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Investigating the effect of the thermal component of atmospheric plasmas on commodity polymers

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Abstract

Atmospheric pressure non-equilibrium plasma (APNEP) has been developed in the UK by EA Technology Ltd and is currently being investigated in a joint project with the University of Surrey. APNEP has been used to induce surface modification changes on commodity polymers such as high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), poly(ethylene terephthalate) (PET) and poly(methyl methacrylate) (PMMA).

A stable atmospheric pressure glow discharge can be formed with a variety of gases, (e.g., nitrogen, air, argon and helium). In all cases, the plasmas are capable of inducing surface modification of commodity polymers in the near-field and remote afterglow regions. However, as APNEP can have a significant thermal component, care must be taken to avoid thermal decomposition of the polymers.

This study has used differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to investigate the thermally induced transitions and thermal decomposition behaviour of commercial polymers. The DSC measurements give melting points, heats of fusion and crystallinities. TGA has been used to measure the onset of thermal degradation in both air and nitrogen atmospheres. In parallel with these experiments, temperature profiles of the downstream region of APNEP have been recorded. As a result, positioning of samples and residence times to avoid thermal damage to the substrates can now be achieved.

Keywords: Atmospheric pressure non-equilibrium plasma; Thermal stability; Polymers

1. Introduction

Although commodity polymers are readily available and have a high strength to weight ratio, they are often unsuitable candidates for many applications due to surface property constraints such as softness, compatibility difficulties, poor adhesion properties. Surface modification by functionalization or surface coating can overcome many of these restrictions. Surface pre-treatments are therefore important for many applications of polymers. Some examples are:

- Adhesion enhancement for bonding and printing [1].
- Surface energy modification [2].
- Generation of barrier layers [3] and protective coatings [4].
- De-greasing [5].
- Preparation of surface coatings [6].

Several methods are currently used to modify polymer surfaces; chemical [7], corona [8], flame [9] and vacuum non-equilibrium plasma [1–6]. However, for

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many industrial applications, these techniques are unsuitable because of reaction, processing or environmental constraints. For example, chemical surface modification uses solvents that can be environmentally unacceptable whereas corona and flame treatments can only perform specific types of modification. Vacuum plasma techniques can be used for a wider variety of surface changes but the need for expensive vacuum apparatus may be unacceptable. Vacuum processing is also often limited to inefficient small-scale batch reactors, rather than to more economically efficient large-scale continuous processes. There is therefore a compelling case for a non-equilibrium plasma that operates under atmospheric conditions.

Atmospheric pressure non-equilibrium plasma (APNEP) has been developed in the UK by EA Technology Ltd [10,11] and is currently being investigated in a joint project with the University of Surrey [12–14]. APNEP is a source of activated gaseous species that can be used to induce in situ and downstream surface modification of polymers and/or plasma enhanced chemical vapour deposition (CVD) [15]. APNEP is a non-equilibrium plasma that can be operated without the need for expensive vacuum apparatus, thus making large-scale cost-effective continuous plasma processing readily available.

APNEPs can be generated with a wide variety of gases over a large flow rate regime. This is illustrated

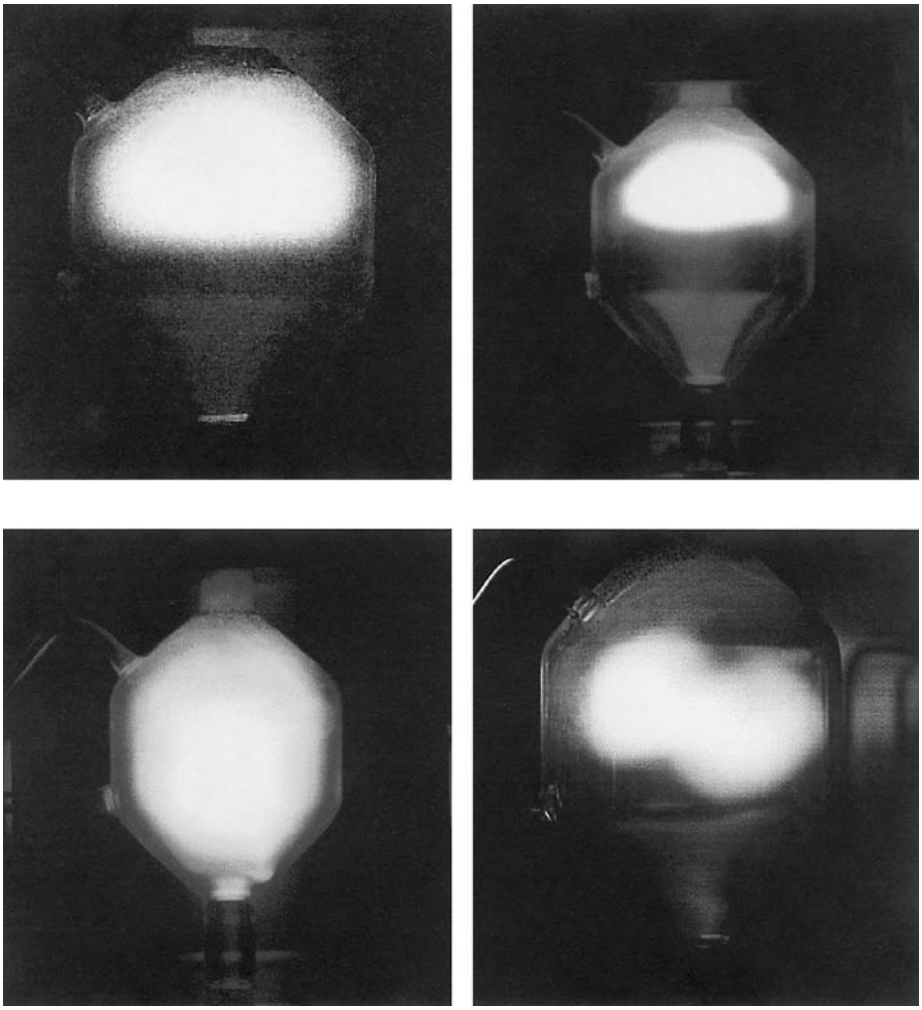

Fig. 1. (a) Zero flow (0 l min^{-1}) air APNEP; (b) 1 l min^{-1} nitrogen APNEP; (c) 1 l min^{-1} argon APNEP; (d) 28 l min^{-1} helium APNEP.

in Fig. 1 where atmospheric pressure glow discharge plasmas in air, nitrogen, argon and helium are illustrated. The flow rates of these plasmas are 0 (zero flow), 1 and 28 l min^{-1}, respectively. However, stable APNEPs have been run at flow rates in excess of 600 l min^{-1}.

APNEP has a significant thermal component. The heat generated by APNEP, can be used to activate the substrate. However as polymers are thermally sensitive materials, care must be taken to avoid unwanted thermal damage. Thermal analysis methods can be used to determine the "safe" operating environment for particular substrates. The variables that require identification are:

- Degradation temperature.
- Melting temperature.
- Maximum residence time (to avoid unwanted thermal effects).
- Substrate location.

The first three variables identified can be determined using thermal analysis. By combining these data, the substrate location for a desired exposure temperature can be calculated. Hence, the aim of this study was to investigate the thermal component of APNEP and to see what effect it is likely to have on a variety of polymeric substrates. Predictions of maximum residence time and substrate location will be estimated from the spatial and temporal temperature profile of the plasma and afterglow regions used for processing and from the thermal stability data obtained from thermal analysis.

2. Experimental and results

2.1. Materials

Research quality grade nitrogen and air were supplied by BOC gases and used as received. High density polyethylene (HDPE) sheet, low density polyethylene (LDPE) film, polypropylene (PP) sheet, poly(ethylene terephthalate) (PET) film and poly(methyl methacrylate) (PMMA) sheet were purchased from Goodfellows. The sheets were 1.0 mm thick whereas the films had a thickness of 0.1 mm. All of the polymeric substrates were washed with iso-propyl alcohol and dried in air before analysis.

2.2. Thermogravimetric analysis (TGA)

TGA was performed using a TA Instruments 2950 Hi-Res TGA. Each substrate was heated at a rate of 10°C min^{-1} from room temperature to 800°C in both air and nitrogen atmospheres. This enables the differences in degradation behaviour between an oxygen-containing and oxygen-free atmosphere to be identified. Fig. 2(a) and (b) contain the TG-curves for all five polymers in air and nitrogen, respectively. Table 1 summarizes the temperatures where 5% and 10% mass loss has occurred.

From these figures and the data in Table 1, it can be seen that most of the polymers are stable at 250°C in air and 300°C in nitrogen. In air, the stability of the polyolefins falls between PMMA (the least stable) and PET, the most stable whereas in nitrogen, the polyolefins and PET all have similar stabilities. Isothermal TG-measurements were made on the polyethylenes at 300°C, 400°C and 500°C to investigate the stability of these polymers at elevated temperatures. It is likely that in a commercial process, high temperatures and short processing times would be desired. Hence the ability to predict the amount of degradation over time at elevated temperatures is important. The TG-curves from these experiments are shown in Figs. 3 and 4. These figures confirm the stability of polyethylenes in both air and nitrogen atmospheres up to 300°C. However, at a temperature of 400°C, only HDPE in nitrogen does not show significant weight loss. At higher temperatures, the polyethylenes can survive for only a few seconds before rapid weight loss occurs. Thermal activation of the surface region of a polyethylene is likely to occur even faster than shown here where bulk degradation properties are investigated. For tempera-

Table 1
TGA data for 5% and 10% mass loss in air and nitrogen (10°C min^{-1})

Polymer	TGA in air		TGA in nitrogen	
	$T_{\text{dec, 5\%}}$ (°C)	$T_{\text{dec, 10\%}}$ (°C)	$T_{\text{dec, 5\%}}$ (°C)	$T_{\text{dec, 10\%}}$ (°C)
HDPE	289	326	445	457
LDPE	289	330	404	418
PP	271	280	397	418
PET	374	372	400	409
PMMA	246	257	292	240

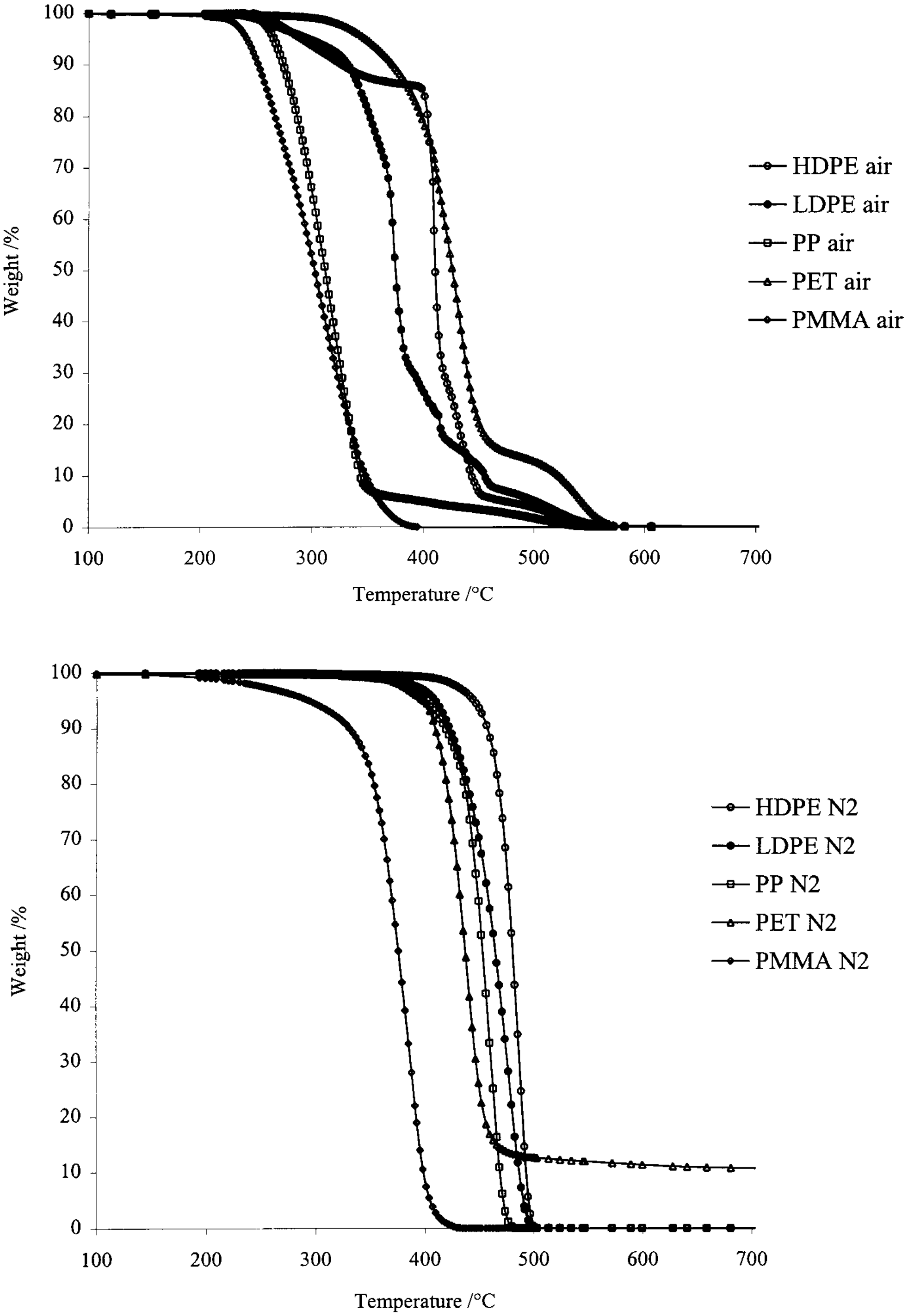

Fig. 2. TGAs of polymers recorded in (a) air and (b) nitrogen.

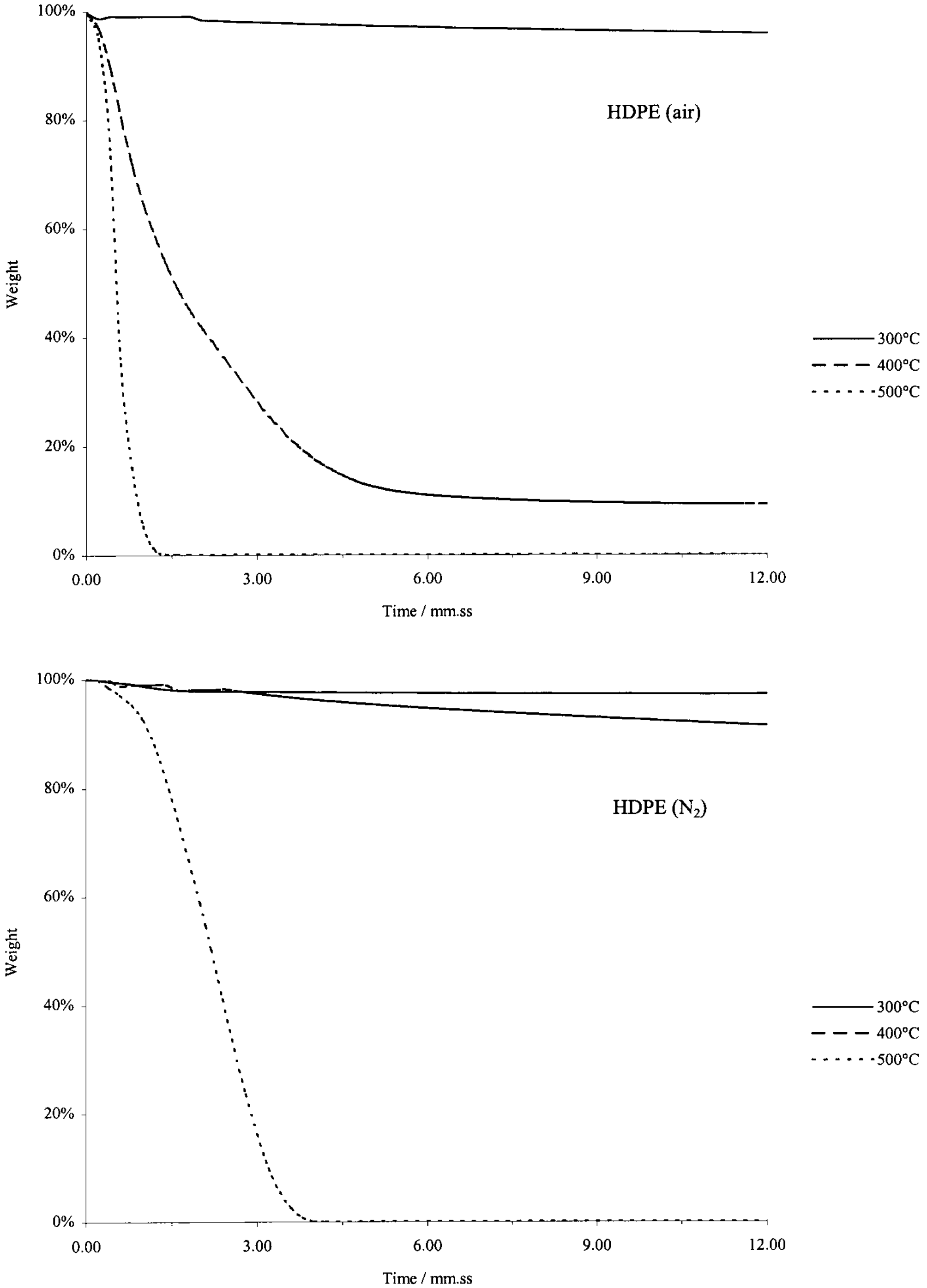

Fig. 3. Isothermal TG-curves for HDPE in (a) air and (b) nitrogen.

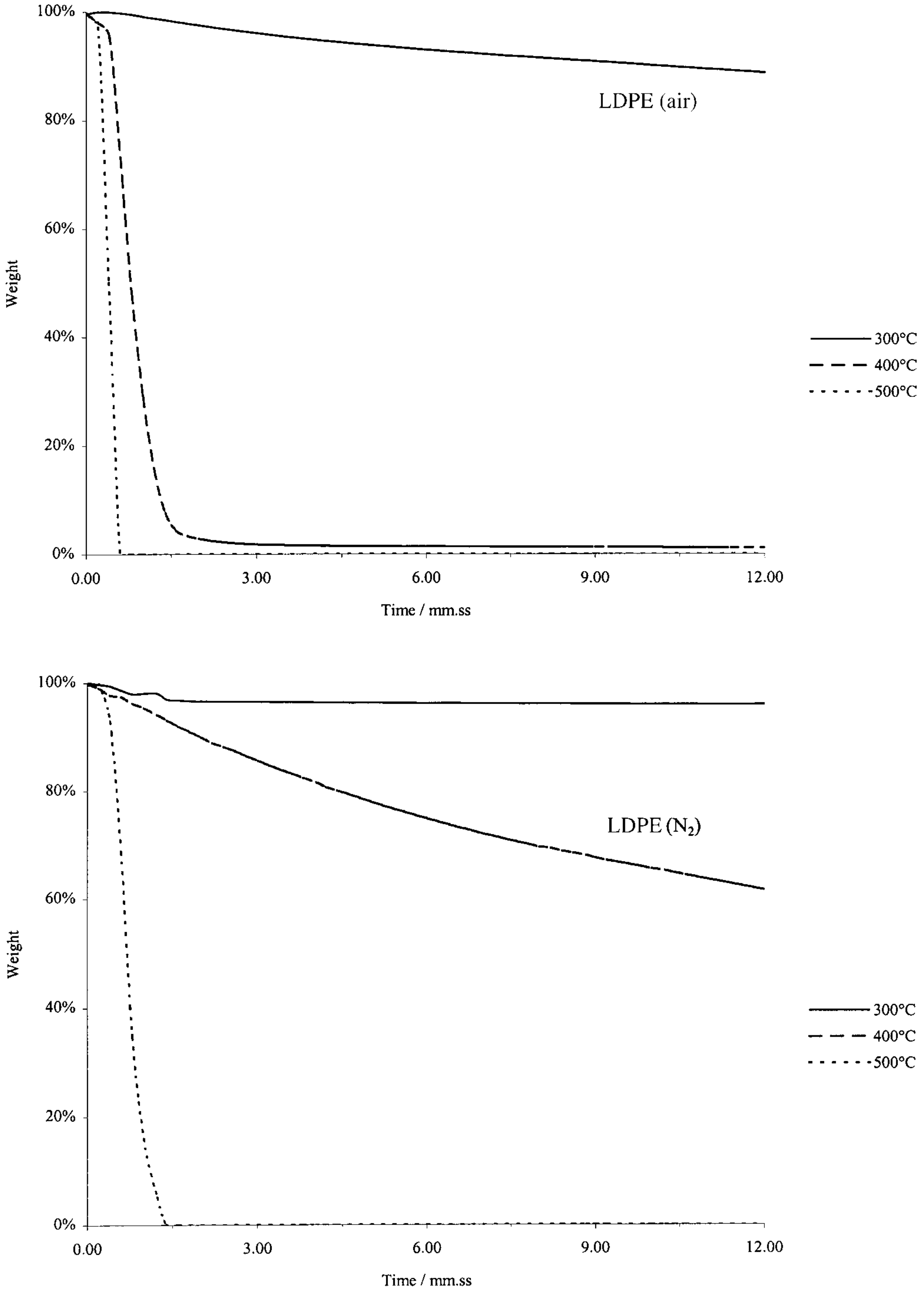

Fig. 4. Isothermal TG-curves for LDPE in (a) air and (b) nitrogen.

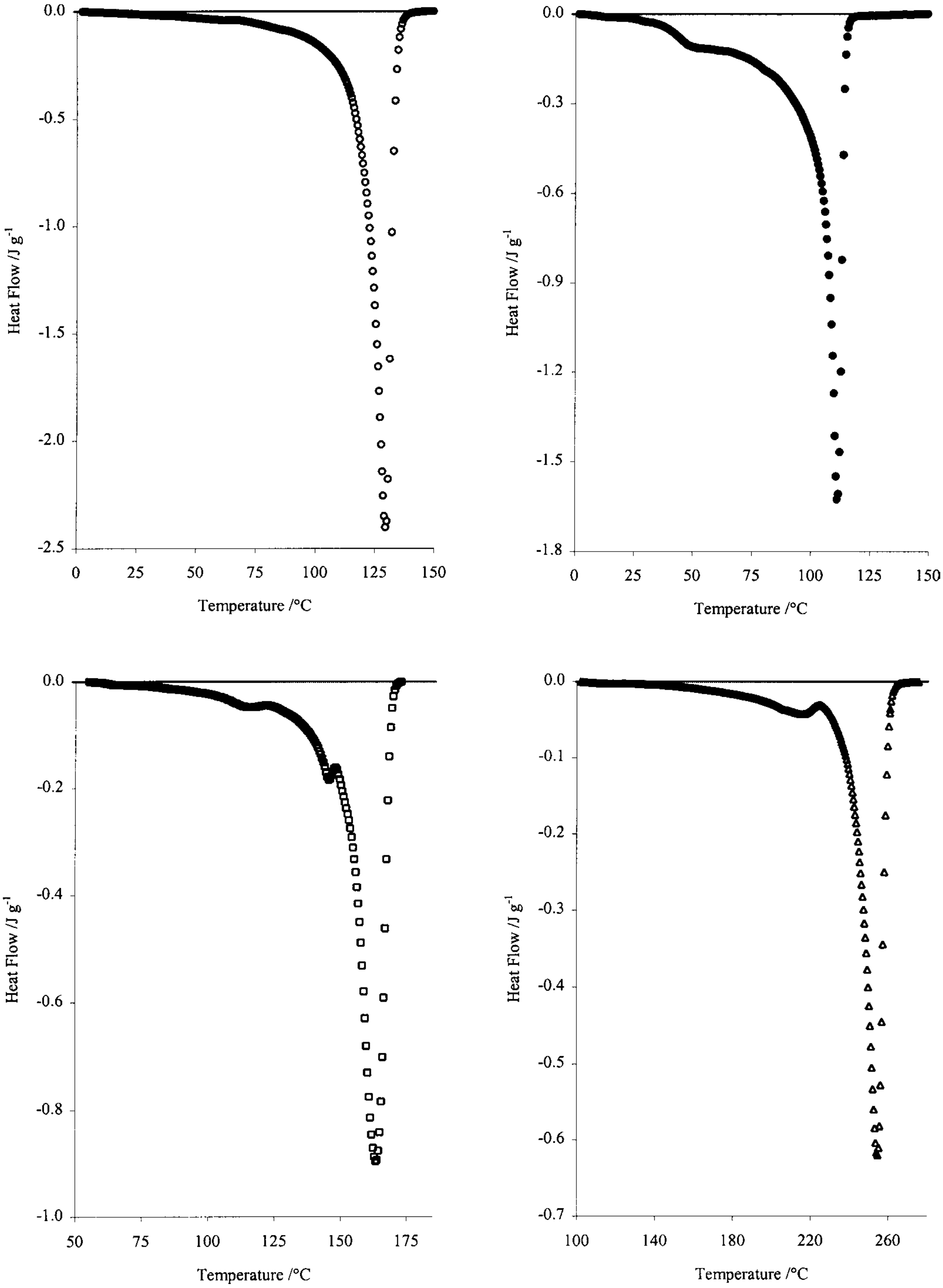

Fig. 5. DSC scan (10°C min^{-1}) of (a) HDPE, (b) LDPE, (c) PP and (d) PET.

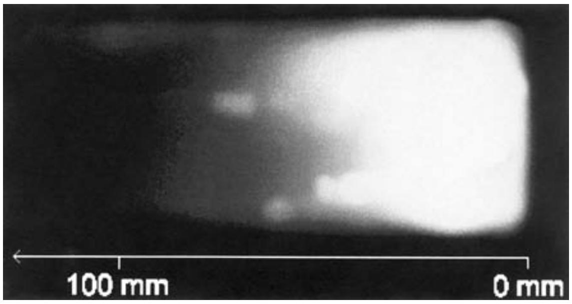

Fig. 6. The downstream afterglow generated by a 12 l min^{-1} nitrogen APNEP.

tures above 400°C, only very short exposures can be sustained.

2.3. Differential scanning calorimetry (DSC)

DSC was performed using a TA Instruments 2910 MDSC at a heating rate of 10°C min^{-1}. Fig. 5(a)–(d) show the DSC curves for HDPE, LDPE, PP and PET. The DSC curve for PMMA showed only a glass transition temperature region (T_g=125.3°C) and has not been illustrated.

On closer inspection of the DSC curve of LDPE Fig. 6, morphological changes (partial melting and rearrangements) can be seen to be occurring at temperatures as low as 30°C, over 80°C below its melting point. For other materials, also morphological changes occur at temperatures much lower than their melting points.

2.4. Downstream afterglow investigations

The atmospheric pressure glow discharge has a source temperature in excess of 2000°C. Therefore, the cooler downstream afterglow region is much more amenable to the processing of polymers. Fig. 6 shows the afterglow induced by a 12 l min^{-1} nitrogen APNEP and this clearly shows that there is an active downstream region within which surface processing is feasible.

Temperature measurements along the afterglow region have been made for various gases and flow rates. Fig. 7 illustrates curves of the temperature variation of the afterglow region along the length of the downstream reaction vessel for a series of nitrogen APNEPs. At high flow rates, this temperature may be in excess of 400°C for up to 100 mm downstream, whereas at lower flow rates, it is only slightly above room temperature.

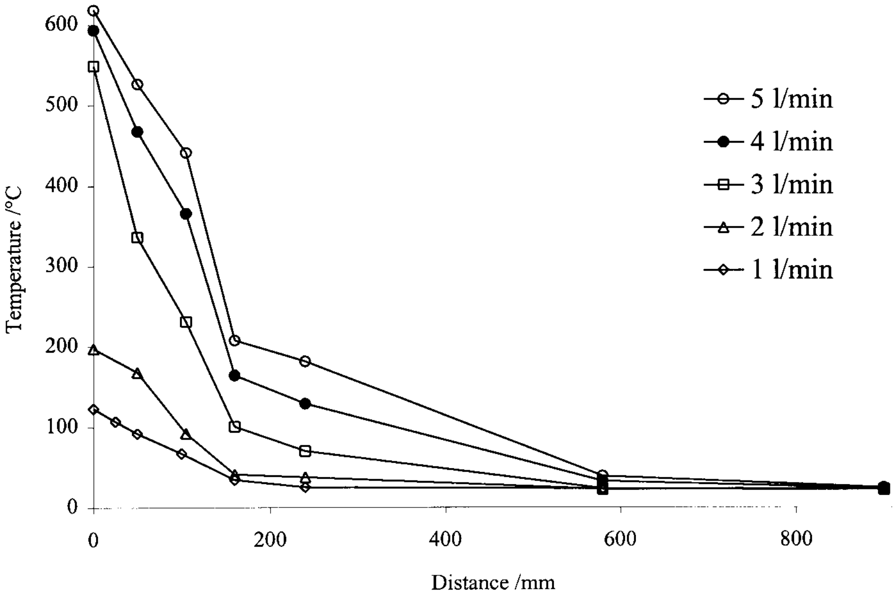

Fig. 7. Temperature profiles of the downstream region of nitrogen APNEPs at flow rates between 1 and 5 l min^{-1}.

3. Discussion

The use of TGA and DSC to investigate the thermal behaviour of commodity polymers emphasizes the wide range of temperatures over which thermal transitions and events occur. For some polyethylenes, partial melting is present at temperatures as low as 30°C. This is significant because the temperature in the near-field downstream region is considerably higher than this, in some cases, above 500°C. The polymers in this study were generally molten before the temperature reached 150°C. The exception was PET which had an onset melting temperature of $\sim$145°C.

In the absence of oxygen, thermally induced decomposition and degradation do not occur until much higher temperatures. With the exception of PMMA, the polymers investigated were stable until $\sim$270°C in oxygen and $\sim$390°C in an oxygen-free environment. Significant PMMA degradation had occurred at temperatures <300°C for both atmospheres. In all cases, melting occurred at least 100°C before degradation and it is the temperature window between melting and degradation that is the most important feature when determining suitable operating conditions for the treatment of polymers using APNEP.

Surface melting is a potentially useful side-effect of the thermal component of APNEP as a molten surface may assist chemical reactions and result in a change of the surface topography, generally making the surface smoother [14]. A molten surface may also allow deeper penetration of active species due to the increased mobility of the surface. On cooling, this will potentially result in a deeper surface treatment region than would have been obtained without surface melting and re-solidification.

Control of the temperature and residence time of the substrates in the plasma region is important in dynamic processing. For a given system, the optimum conditions for controllable and efficient surface modification can be determined by a combination of thermal methods.

4. Conclusions

To process polymers in the downstream afterglow region of APNEP, care must be taken to avoid undesirable thermally induced effects. This is achieved by placing the substrate in a cooler region of the downstream reactor. For example, polyethylene can be safely exposed to the activated gas stream of a $3\,\mathrm{l\,min^{-1}}$ nitrogen APNEP for 10 min if placed 800 mm downstream. Only 5 mm downstream from a similar plasma, rapid melting and degradation ensue. However, this does not mean that the near-field afterglow region is unsuitable for polymer treatment. For residence times of fractions of a second, such as those found for a continuous feed process, thermal damage may be avoided.

In fact, the thermal component of APNEP is potentially very useful. In many cases, partial surface melting and/or thermal activation are desired. This can result in surface smoothing and also generates thermally activated species to further accelerate or promote additional reactions.

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