
Comparative Study of Thermal Degradation Behavior of PMMA:Organotin(IV) Phenoxides Blends

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ABSTRACT

This paper reports the comparative study of thermal degradation of different poly methyl methacrylate (PMMA):organotin(IV) phenoxide blends. PMMA was synthesised by -irradiation method by irradiating MMA in a -chamber. PMMA:organotin(IV) phenoxides blends have been prepared by dissolving PMMA (1 g) and organotin(IV) phenoxides (1 g/ 2g) in acetone and solutions were stirred for about 24 hours. These were then treated with methanol whereupon the PMMA- organotin(IV) phenoxides blends were separated out. The resulting polymer was dried in oven at 40 °C overnight and characterized by FTIR. Thermal investigations by simultaneous TG-DT study on PMMA-organotin(IV) phenoxides blends have shown increased thermal stability compared to pure PMMA. A comparative study of have shown some organotin(IV) phenoxides better thermal stabilisers than others.

Keywords: Poly (methyl methacrylate), PMMA, Thermal degradation, Organotin compounds, Thermal stabilizers.

INTRODUCTION

Owing to the deterioration in properties and uncontrolled change in the constitution of polymers at high temperature flux, these are not preferred materials for elevated temperature. Over the years, several compounds have been screened for thermal stabilization of polymers. Among these complexes, organotin complexes have shown marked effect as stabilizers for PVC.¹⁻⁵ Poly methyl methacrylate or PMMA polymer presents much scope for such studies as it has predominant structural and mechanical properties and it solely and steadily decays to monomer. PMMA has good processing and thermoforming properties and which can be tailored with pigments, flame retardant additives, UV absorbent additives and scratch resistant coatings.⁶ There are reports on thermal degradation of poly (methyl methacrylate) in the presence of triphenyltin chlorides,⁷ tin(IV) chloride and tetraphenyltin.⁸ Many workers have investigated thermal degradation of PMMA. Manuring⁹ and Kashiwagi^{et.al.},¹⁰ recognized that the degradation of PMMA advances by combination of side chain and main chain scission producing methyl methacrylate monomer. It is well acknowledged that degradation process is a radical chain reaction involving initiation, propagation, transfer and termination reactions. It is clear that organotin compounds are very effective stabilizers because they are multifunctional in nature and can interact in various ways, with polymer undergoing degradation. It is worth mentioning here that the growing demand for polymeric materials with good mechanical properties, high service temperature and improved chemical resistance has led to active research in the development of new high performance polymeric materials blending is a particularly interesting way to new engineering polymers, which allows a number of properties to be obtained that are difficult to achieve in a single polymer. Furthermore, blending gives rise to a range of properties in the final product by changing the blend compositions. In view of the above interesting observations, it has been thought worthwhile to study the effect of organotin(IV) phenoxides in the thermal stabilisation of PMMA. The aim of interacting PMMA with organotin(IV) phenoxides is to gather some useful information regarding the effect of organotin compounds as additives on the thermal stability and degradation of PMMA. In continuation of our endeavours in the thermal stabilization of polymers,^{11,12} author report herein comparative study of thermal degradation behaviour of PMMA:organotin(IV) phenoxides blends.

EXPERIMENTAL

The monomer methyl methacrylate (Aldrich) was freed from initiator by repeated washing with aqueous NaOH followed by water until the washing became neutral. After drying over anhydrous Na₂SO₄, it was distilled carefully at 100 °C under vacuum. FTIR spectra were collected with Nicolet 5700 spectrophotometer and ¹H NMR spectra on JEOL PMX 60 SI spectrometer using CDCl₃ as solvent. ¹³C NMR spectra of the complexes were recorded on Bruker AC-3000 MHz NMR spectrometer. Thermal degradation behaviour of the PMMA:organotin(IV) phenoxides blends were recorded on the simultaneous DT-TG Shimadzu Thermal Analyzer DT-40 instrument. Thermocouple used was Pt/Pt-Rh (10%). The temperature range of the instrument was from room temperature to 1300 °C. The PMMA: organotin(IV) phenoxides blends were heated in a static air atmosphere and α -alumina was taken as a reference material. A heating rate of 10°C/min was employed. The monomer methyl methacrylate (Aldrich) was freed from initiator by repeated washing with aqueous NaOH and then with water until the washing became neutral. After drying over anhydrous Na₂SO₄, the monomer methyl methacrylate was used for polymer preparation after distilling carefully at 100 °C under vacuum. (lit. b. pt. 100 °C).

PMMA {poly (methyl methacrylate)} was synthesised by γ -irradiation method reported earlier by us.^{11, 12} The resulted polymer was characterized by IR, ¹H and ¹³C NMR. In a typical reaction of preparation of PMMA:Organotin(IV) phenoxide blends, PMMA (1 g/ 2g) and Ph₃Sn(OAr) (1 g/ 2g) used to prepare 1:1 and 1:2 blends, were dissolved separately in acetone and were mixed together. The solutions were stirred for about 24 hours. It was then treated with methanol whereupon the polymer: tin blends were separated out. The resulting polymer was dried in oven at 40 °C overnight.

RESULTS AND DISCUSSION

The PMMA polymer synthesized by gamma radiations has been characterized by IR, ¹H and ¹³C NMR spectral techniques. The ¹H NMR spectrum of pure PMMA showed singlet at 1.5, 2.3 and 3.6 ppm assigned to ethylene, methyl and methoxy protons respectively.¹³ The resonances observed at 54, 45 and 177 ppm in pure PMMA ascribed to methylene group (-CH₂), quaternary carbon (>C<) and carbonyl carbon group (>C=O) respectively. The methyl carbon (-CH₃) and methoxy carbon (-OCH₃) showed peaks at 18 ppm and 51 ppm respectively.

The ¹³C-NMR spectra revealed the exact structure of the poly (methyl methacrylate), which was not associated with any other impurities.¹⁴ A comparison of the IR spectra of pure PMMA, parent organotin(IV) phenoxides and modified PMMA have suggested the formation of blends. In the IR spectrum of PMMA, the disappearance of peak after polymerization at 1650 cm⁻¹ due to terminal methylene group of the monomer methyl methacrylate confirmed the complete polymerization of vinyl group. A sharp band at 1730 cm⁻¹ attributed to the ester carbonyl (>C=O) group and bands in 1300-1060 cm⁻¹ region have been assigned to (C-O-C) mode. A sharp band of medium intensity observed ~ 2930 cm⁻¹ has been attributed to (C-H) mode. In the i.r. spectra of PMMA: tin blends, the sharp absorption band observed ~ 1720 cm⁻¹ compared to that of 1730 cm⁻¹ in case of pure PMMA due to (C=O) mode is indicative of weak coordination between tin metal and carbonyl oxygen of the polymer. The occurrence of bands in 1650-1420 cm⁻¹ region assigned to phenolic (C=C) mode has also supported the formation of blends. In the present investigations, thermal properties of PMMA-organotin(IV) phenoxides blends are investigated using TG/DT studies. Figure 1 shows the comparative IDT, FDT, % weight loss and DTA peak temperature for different PMMA:organotin(IV) phenoxide blends. In Figure 2, TGA curves and DTA peak temperature of different PMMA:organotin(IV) phenoxide blends have been represented.

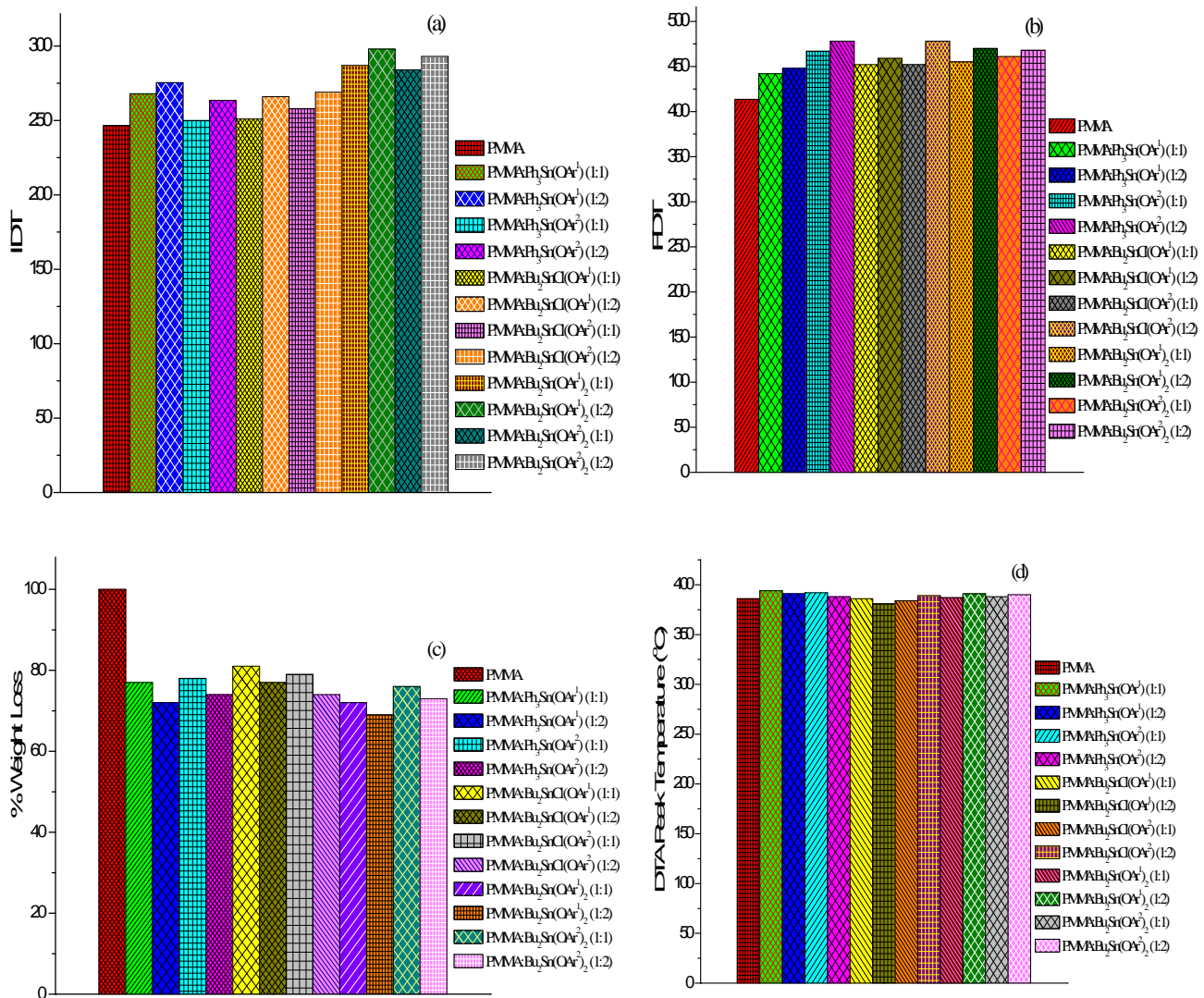
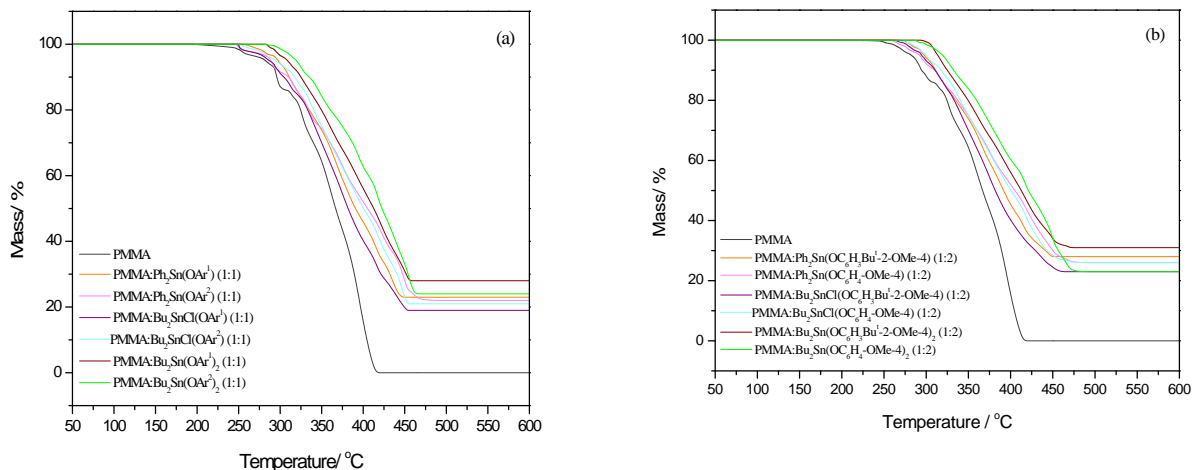


Figure 1. Comparative (a) IDT (b) FDT (c) % weight loss and (d) DTA peak temperature of PMMA and PMMA:Organotin(IV) phenoxides blends; OAr¹=OC₆H₃-Bu¹-2-OMe-4 and OAr²=OC₆H₄-OMe-4.



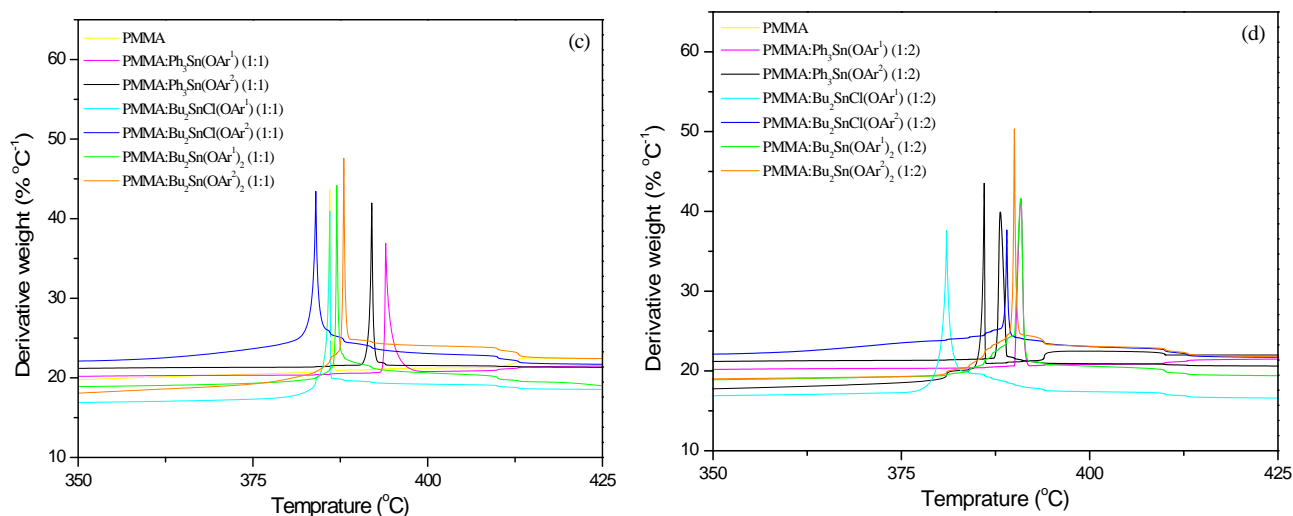


Figure 2. (a) TGA (1:1) (b) TGA (1:2) (c) DTA (1:1) (d) DTA (1:2) of PMMA and PMMA: organotin(IV) phenoxides blends; OAr¹ = OC₆H₃-Bu^t-2-OMe-4 and OAr²=OC₆H₄-OMe-4).

The thermal behavior of the PMMA: organotin(IV) phenoxides and pure PMMA has provided following information. The TG-DT curve of pure PMMA has shown it to decompose in two stages. The initial decomposition temperature (IDT) is 246.6 °C showing its appreciable thermal stability. The first stage decomposition in the region 246.6-315 °C (weight loss is 14%) while second stage decomposition in the temperature range 315-413.6 °C has been observed (weight loss is 86%). The PMMA-organotin(IV) phenoxides blends have shown to decompose in single stage compared to two stage decomposition for the pure PMMA. There is significant increase in the initial decomposition temperatures of the PMMA-organotin(IV) phenoxides blends compared to pure PMMA. Initial decomposition temperatures (IDT) are highest for dibutyltin(IV) diphenoxides. PMMA:dibutyltin(IV) –di-2-tert.-butyl-4-methoxy phenoxide has higher IDT than 4-methoxy analogue. Out of 1:1 and 1:2 compositions, 1:2 blends have higher IDT than 1:1 blends. There is increase in the final decomposition temperatures (FDT) of the PMMA-organotin(IV) phenoxides blends compared to pure PMMA. PMMA:triphenyltin(IV) -4-methoxy phenoxide and PMMA:dibutyltin(IV) chloro –di-4-methoxy phenoxide have shown higher final decomposition temperature than the others in 1:2 composition. There is a appreciable decrease in percentage weight losses of the PMMA-organotin(IV) phenoxides blends compared to 100% weight loss in case of pure PMMA. PMMA:dibutyltin(IV)- 2-tert.-butyl-4-methoxy phenoxide in 1:1 and 1:2 composition, PMMA:triphenyltin(IV)- 2-tert.-butyl-4-methoxy phenoxide (1:2) have shown least percentage weight loss than the others. There is a marked increase in the decomposition temperature at every 10% weight loss for PMMA-organotin(IV) phenoxides blends compared to pure PMMA. Thermal data inferred from TG-DT curves of PMMA-organotin(IV) phenoxides blends are presented in Table 1. The decomposition temperatures for every 10% weight loss for PMMA-organotin(IV) phenoxides blends are given in Table 2.

CONCLUSIONS

It may be concluded from our results that the organotin(IV) phenoxides have marked influence on the thermal degradation of Poly (methyl methacrylate). In future, these materials can also be utilized for the thermal stabilization of other types of polymers also.

Table 1. TG/DTA Data of PMMA:Organotin(IV) phenoxides blends.

Organotin: polymer blends	IDT /°C	FDT /°C	% Wt. Loss	Stages of decomp.	Decomp. Range	DTA Peak Temp /°C	DTA Peak Nature
PMMA	246.6	413.6	14% 86%	1 st 2 nd	246.6-315 315-413.6	386	Exo
PMMA:Ph ₃ Sn(OAr ¹). (1:1)	268	442	77%	Single	668-442	394	Exo
PMMA:Ph ₃ Sn(OAr ¹) (1:2)	275.4	448	72%	Single	275.4-448	391	Exo
PMMA:Ph ₃ Sn(OAr ²). (1:1)	250	467	78%	Single	250-467	392	Exo
PMMA:Ph ₃ Sn(OAr ²). (1:2)	263.6	478	74%	Single	263.6-478	388	Exo
PMMA:Bu ₂ SnCl(OAr ¹). (1:1)	251	452	81%	Single	251-452	386	Exo
PMMA:Bu ₂ SnCl(OAr ¹). (1:2)	266	459	77%	Single	266-459	381	Exo
PMMA:Bu ₂ SnCl(OAr ²). (1:1)	258	452	79%	Single	258-452	384	Exo
PMMA:Bu ₂ SnCl(OAr ²). (1:2)	269	478	74%	Single	269-455	389	Exo
PMMA:Bu ₂ Sn(OAr ¹) ₂ . (1:1)	287	455	72%	Single	287-452	387	Exo
PMMA:Bu ₂ Sn(OAr ¹) ₂ . (1:2)	298	470	69%	Single	298-470	391	Exo
PMMA:Bu ₂ Sn(OAr ²) ₂ . (1:1)	284	461	76%	Single	284-461	388	Exo
PMMA:Bu ₂ Sn(OAr ²) ₂ . (1:2)	293	468	73%	Single	293-468	390	Exo

Where OAr¹ = OC₆H₃-Bu^t-2-OMe-4 and OAr²=OC₆H₄-OMe-4.

Table 2. Decomposition temperature for PMMA:Organotin(IV) phenoxides blends.

Complex	IDT /°C	FDT /°C	Decomposition Temperature at every 10% weight loss								
			10%	20%	30%	40%	50%	60%	70%	80%	90 %
PMMA	246.6	413.6	268	320	328	335	352	369	382	390	404
PMMA:Ph ₃ Sn(OAr ¹). (1:1)	268	442	274	280	305	331	350	372	390	-	-
PMMA:Ph ₃ Sn(OAr ¹) (1:2)	275.4	448	293	304	325	350	372	393	415	-	-
PMMA:Ph ₃ Sn(OAr ²). (1:1)	250	467	290	300	353	362	398	410	422	-	-
PMMA:Ph ₃ Sn(OAr ²). (1:2)	263.6	478	296	303	354	368	387	411	424	-	-
PMMA:Bu ₂ SnCl(OAr ¹). (1:1)	251	452	309	336	353	379	392	406	417	-	-
PMMA:Bu ₂ SnCl(OAr ¹). (1:2)	266	459	291	313	337	358	374	386	399	-	-
PMMA:Bu ₂ SnCl(OAr ²). (1:1)	258	452	299	316	328	348	364	375	384	-	-
PMMA:Bu ₂ SnCl(OAr ²). (1:2)	269	455	282	299	320	345	364	382	403	-	-
PMMA:Bu ₂ Sn(OAr ¹) ₂ . (1:1)	287	452	315	326	338	373	382	387	406	-	-
PMMA:Bu ₂ Sn(OAr ¹) ₂ . (1:2)	298	470	318	339	354	375	384	387	-	-	-
PMMA:Bu ₂ Sn(OAr ²) ₂ . (1:1)	284	461	294	310	332	345	367	378	382	-	-
PMMA:Bu ₂ Sn(OAr ²) ₂ . (1:2)	293	468	311	335	354	380	384	391	423	-	-

Where OAr¹ = OC₆H₃-Bu^t-2-OMe-4 and OAr²=OC₆H₄-OMe-4.

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