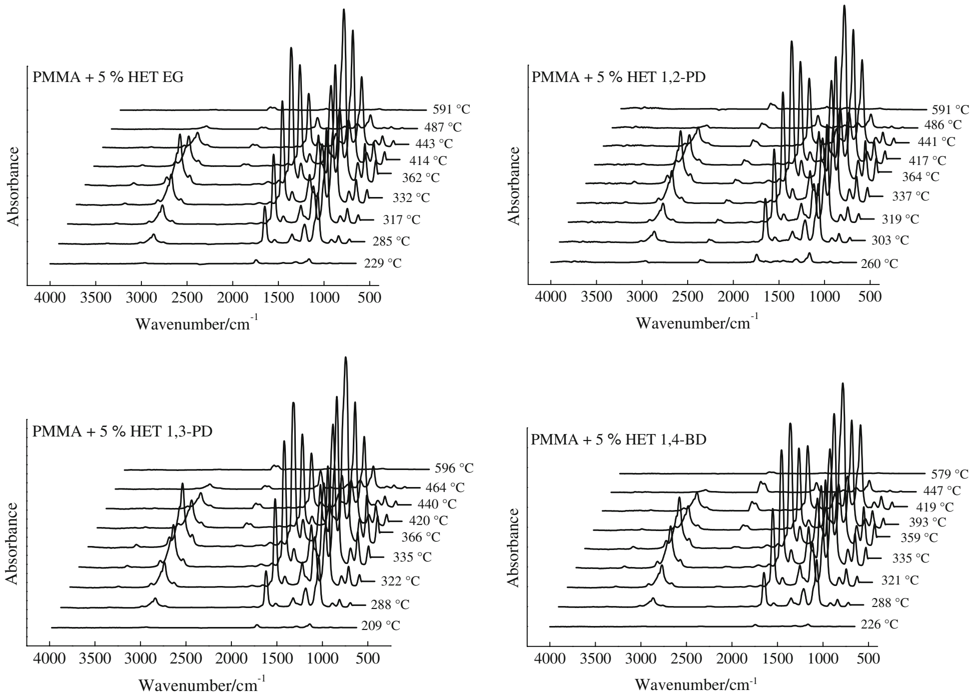


Fig. 7 FTIR spectra of the gases evolved during thermal degradation of PMMA containing 5% of HET acid based oligoesters

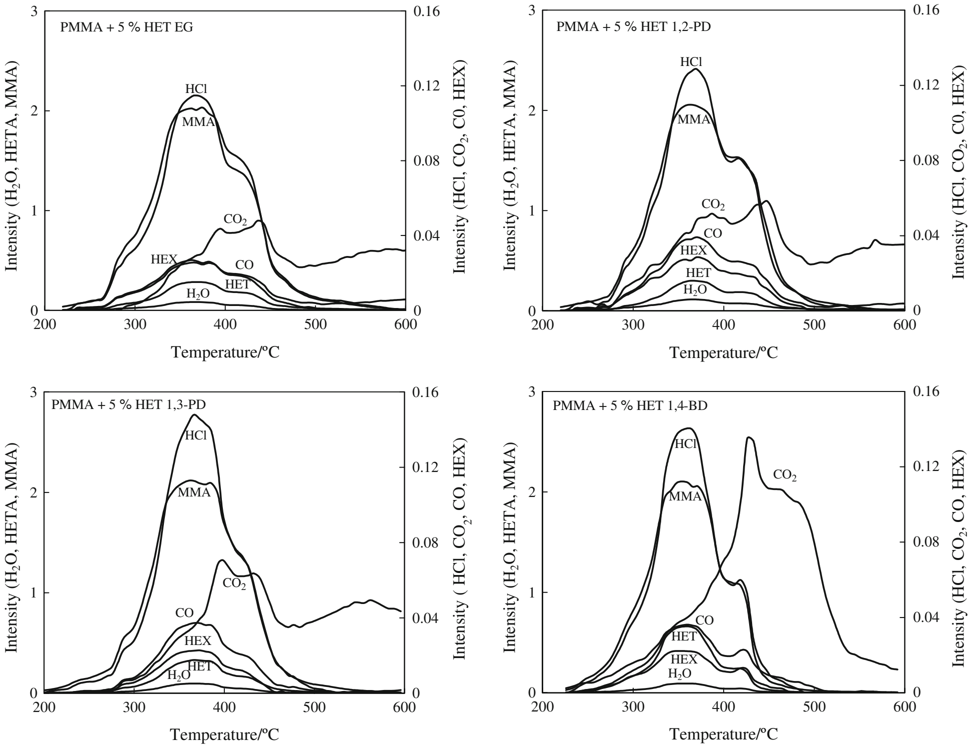


Fig. 9 The profile of the volatile gases evolved during the thermal degradation of PMMA containing HET acid based oligoesters

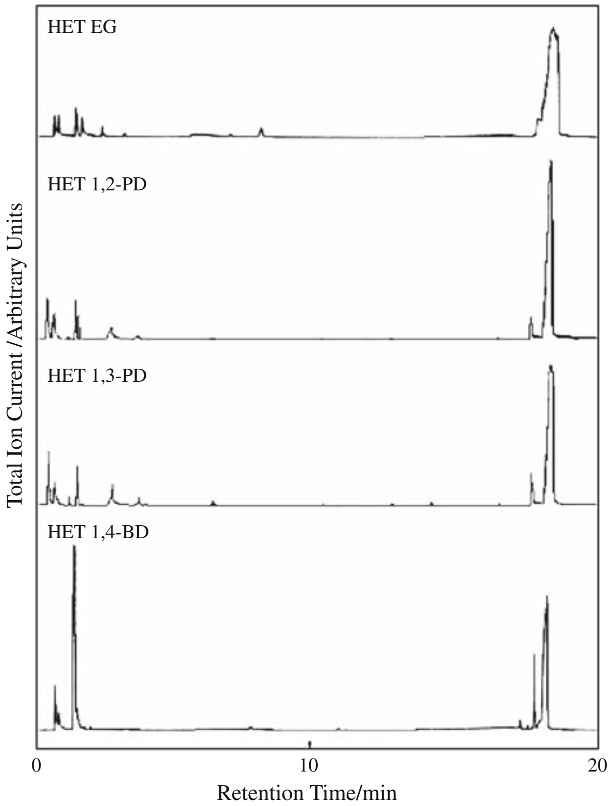


Fig. 10 Total ion chromatograms of the volatile fractions obtained in the isothermal degradation of HET acid based oligoesters

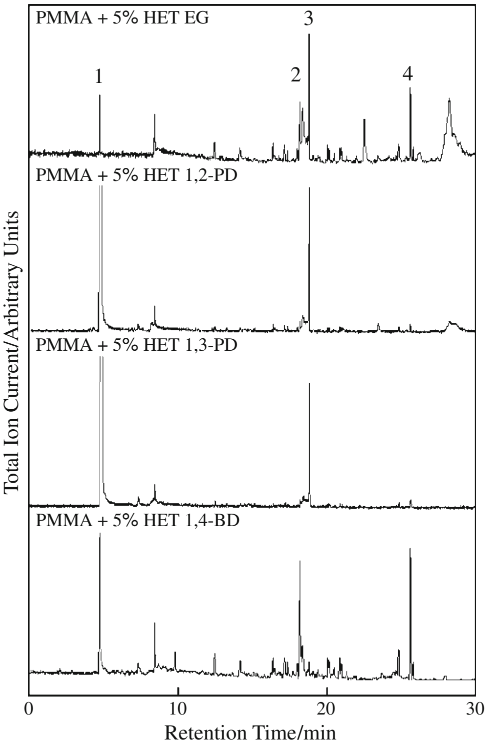


Fig. 11 Total ion chromatograms of the volatile fractions obtained in the isothermal degradation of PMMA containing 20% of HET acid based oligoesters: 1—PMMA, 2—Complex ester, 3—HEX and 4—Ester containing HET acid unit

Table 3 Products identified in the volatile fractions obtained during isothermal degradations (400 °C for 10 min in nitrogen atmosphere) of the HET acid based oligoesters

Retention time/min	Molecular formula	Proposed compound	HET EG	HET 1,2-PD	HET 1,3-PD	HET 1,4-BD	Remarks
0.56	CO_2/C_2H_4O	Carbon dioxide/Acetaldehyde	*				B
0.61	C_2H_3Cl	Vinyl chloride	*				B
0.62	C_4H_6	1,3-Butadiene				*	B
0.71	C_3H_6O	Acetone	*		*	*	A
0.84	C_3H_6O	Allyl alcohol			*		A
1.20	C_4H_8O	Tetrahydrofuran				*	A
1.25	$C_2H_4Cl_2$	1,2-Dichloroethane	*				A
1.44	C_2H_5ClO	2-Chloroethanol	*				A
1.67	$C_3H_6Cl_2$	1,2-Dichloropropane		*			B
1.70	$C_5H_{10}O$	2-Methyltetrahydrofuran				*	B
1.75	C_3H_8O	2-Propanol		*			A
2.01	C_3H_8O	1-Propanol		*			A
2.07	C_4H_7ClO	2-Chloroethyl vinyl ether	*				B
2.09	$C_6H_{12}O_2$	2,2,4-Trimethyl-1,3-dioxolane		*			B
2.75	C_7H_8	Toluene	*	*			A
3.15	$C_6H_{12}O_2$	Dimethyl-1,4-dioxane (I)		*			A
3.36	$C_6H_{12}O_2$	Dimethyl-1,4-dioxane (II)		*			A
4.94	$C_4H_2O_3$	Maleic anhydride	*	*	*	*	A
6.06		Compound with C_3H_6ClO unit	*				C
7.00	$C_4H_8Cl_2O$	Di(2-chloroethyl)ether	*				B
9.60		Compound with $C_5H_9O_2$ unit (I)				*	C
15.36		Compound with $C_5H_9O_2$ unit (II)				*	C
15.59		Compound with $C_5H_9O_2$ unit (III)				*	C
15.70	C_5HCl_5	Pentachlorocyclopentadiene	*	*	*	*	A
16.08	C_5Cl_6	Hexachlorocyclopentadiene	*	*	*	*	A

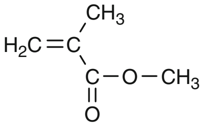
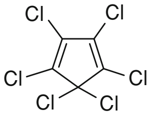
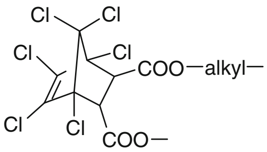
*Products identified, *A* Structure proved by injecting authentic sample, *B* Structure proposed on the basis of library documented mass spectrum, *C* Structure proposed on the basis of fragmentation pattern

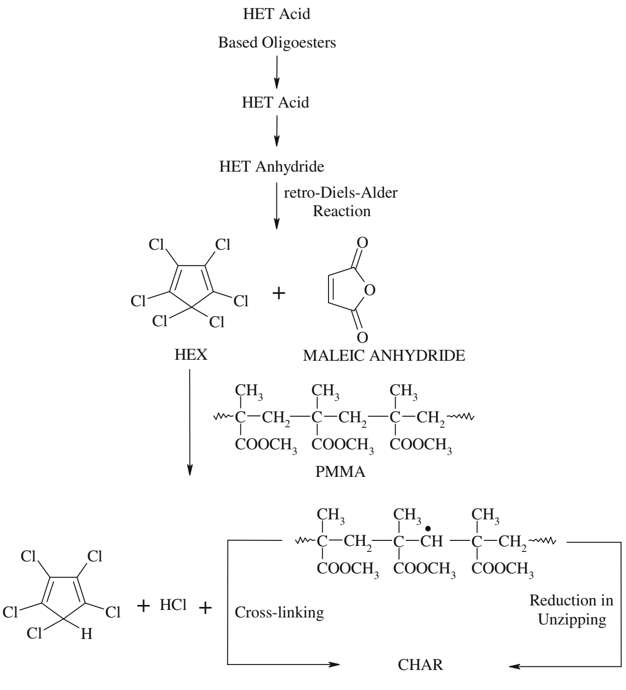
2-chloroethanol, toluene, maleic anhydride, 2-chloroethyl vinyl ether and di(2-chloroethyl)ether. The compounds tetrahydrofuran and 2-methyltetrahydrofuran are mainly due to the degradation of the diol unit in the oligoesters. The results obtained are consistent with the earlier work [8, 34]. In all the cases, the major volatile degradation product evolved is HEX through retro Diels–Alder reaction of the HET acid moiety present in the oligoesters.

The total ion chromatograms of the volatile products obtained in the isothermal degradation of PMMA containing 20 wt% of HET acid based oligoesters are presented in Fig. 11. The depolymerization of PMMA to the original monomer, methyl methacrylate, through unzipping reaction was the major reaction resulting from the thermal degradation of PMMA [35–38]. Several new products noted in the volatile fractions of the PMMA blended with 20 wt% of HET acid based oligoesters are listed in Table 4. The consequence of adding HET acid based oligoesters to the PMMA system is the evolution of detectable quantities of HETA, HEX and small quantities of compounds containing HET moiety along with the major component MMA in the thermal degradation products.

The major compound released during the decomposition of the HET acid based oligoesters is HET anhydride. The release of HEX and the subsequent production of HCl during degradation are taking place in the same temperature region. The chlorinated products will definitely act as radical scavengers during the degradation of PMMA. The chlorine radical produced during the degradation of HEX will affect the normal unzipping reaction of PMMA. Hydrogen abstraction from the PMMA chain and the alteration of the course of unzipping processes will lead to increased char in the condensed phase (Scheme 2).

Table 4 Details of compounds identified in the volatile fraction obtained during thermal degradation of blends of PMMA with oligoesters

S. No.	Retention time/min	Compound name	Structure
1	4.817	Methyl methacrylate	
2	18.177	Complex ester	-
3	18.784	Hexachlorocyclo-pentadiene	
4	25.595	Ester containing HET acid unit	



Scheme 2 Role of HET acid based oligoesters on the thermal degradation of PMMA

Conclusions

Polymethyl methacrylate and PMMA containing four different HET acid based oligoesters having loading per cent of five and 20 were synthesized by bulk polymerization technique. It was found that loading of HET acid based oligoesters did not affect the optical clarity of PMMA. The thermal stability and the energy of activation for the major degradation were assessed and show that PMMA containing 5 wt% of HET 1,3-PD is thermally more stable than the other blends. The acceleration of thermal degradation by the incorporation of oligoesters was predicted from the mass loss order measured at 350 °C. The release of non-flammable gases like HCl, CO, CO_2, H_2O, HEX, HET acid/anhydride and MMA in the same temperature region predicted using TG coupled with FTIR study confirms the interference of chlorinated compounds released on the unzipping reaction of PMMA. The major volatile products identified using GC–MS technique in the isothermal degradation of PMMA containing 20 wt% of oligoesters are HEX and HETA along with certain minor products may act as diluents for the flammable gaseous degradation products from PMMA matrix. Especially, HEX acts as a radical scavenger owing to its capacity to transfer chlorine both in the condensed and gaseous phases. It is concluded that the evolution of MMA could be effectively suppressed by adding HET acid based oligoesters.

Acknowledgements The authors gratefully acknowledge the Management and the Principal of Kamaraj College of Engineering and Technology, K. Vellakulam Post and Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi for their encouragement and providing facilities to carry out this work successfully. The authors thank Prof. Dr. J. K. Fink, Institut für Chemie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben, Austria for his help in pyrolysis studies.

References

1. Troitzsch JH. Plastics flammability handbook: principles, regulations, testing, and approval. 3rd ed. Munich: Hanser Publishers; 2004.
2. Grand AF, Wilkie CA, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker; 2000.
3. Hindersinn R. Encyclopedia of polymer science and technology. 2nd ed. New York: Wiley; 1977.
4. Novikov SN, Gitina RM, Antonov AV. High molecular weight halogenated fire retardants. Int J Polym Mater. 1993;20:19–30.
5. Harper CA. Modern plastics handbook. New York: McGraw-Hill; 2000.
6. Zeng WR, Li SF, Chow WK. Review on chemical reactions of burning poly(methyl methacrylate) PMMA. J Fire Sci. 2002;20: 401–33.
7. Etienne S, Becker C, Ruch D, Grignard B, Cartigny G, Detrembleur C, et al. Effects of incorporation of modified silica nanoparticles on the mechanical and thermal properties of PMMA. J Therm Anal Cal. 2007;87:101–4.
8. Vijayakumar CT, Lederer K. An insight into the degradation aspects of 1,4,5,6,7,7-hexachloro-5-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid based two component polyesters. Thermochim Acta. 1990;173:129–35.
9. Rajkumar T, Vijayakumar CT, Sivasamy P. HET acid based oligoesters: TGA/FTIR studies. Eur Polym J. 2008;44:1865–73.
10. Atkinson PA, Haines PJ, Skinner GA, Lever TJ. Studies of fire-retardant polyester thermosets using thermal methods. J Therm Anal Cal. 2000;59:395–408.

11. Vijayakumar CT. Investigations on the thermal degradation of polyesters. Doktor Der Montanistatischen Wissenschaften Dissertation. Montanuniversität Leoben, A-8700 Leoben, Austria; 1987.
12. Dharwadkar SR, Kharkhanavala MD. Thermal analysis, calculation of activation energy of decomposition reactions from thermogravimetric analysis. Thermal analysis. New York: Academic Press; 1969. p. 1049–69.
13. Vijayakumar CT, Sivasamy P, Rajkumar T. Synthesis and characterization of 1,3-bis(2-hydroxyethoxy)benzene based saturated and unsaturated polyesters. Eur Polym J. 2007;43:3028–35.
14. Chen W, Feng L, Qu B. In situ synthesis of poly(methyl methacrylate)/MgAl layered double hydroxide nanocomposite with high transparency and enhanced thermal properties. Solid State Commun. 2004;130:259–63.
15. Wang H, Meng S, Zhong W, Du W, Du Q. Poly(methyl methacrylate)/silica/titania ternary nanocomposites with greatly improved thermal and ultraviolet-shielding properties. Polym Degrad Stab. 2006;91:1455–61.
16. Kim S, Wilkie CA. Transparent and flame retardant PMMA nanocomposites. Polym Adv Technol. 2008;19:496–506.
17. Gao Z, Xie W, Hwu JM, Wells L, Pan WP. The characterization of organic modified montmorillonite and its filled PMMA nanocomposite. J Therm Anal Cal. 2001;64:467–75.
18. Kashiwagi T, Gilman JW. Silicon based flame retardants. In: Grand AF, Wilkie CA, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker; 2000. p. 363.
19. Inoue E, Tsuchiya M, Ishimaru K, Kojima T. Thermogravimetric studies on poly(methyl methacrylate), poly(tetrahydrofuran) and their blends. J Therm Anal Cal. 2002;70:747–53.
20. Durães JA, Drummond AL, Pimentel TAPF, Murta MM, Moreira SGC, Sales MJA. Thermal and structural behavior of Buriti oil/poly(methyl methacrylate) and Buriti oil/polystyrene materials. J Therm Anal Cal. 2008;92:529–34.
21. Hirschler MM. Chemical aspects of thermal decomposition. In: Grand AF, Wilkie CA, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker; 2000. p. 61.
22. Peterson JD, Vyazovkin S, Wight CA. Kinetic study of stabilizing effect of oxygen on thermal degradation of poly(methyl methacrylate). J Phys Chem B. 1999;103:8087–92.
23. Stoliarov SI, Westmoreland PR, Nyden MR, Forney GP. A reactive molecular dynamics model of thermal decomposition in polymers: I. Poly(methyl methacrylate). Polymer. 2003;44:883–94.
24. Kashiwagi T, Inaba A, Hamins A. Behavior of primary radicals during thermal degradation of poly(methyl methacrylate). Polym Degrad Stab. 1989;26:161–84.
25. Holland BJ, Hay JN. The kinetics and mechanisms of the thermal degradation of poly(methyl methacrylate) studied by thermal analysis-Fourier transform infrared spectroscopy. Polymer. 2001;42:4825–35.
26. Madorsky SL. Thermal degradation of organic polymers. New York: Interscience Publishers; 1964.
27. Hirata H, Kashiwagi T, Brown JE. Thermal and oxidative degradation of poly(methyl methacrylate): weight loss. Macromolecules. 1985;18:1410–8.
28. Lomakin SM, Brown JE, Breese RS, Nyden MR. An investigation of the thermal stability and char-forming tendency of cross-linked poly(methyl methacrylate). Polym Degrad Stab. 1993;41: 229–43.
29. Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. New York: Wiley; 1986.
30. Hummel DO, Scholl F. Atlas of polymer and plastics analysis. Munich: Hanser Verlag; 1984.
31. Mullens J, Reggers G, Ruysen M, Carleer R, Yperman J, Franco D, et al. The determination of the gases released during heating of a flame retardant for polymers, coupling of TG with FTIR, MS and GC-MS. J Therm Anal. 1997;49:1061–7.
32. Pielichowski K, Hamerton I. TGA/FTIR studies on the thermal stability of poly(vinyl chloride) blends with a novel colourant and stabilizer: 3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole. Polymer. 1998;39:241–4.
33. Reggers G, Ruysen M, Carleer R, Mullens J. TG–GC–MS, TG–MS and TG–FTIR applications on polymers and waste products. Thermochim Acta. 1997;295:107–17.
34. Vijayakumar CT, Fink JK. Some aspects of tailoring flame retardancy in HET acid based flame retardants. J Polym Sci Polym Chem Ed. 1983;21:1617–25.
35. Grassie N, Melville HW. The thermal degradation of polyvinyl compounds. II. The degradation of benzoyl peroxide catalyzed polymethyl methacrylates. Proc R Soc London. 1949;A199: 14–23.
36. McNeill IC. A study of the thermal degradation of methyl methacrylate polymers and copolymers by thermal volatilization analysis. Eur Polym J. 1968;4:21–30.
37. Gritter RJ, Seeger M, Johnson DE. Hydrocarbon formation in the pyrolytic decomposition of methacrylate copolymers. J Polym Sci Polym Chem Ed. 1978;16:169–77.
38. Gao F, Price D, Milnes GJ, Eling B, Lindsay CI, McGrail PT. Laser pyrolysis of polymers and its relation to polymer fire behaviour. J Anal Appl Pyrolysis. 1997;40–41:217–31.