The effect of AlBr₃ additive on the thermal degradation of PMMA A study using TG-DTA-DTG, IR and PY-GC-MS techniques

M. Arshad · K. Masud · M. Arif ·
S. Rehman · M. Arif · J. H. Zaidi ·
Z. H. Chohan · A. Saeed · A. H. Qureshi

Abstract The thermal behavior of poly(methyl methacrylate) (PMMA) was studied in the presence of AlBr₃ using TG-DTA-DTG, IR and Py-GC-MS techniques. Degradation products were identified. It was found that PMMA started degrading at a lower temperature due to the generation of free radicals (Br$^\bullet$), being the product of decomposition of AlBr₃. Despite early destabilization of the system, stabilization zone was also highlighted. Flammability test was conducted to check the affectivity of AlBr₃. Degradation mechanism has been proposed. Pyrolysis of the system (PMMA–AlBr₃) was also monitored by heating it at different temperatures.

Keywords Thermal degradation · PMMA · Aluminum tribromide · Thermoanalytical study · IR spectroscopy · Py-GC-MS · Flammability test · Degradation mechanism

M. Arshad (✉) · M. Arif · J. H. Zaidi
Chemistry Division, PINSTECH, Nilore, Islamabad, Pakistan
e-mail: marshads53@yahoo.com.sg

K. Masud
NLP, PINSTECH, Nilore, Islamabad, Pakistan

M. Arif · Z. H. Chohan
Department of Chemistry, Bahauddin Zakariya University, Multan, Pakistan

S. Rehman
Department of Chemistry, University of Peshawar, Peshawar, Pakistan

A. Saeed
Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

A. H. Qureshi
Materials Division, PINSTECH, Nilore, Islamabad, Pakistan

Introduction

For the last few decades, the thermal degradation behavior and other related physical parameters of various homopolymers and copolymers have been studied extensively [1–3] due to their commercial importance [4–6]. It has been the interest of many researchers to extend these investigations to the examination of polymeric and copolymeric systems especially in which various physical properties [7, 8] and mechanisms of the degradation have already been probed [9–12]. Since thermal properties of polymers/copolymers provide valuable information regarding toughness, stiffness, stability, compositions of intermediates and types of residues formed, these have become topics of several publications [13–15].

Poly(methyl methacrylate) (PMMA), is a completely amorphous vinyl polymer but it possesses high strength and excellent dimensional stability due to its rigid polymer chains. It shows exceptional optical clarity, very good weatherability, and impact resistance. PMMA has many applications like indoor and outdoor lighting, diffusers, lenses and contact lenses [16]. The thermal as well as other properties of poly (methyl methacrylate) alone [17–19] and in the presence of a number of additives have been studied by many workers [20–22].

In continuation of our previous investigations on homopolymer and copolymer of PMMA with organometallic additives [12, 23, 24], we have now decided to concentrate more on purely inorganic additives to study the mode of their (blends, additives and polymers/copolymers) decomposition along with mechanistic pathways. This

shifting in our interest was based on the exclusion of flammable degradation products bound to arise from the disintegration of organic part of the additive/s.

The purpose of the present work was to gain additional evidence to propose a detailed mechanism of the degradation of PMMA mixed film with aluminum tribromide while getting insight into the behavior of polymeric system in the presence of additive. The nature of degradation products and the changes produced in PMMA–AlBr₃ blend during pyrolysis are studied using FTIR, TG-DTA-DTG and Py-GC-MS techniques. Activation energy and order of reaction were determined by Horowitz and Metzger method [25], whereas the flammability test of polymer and its blends were performed by using standard method [26].

Experimental

Reagents, synthetic procedures and instrumentations

All the chemicals obtained from standard source suppliers were of analytical grade. Aluminum tribromide (Aldrich-Sigma; 99% purity) was used without purification whereas the monomer, methyl methacrylate (E. Merck), 2,2′-Azobisisobutyronitrile (AIBN, E. Merck), absolute ethanol (E. Merck), acetone (E. Merck), diethyl ether (BDH) were used with further purification.

Preparation of poly (methyl methacrylate)

The homopolymer was prepared by the reported method [27]. The molecular mass was found as 120,000.

Method of preparing thin film for analysis

The samples of polymer with additive for degradation were prepared by the selection of common solvent, i.e., acetone. The known amounts of both polymer and additive were dissolved separately in a sufficient quantity of acetone and both were left to stand overnight in closed Pyrex tubes. Later on both the solutions were mixed and shaken thoroughly and poured into a well-cleaned transparent Pyrex dish. Complete evaporation of the solvent was effected at STP. The resultant mixed film was transparent in the dish confirming the compatibility of the pair studied.

Method of preparing strip for horizontal burning test

For PMMA and blends the solid samples were added to acetone and kept overnight to dissolve completely. The strips were chipped off from aluminum mold according to the reported procedure [26]. The dried strips were kept in desiccator for the required test. The results are shown in Fig. 8.

Instrumentations

The liquid chromatograph, Hitachi 655-A-11 with GPC software and integrator (D-2200 GPC along with column GLA-100 m (Gelko)) was employed for molecular mass determination of polymer at room temperature. The thermoanalytical measurements were carried out with NET-ZSCH Simultaneous Thermal Analyzer STA 429. The measurements were made in an atmosphere of nitrogen, in the temperature range of ambient to 800 °C, at a heating rate of 10 °C min⁻¹ using kaolin as reference material. The infrared spectra of polymer, additives and those of residues produced after heating the blends at different temperatures were recorded with Nicolet 6700 FT-IR spectrometer in the range 4000–400 cm⁻¹. The GC-MS system was an Agilent 6890 N type coupled with 5973 inert MSD, by Agilent Analytical Instruments, Agilent Technologies, USA. Analysis of the product in acetone was performed with a DB-5MS column. The activation energy (E_o) and order of reaction (n) of polymer and blends were calculated using Horowitz and Metzger method [25] from TG curves.

Results and discussion

Thermoanalytical characterization

The thermal curves (TG, DTA and DTG) of pure additive, homopolymer and blends (polymer-additive), recorded in inert (nitrogen) atmosphere from ambient to 800 °C, are produced in Figs. 1, 2, 3, and 4. The relevant data and stages of pyrolysis regarding the thermal behavior of additive, polymer and blends are presented in Table 1. The thermal degradation study on AlBr₃ has not been
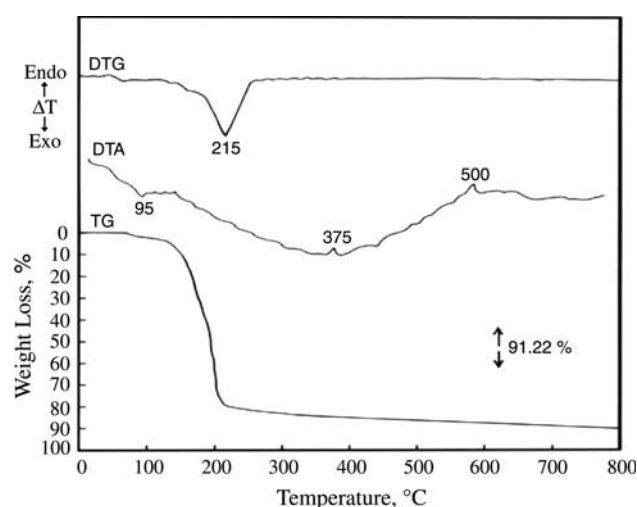

Fig. 1 Thermoanalytical curves (dynamic nitrogen, heating rate 10 °C/min) for aluminum tribromide additive in nitrogen atmosphere
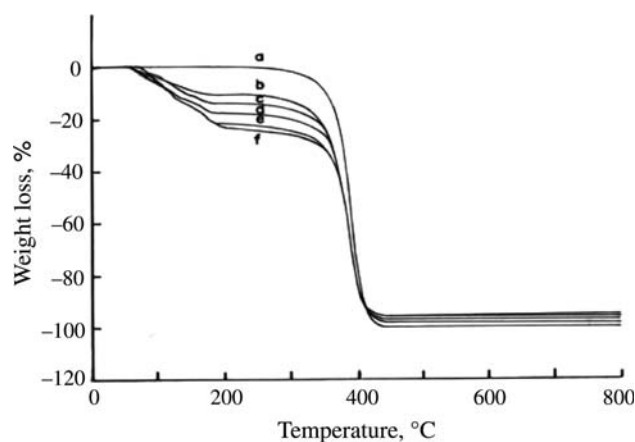
Fig. 2 TG curves (dynamic nitrogen, heating rate 10 °C/min) for PMMA–AlBr₃ blends: 100% PMMA (*a*), 97.5% PMMA (*b*), 95% PMMA (*c*), 92.5% PMMA (*d*), 90% PMMA (*e*) and 87.5% PMMA (*f*)
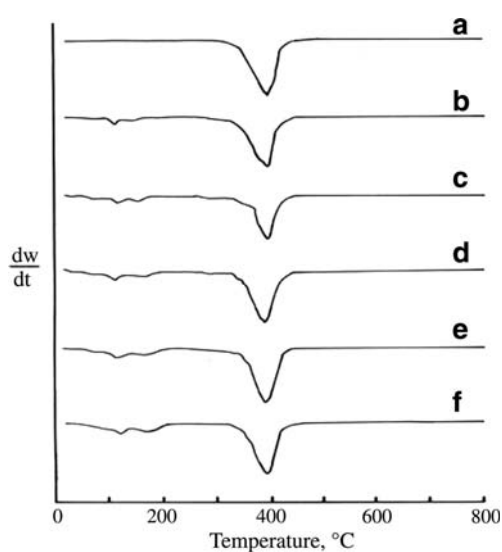

Fig. 3 DTG curves (dynamic nitrogen, heating rate 10 °C/min) for PMMA–AlBr₃ blends: 100% PMMA (*a*), 97.5% PMMA (*b*), 95% PMMA (*c*), 92.5% PMMA (*d*), 90% PMMA (*e*) and 87.5% PMMA (*f*)

Fig. 4 DTA curves (dynamic nitrogen, heating rate 10 °C/min) for PMMA–AlBr₃ blends: 100% PMMA (*a*), 97.5% PMMA (*b*), 95% PMMA (*c*), 92.5% PMMA (*d*), 90% PMMA (*e*) and 87.5% PMMA (*f*)

performed earlier to the best of our knowledge, though the corresponding salt with chlorine was blended with polystyrene to investigate the catalytic effect [28]. TG trace of AlBr₃ exhibits a two-step degradation process starting to decompose around 70 °C (Fig. 1). The first mass-loss (about 5–6%) appears to be the result of elimination of moisture. The major disintegration step commences at 108 °C and ends at 223 °C indicating an overall mass-loss of ∼76%. This part of decomposition is believed to be the outcome of Br, Br₂ and Br• (free radical) production. A DTG peak at 215.4 °C marks the temperature of maximum mass-loss for this stage. The final stage of degradation shows a very slow rate of mass-loss over a temperature range of 223–800 °C. Up to 660 °C, the mass-loss is only 6–7% which may be assigned to the loss of bromine (either
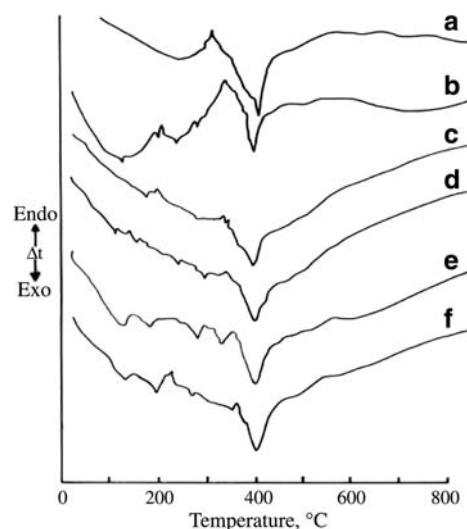
in nascent or radical form). At 660 °C, aluminum metal starts melting and shows a mass-loss of 2.5% due to its evaporation. The three DTA peaks at 95, 375 and 588 °C and one DTG peak at 215 °C support the current degradation behavior of metal halide. The residue is almost 9% of the original mass and is pure aluminum metal. Thermal degradation of PMMA is well-known both in air and under nitrogen atmosphere. The degradation of PMMA proceeds by combination of end-chain and main-chain scissions. It is one-step degradation and yields monomeric methyl methacrylate with no residue at the end [29, 30]. Our investigation confirms the already known thermal degradation pattern of PMMA (Fig. 2*a*) in the nitrogen atmosphere. It begins to lose mass around 250 °C with single stage decomposition terminating around 440 °C. Two DTA peaks at 318 and 412 °C and a DTG peak (for maximum mass-loss in the only step of pyrolysis) at 396 °C support the well-established thermal degradation of PMMA. The degradation is initiated near the chain ends (next to double bonds—DTA peak at 318 °C) and the monomers are furnished by unzipping of chains. Random backbone scission (DTA peak at 412 °C) also contributes towards the production of monomers at some later part of degradation.

The TG traces obtained from blends of 2.5–12.5% AlBr₃ in PMMA compared to that of pure PMMA indicate the low-temperature degradation in the early stages (Fig. 2*a*–*f*). The thermal degradation of blend (PMMA:AlBr₃, 90:10%—this is chosen from the whole percentage series as representative sample for interpretation-sake; the other members of this series behave in a similar fashion) begins at low temperature (50 °C) and occurs in two stages. In the first temperature zone, 50–190 °C, 21% of the blend

Table 1 Comparative TG, DTG and DTA data for PMMA–AlBr$_3$ blends

Blend composition (%) PMMA–AlBr$_3$	Temperature range (°C)	Stage	Weight loss (%)	TG (°C)			DTG (°C)			DTA (°C)
				T_o	T_{50}	T_{max}	I	II	III	Peaks (Thermal effect)
100–00	250–440	I	100	250	390	440*	396	–	–	319 (Endo), 412 (Exo)
97.5–2.5	50–170	I	10	50	384	440	120	160	390	124 (Exo), 206 (Endo),
	170–440	II	88.81							341 (Endo), 400 (Exo)
95–5	50–180	I	14	50	384	440	120	170	390	130 (Exo), 200 (Endo),
	180–440	II	83.13							280 (Exo), 340 (Exo),
										370 (Exo), 406 (Exo)
92.5–7.5	50–200	I	17	50	380	440	125	170	393	130 (Exo), 150 (Endo),
	200–440	II	80.68							160 (Exo), 250 (Exo),
										300 (Exo), 345 (Endo), 408 (Exo)
90–10	50–210	I	21	50	390	440	121	170	395	131 (Exo), 148 (Endo), 181 (Exo),
	210–440	II	75.44							288 (Exo), 335 (Exo), 400 (Exo)
87.5–12.5	65–200	I	22	65	300	440	125	166	392	130 (Exo), 150 (Endo), 193 (Exo),
	200–440	II	72.54							227 (Endo), 272 (Exo), 356 (Exo),
										360 (Endo), 399 (Exo)
00–100	70–223	I	86	70	200	800	215	–	–	95 (Exo), 375 (Endo), 588 (Endo)
	223–800	II	7.22							

* 100% weight loss

volatilizes. This portion of pyrolysis is due to the degradation of additive (AlBr$_3$). It is noteworthy that AlBr$_3$ commenced to decompose at 70 °C when heated alone (Fig. 1). It is also observed that more mass-loss is found for this stage of degradation than the overall percentage of additive in the blend. It is believed that although additive begins to disintegrate earlier than the temperature at which it started to decompose alone, it causes polymer degradation at an early temperature. Similarly, in the presence of polymer, the additive (due to interaction with polymer pendant groups and heat transfer) exhibited an early splitting. This shows destabilization of additive and polymer in this part of heating. However, it certainly gives an indication of interaction (physical as well as chemical) between the two components of the system. Formation of atomic bromine (Br) and generation of bromine free radicals (Br$^•$) are believed to be the cause of destabilization of polymer. Two DTG peaks (121 and 170 °C) and two DTA peaks (131 and 181 °C) are found for this stage of pyrolysis. The second stage starts soon after the completion of first stage (190 °C) and gives a mass-loss of 76%. The slow rate of decrease in mass of the degrading blend from 190 to 360 °C suggests that the splitting is being hindered due to the interaction of degrading species (formation of new bonds which prevent quick mass-loss can not be excluded in this zone). Alternatively, the degrading system seems stabilized in this region. However, around 360 °C the energy content overcomes the holding forces (binding forces) and the system degrades rapidly. The degradation

process ends at 440 °C with the removal of a number of products including those which were not found when the components of the blend were pyrolyzed alone. For the slower portion of degradation of the final step, two DTA peaks (288 and 335.7 °C) are observed which give the energy changes occurring due to the chemical interaction of blended components. For the faster portion of the final degradation step, one DTA peak (400 °C) and one DTG peak (395 °C) arise. The residue is only 4% of the original mass of the blend and is identified as aluminum attached with oxygen and carbon, aluminum metal and char [12, 31]. It has been noticed (Fig. 2b–f) that when the amount of additive in the blend is increased to 12.5% from 2.5%, sample volatilizes quickly from the temperature range of 50–360 °C to 50–300 °C. This may be attributed to the higher content of AlBr$_3$ which generates more bromine free radicals (Br$^•$) hastening the decomposition of undegraded part of the blends. The TG data indicate that aluminum tribromide initiates the early degradation of PMMA at a lower temperature. The degradation begins at a relatively low temperature (50 °C, except for the blend 87.5% PMMA with 12.5% additive, which starts at 65 °C) as compared to that of pure PMMA (250 °C). It has also been observed that progressive percent mass-loss increases for 1st stage of degradation, when the amount of AlBr$_3$ in the blend is increased (i.e., from 2.5% additive to 12.5% additive in the blend). This supports the observation made earlier that both constituents of the system disintegrate in the presence of each other at lower temperatures.

The plots (not shown) of T$_o$, T$_{25}$, T$_{50}$ and T$_{max}$ of polymer and its blends show a very clear trend of destabilization when T$_o$ is taken into account. It is the temperature corresponding to the start of mass-loss. As the percentage of additive in the blends is increased, a slight stabilization of 20 °C is noted which may be attributed to the number of links which are developed between Al and pendent oxygens of polymer per unit volume of additive. However, for T$_{25}$ (temperature at which 25% mass-loss occurs), the trend of destabilization is more pronounced when mass% of additive goes from 2.5 to 12.5. This seems to be due to the production of Br$^\bullet$ which causes the accelerated degradation of polymer. At T$_{50}$ (temperature at which 50% mass-loss is observed), a very inappreciable stabilization is noted as energy content is too great to be resisted by the different types of interactions or bonds between additive and polymer irrespective of the mass% of additive. T$_{max}$ (temperature for maximum mass-loss) is same for polymer and blends which is indicative of the region very close to the completion of decomposition process. In this zone, almost all kinds of bonds are prone to breakage. This graph, however, does not shed any light as to how much residue is left at the termination of disintegration of the system.

Infrared spectroscopy and gas chromatography–mass spectrometry

IR spectrum of the pure additive gives typical stretchings for AlBr$_3$. As additive is hygroscopic so a broad band in the region 3600–3000 cm^{-1} hints at the presence of H$_2$O. The other peaks at 1603, 1089, 676, 580, 478 cm^{-1} arise due to Al–Br bond.

The bands in the region 1725–1735 cm^{-1} evidence the presence of ester linkages for PMMA. The absence of peaks in the region 1630–1640 cm^{-1} clearly indicates the conversion to polymeric form of the compound and absence of monomeric C=C double bonds. The saturated C–H stretchings appear around 3000 cm^{-1} [31]. The IR spectrum of the blends—films were produced with different percentage ratios of PMMA to AlBr$_3$—gives characteristic peaks for PMMA with displaced positions. This may be due to the presence of additive and the physical interactions the additive may have developed with the polymer. For instance, the peaks for ester linkages of PMMA appear now at lower frequencies, i.e., around 1716 cm^{-1}. On the other hand, Al-Br stretchings either seem suppressed or appear at higher frequencies. Peaks at 1616, 686, 593 cm^{-1} are ample proof for the interaction between PMMA and AlBr$_3$. The film cast by common solvent was transparent which confirmed the compatibility of the components and mixing at molecular level.

For gaining conclusive evidence regarding the products identification, the blends were heated at 300, 400 and
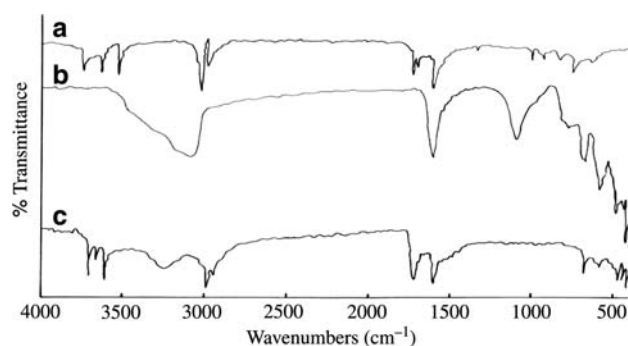

Fig. 5 Infrared spectra of PMMA (*a*), Additive, AlBr$_3$ (*b*) and blend, PMMA (90%) + AlBr$_3$ (10%) (*c*)
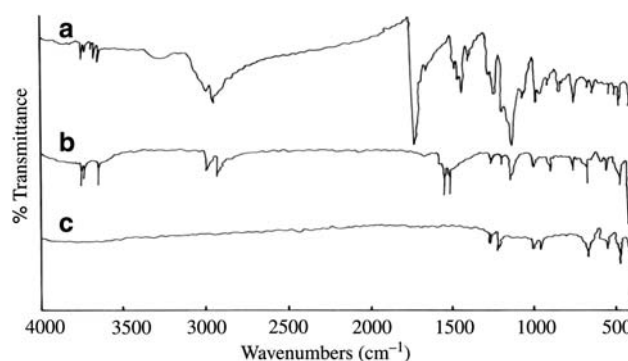

Fig. 6 Infrared spectra of blend PMMA (90%) + AlBr$_3$ (10%) after heated at 300 °C (*a*), 400 °C (*b*) and 500 °C (*c*)

500 °C for a minute and the residue (in each case) was dissolved in acetone. IR spectra of residues were taken as KBr discs while the dissolved residues were subjected to GC-MS. The IR spectra of residues coupled with GC-MS helped in identifying the nature of residues at different temperatures.

The IR spectrum (Fig. 5c) of the blend (90% PMMA:10% AlBr$_3$) and residue of this blend after heated at 300 °C (Fig. 6a) are not showing much difference thereby revealing that after the initial low-temperature decomposition of additive (it is believed that Br$^\bullet$ (free radical), Br, Br$_2$, HBr, CH$_4$, CO, CO$_2$, CH$_3$Br, CH$_3$OH and certain other smaller molecules evolve as the temperature rises to 300 °C) which also causes a minor degradation of polymer, the system is intact with aluminum forming bonds with ester oxygen of several chains, thus, stabilizing the blend in this temperature zone. The amount of moisture appears to have diminished which may be attributed to its complete elimination by 300 °C and then reabsorbance by the undegraded AlBr$_3$ in the residue. TG curve is in agreement with IR findings as rate of mass-loss is slow around 300 °C. GC-MS results (gas chromatograms combined with mass spectra) confirm the observations made on the basis of IR spectra. No peaks (chromatograms) are present for smaller molecules as these
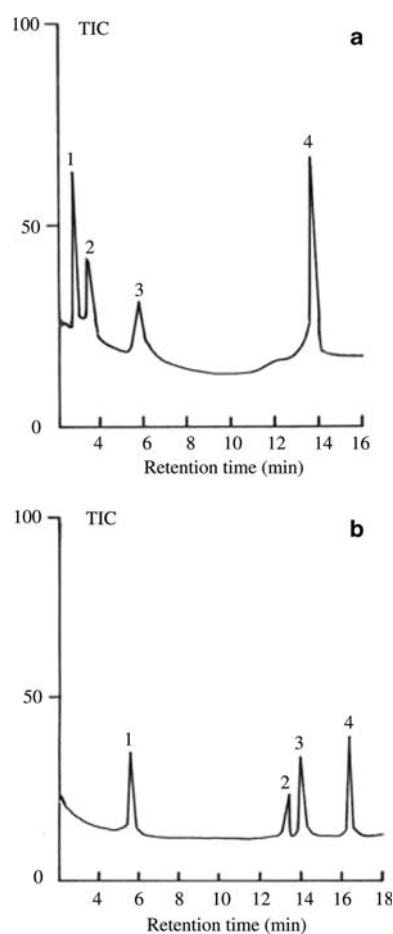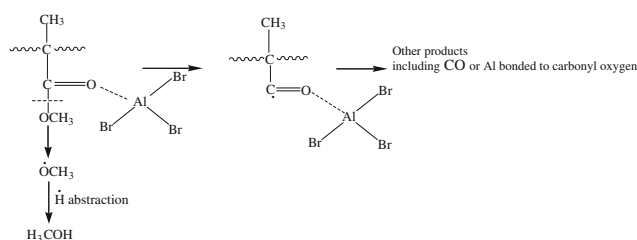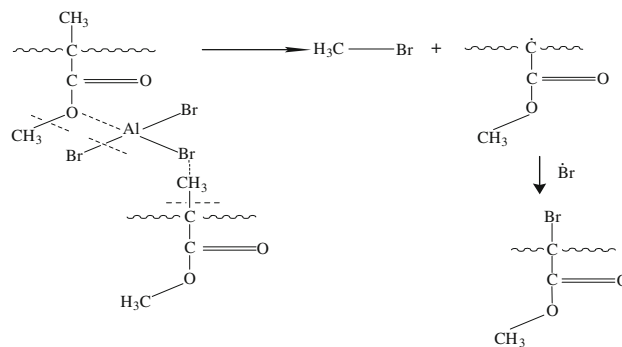
Fig. 7 GC-MS results of blends: **a** heated at 300 °C, **b** heated at 400 °C

have already left the scene. The products are either fractions of degraded polymer, i.e., methacrylic acid, cyclic products having few carbons, more than trace MMA units forming compounds which are cyclic in nature involving unsaturation etc. or oligomers bonded [32] to aluminum through ester oxygen or oligomers with bromine that replaces the –CH$_3$ group other than ester –CH$_3$ (Fig. 7a). The production of methanol (its identification was made possible through Py-GC-MS) clearly shows the involvement of another interaction, i.e., Al…O=C< (Schemes 1, 2).

The IR and GC-MS (Figs. 6b, 7b, respectively) of residue (when the blend was heated at 400 °C) were markedly different from those which were recorded for the residue when the blend was heated at 300 °C (Table 2). As the major and quick (sharp fall in TG traces, Fig. 2) mass-loss is observed in this region (300–400 °C), the products seem to be those which are expected prior to completion of degradation process, i.e., undegraded portion of polymer end chains, Al–O linked with smaller carbon moieties, absence of ester linkages, branched hydrocarbons with limited chain length, etc. (Schemes 3, 4). However, some C–H stretchings of
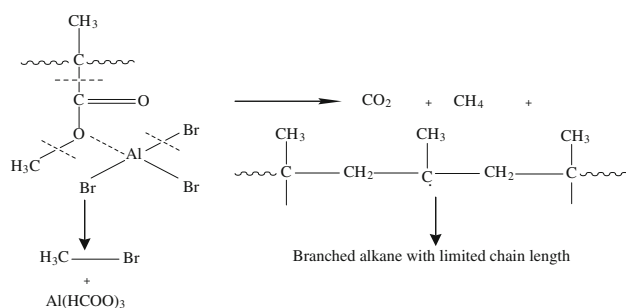

Scheme 1

Scheme 2

**Table 2** GC-MS results of blend (PMMA 90% + AlBr$_3$ 10%) after heating at 300 °C and 400 °C

Blend heated at 300 °C		Blend heated at 400 °C	
Peak no.	Product identified	Peak no.	Product identified
1	$C_4H_6O_2$	1	$C_3H_3O_6Al$
2	$C_6H_{10}O_2$	2	$C_8H_{14}O_4AlBr$
3	$C_{10}H_{12}O_2$	3	$C_{14}H_{25}O_6Al$
4	$C_{10}H_{16}O_4Br$	4	$C_{23}H_{41}O_5Al_2Br$

–CH$_3$ and –CH$_2$– can still be observed (3749, 3675, 3648 cm^{-1}). The bromine content has almost vanished. Few bromine atoms are believed to be still bonded to aluminum which, in turn, appears to have developed true bonds with oxygen of ester linkages [33, 34].

The heating of blend to 500 °C was carried out to study the nature of residue only. The degradation of the blend completed around 440 °C (Fig. 2). The IR spectrum of the residue (Fig. 6c) gives evidence for Al–O–C linkages (900–1200 cm^{-1}), C–C bonds (1300–800 cm^{-1} which may be ascribed to char) and Al–C linkages (400–900 cm^{-1} that may be attributed to Al$_4$C$_3$). The presence of aluminum metal cannot be excluded on visual inspection-basis. The GC-MS studies only confirm the Al–O–C bonds in the form of Al(HCOO)$_3$ [33].

Scheme 3
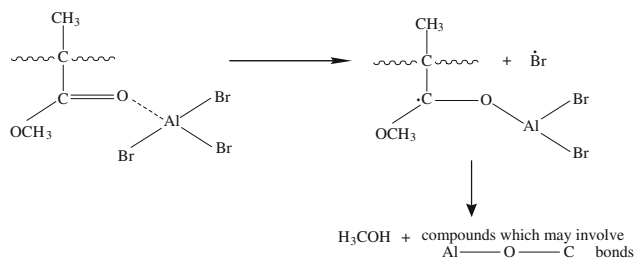
Scheme 4

The IR and GC-MS investigations of residues at 300, 400 and 500 °C helped monitor the progress of degradation. These studies provided enough insight which suggests that apart from earlier low-temperature degradation, the blend is stable around 300 °C (the nature of products found around this temperature is a convincing clue). In the region around 400 °C, the energy content is so high that the links between Al and O (both ester as well as carbonyl) cannot block the unzipping of main chain. The presence of Al–O and Al–C linkages in residue at 500 °C indicates the role played by aluminum of the additive in modifying the overall degradation mechanism of polymer. Bromine (free radicals) was thought to initiate the early decomposition of the PMMA. In later part of the degradation, it is Al which interacts with disintegrating polymer, thus, modifying the pattern of pyrolysis and mode of formation of degradation products.

Flammability of polymer and blends

Figure 8 depicts the burning rate of PMMA–AlBr$_3$ blends (Table 3) determined by horizontal burning test. The burning rate of blend with 12.5% of additive (Mix F) decreases to 5 times when compared with that of neat polymer whereas the effectivity, in this connection, is very pronounced even for the lowest proportion (Mix B). This attributes to the retarding effect caused by AlBr$_3$ additive to PMMA. The trend is clearly linear one, i.e., higher the concentration of additive, lower is the rate of burning and vice versa. This also confirms the uniform distribution of additive in the polymer.
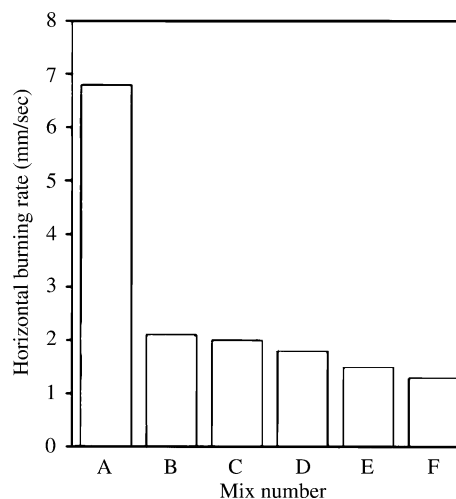

Fig. 8 Horizontal burning rate of mixes *A–F*

Table 3 Formulation of the mixes

Ingredients	Blend mix number					
	A	B	C	D	E	F
PMMA (%)	100	92.5	95	92.5	90	87.5
AlBr$_3$ (%)	–	2.5	5	7.5	10	12.5

Table 4 Activation energies and order of reaction for PMMA, additive and PMMA-additive blends

Blend composition (%) PMMA–AlBr$_3$	E_o (KCal/mol)	Order of reaction (n)
100–0	138.9	3/2
97.5–2.5	39.105	3/2
95–5	37.278	1
92.5–7.5	39.470	1
90–10	41.423	1/2
87.5–12.5	40.567	1
0–100	11.114*	0

* overall activation energy

Activation energy and order of reaction of polymer and blends

Activation energy and order of reaction are tabulated in Table 4 for polymer, additive and blends. The trend confirms the findings from TG curves. PMMA is more stable than the blends of all compositions. As the percentage of additive (AlBr$_3$) is enhanced, a slight increase in activation energy is noticed. This not only points out the early destabilization of the system but also indicates the interaction associated with the additive's degradation (concentration-based) for the promotion of polymer's disintegration at lower temperatures.

Conclusions

Based on the preceding results the following conclusions can be drawn:

I.   The system—PMMA/AlBr$_3$—showed interaction between both components, when polymer and additive are mixed at molecular level.

II. IR results shed convincing light on chemical interaction between the components of blend.

III. In the early stages of degradation of blends, destabilization dominates which is attributed to the decomposition/partial sublimation of the additive. However, as the pyrolysis progresses and the interaction binds the degrading members of the systems, the stabilization can be observed in different temperature zones.

IV. Aluminum may also act as heat sink, hence, providing evidence for physical interaction.

V.   Activation energies also substantiate the destabilization factor for blends in the initial stages of degradation when compared to the degradation of neat PMMA.

VI. Emergence of new degradation products can be ascribed to the chemical interaction between the components of blend. The path of decomposition of polymer has certainly been changed in the presence of additive.

VII. Pure PMMA is the most stable of the polymer-blend systems when T_o is taken into account, however, as the concentration of additive is increased, T_o shifts to higher temperatures for blends. T_{25} shows a destabilization effect for higher additive concentration in the blends whereas T_{50} follows the trend observed for T_o. T_{max} exhibits identical behavior for PMMA and blends. By and large, stability prevails and interactions strengthen.

VIII. The effective flame retardance of AlBr$_3$ is proven beyond all doubts. As the concentration of additive goes up in the blends, the rate of burning goes down.

References

1. Osowiecka B, Bukowski A, Zielinski J, Ciesinska W, Zielinski T. Investigations on nucleated polyproplyne with using thermal analysis method. J Therm Anal Calorim. 2003;74(2):673–79.

2. Szocik H, Jantas R. Multimonomer and cross-linked polymers formed by its copolymerization—thermal studies. J Therm Anal Calorim. 2004;76(1):307–12.

3. Majumdar J, Cser F, Jollands MC, Shanks RA. Thermal properties of polypropylene post-consumer waste (PP PCW). J Therm Anal Calorim. 2004;78(3):849–64.

4. Prolongo MG, Arribas C, Salom C, Masegosa RM. Mechanical properties and morphology of epoxy/poly (vinyl acetate)/poly (4-vinyl phenol) brominated system. J Therm Anal Calorim. 2007;87(1):33–40.

5. Prolongo SG, Prolongo MG. Epoxy/poly(4-vinylphenol) blends Cross linked by imidazole initiation. J Therm Anal Calorim. 2007;87(1):259–68.

6. Prolonga SG, Buron M, Salazar A, Urena A, Rodriguez J. Morphology and dynamic mechanical properties of epoxy/poly (styrene-co-allyl alcohol) blend-influence of hardener nature. J Therm Anal Calorim. 2007;87(1):269–76.

7. Vyazovkin S, Stone J, Sbirrazzuoli N. Hoffman–Lauritzen, parameters for non-isothermal crystallization of poly (ethylene terephthalate) and poly(ethylene, oxide) melts. J Therm Anal Calorim. 2005;80(1):177–80.

8. Zuoyun H, Xingzhou H, Gang S. Study of the mechanism of thermal degradation of poly (vinyl chloride). Polym Degrad Stab. 1989;24:127–35.

9. McNeill IC, Liggat JJ. The effect of metal acetlyacetonates on the thermal degradation of poly (methyl methacrylate): part II-manganese (III) acetylacetonate. Polym Degrad Stab. 1992;37(1):25–32.

10. Wochnowski C, Shams Eldin MA, Metev S. UV-Laser—assisted degradation of poly (methyl methacrylate). Polym Degrad Stab. 2005;89(2):252–64.

11. McNeill IC, Neil D. Degradation of polymer mixtures—III: poly(vinyl chloride)/poly(methyl methacrylate) mixtures, studied by thermal volatilization analysis and other techniques. The nature of the reaction products and the mechanism of interaction of the polymers. Eur Polym J. 1970;6(4):569–83.

12. Zulfiqar S, Masud K, Ameer Q. Thermal degradation behavior of blends of phenyl methacrylate-styrene copolymers with aluminum isopropoxide. J Therm Anal Calorim. 2003;73(3):877–86.

13. Turi EA, editor. Thermal characterizations of polymeric materials. New York: Academic Press; 1972.

14. Mothe CG, Tavares MIB. Study of phenolic resin/EVA blends by thermal analysis. J Therm Anal. 1997;49:477–81.

15. Amin MB, Maadhah AG, Halim SH, editors. Handbook of polymer degradation. New York: Marcel Dekker; 1992.

16. Nemec JW, Bauer WI Jr. In: Mark HF, Bikales NM, Overberger CG, Marges G, editors. Encyclopedia of polymer science and engineering, vol. 1. New York: Wiley Interscience; 1985. p. 211.

17. Dakka SM. TG/DTA/MS OF poly(methyl methacrylate)—the effect of particle size. J Therm Anal Calorim. 2003;74(1):729–34.

18. Dakka SM. TG/MS of poly (methyl methacrylate)—the effect of heating rate on the rate of production of evolved gases. J Therm Anal Calorim. 2004;75(3):765–72.

19. Dakka SM. The role of the oxidative environment. J Therm Anal Calorim. 2003;73(1):17–24.

20. Etienne S, Becher C, Ruch D, Grignard B, Cartigny G, Detrenbleur C, et al. Effects of incorporation of modified silica nanoparticles on the mechanical and thermal properties of PMMA. J Therm Anal Calorim. 2007;87(1):101–4.

21. Cardelli C, Conti G, Giann P, Porta R. Blend formation between homo and co-polymers at 289.15 K.PMMA.SAN bends. J Therm Anal Calorim. 2003;71(2):353–65.

22. McNeill IC, McGuiness RC. The effect of zinc bromide on the thermal degradation of poly (methyl methacrylate) part-I, thermal analysis studies and general nature of the interaction. Polym Degrad Stab. 1984;9(3):167–83.

23. Zulfiqar S, Masud K. Thermal degradation of blends of allyl methacrylate-methyl methacrylate copolymers with aluminum ethoxide. Polym Degrad Stab. 2000;70:229–39.

24. Zulfiqar S, Masud K, Ameer Q. Thermal degradation of blends of phenyl methacrylate–styrene copolymers with aluminium ethoxide. Polym Degrad Stab. 2002;77:457–64 (references therein).

25. Horowitz HH, Metzger G. A new analysis of thermogravimetric traces. Anal Chem. 1963;35:1464–68.

26. Sain M, Park SH, Suhara F, Law S. Flame retardant and mechanical properties of natural fibre-PP composite containing magnesium hydroxide. Polym Degrad Stab. 2004;83:363–7.

27. Grassie N, McNeill IC, Cooke I. Thermal degradation of polymer mixtures. (I) Degradation of polystyrene- poly methyl methacrylate mixture and a comparison with the degradation of styrene-methyl methacrylate copolymers. J Appl Polym Sci. 1968;12: 831–7.

28. Nanbu H, Sakuma Y, Ishihara Y, Takesue T, Ikemura T. Catalytic degradation of polystyrene in the presence of aluminium chloride catalyst. Polym Degrad Stab. 1987;19(1):61–76.

29. Manring LE. Thermal degradation of poly(methyl methacrylate): 4. Random side-group scission. Macromolecules. 1991;24(11): 3304–9.

30. Chang TC, Chen YC, Chiu YS, Ho SY. The effect of silicon and phosphorus on the degradation of PMMA. Polymer. 1996;37(14): 2963–68.

31. The Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, PA 5;1974.

32. Ebdon JR, Hunt BJ, Joseph P. Thermal degradation and flammability characteristics of some polystyrenes and poly(methyl methacrylate)s chemically modified with silicon-containing groups. Polym Degrad Stab. 2004;83(1):181–5.

33. Robinson JW, editor. CRC handbook of spectroscopy, vol. II. USA: CRC Press Inc.; 1974.

34. Szymanski HA, Erikson RE, editors. Infrared band handbook, vol. 1 and 2. 2nd ed. New York: IFI/Plenum; 1970.