ATMOSPHERIC PRESSURE NON-EQUILIBRIUM PLASMA PROCESSING OF POLYMERS

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1. Introduction

The ability to perform controlled surface engineering of polymers is of academic and commercial importance. In industry, the use of plasmas to perform this task has often been ruled out due contraints imposed by the need for low pressure/vacuum environments to sustain the plasmas. However, EA Technology Ltd. has developed a non-equilibrium plasma process that operates without the need of vacuum equipment but under atmospheric conditions [1,2]. This system, known as the atmospheric pressure non-equilibrium plasma, (APNEP) has many of the advantages of conventional vacuum non-equilibrium plasmas with the additional feature that it operates at atmospheric pressure. The key operational features of APNEP are as follows:

- it operates at atmospheric pressure
- it is a non-equilibrium plasma (glow discharge), $T_e >> T_{gas}$
- can operate at flow rates of 0 to > 120 l min^{-1} (high gas volume throughput)
- thermal component available if required
- suitable for both continuous and batch processes
- operates at standard microwave (MW) frequency of 2.45 GHz
- adapted from readily available components
- downstream processing – suitable for processing films and complex shaped substrates
- stable plasmas can be formed for a variety of gases (air, N_2, He, Ar and others)
- control of the vac-UV/UV component

These features give APNEP the potential to perform the following processes:

- surface cleaning
- produce uniform surface modification
- downstream processing of thermally sensitive materials
- processing of large areas and irregular shapes

- in-situ processing of thermally stable materials (metals, ceramics)
- APNEP enhanced chemical vapour deposition (CVD)

2. APNEP Apparatus

The original APNEP is based on a modified commercial microwave oven that contains a plasma containment vessel. A source gas is flowed through the containment vessel (where the atmospheric pressure glow discharge exists) and vents into a downstream reactor or an open exposure region where most of the processing of polymers is performed.

2.1. APNEP Induced Surface Cleaning

Surface cleaning/de-greasing/removal of weak boundary layers (WBL) is of importance for many processes, e.g. printing, bonding. Surface infrared (ATR-FT-IR) spectroscopy has been used to demonstrate APNEP induced surface cleaning of high density polyethylene (HDPE). As received HDPE has two broad bands at 1250 - 1200 cm^{-1} and 1150 - 1000 cm^{-1} that can be attributed to hydrocarbon contamination. After downstream exposure to a N_2 APNEP, these contaminant bands are removed, (a similar effect is observed by rigorous solvent cleaning of the HDPE).

2.2. APNEP induced Chemical Modification

Five commodity polymers (high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), poly(ethylene terephthalate) (PET) and poly(methyl methacrylate) (PMMA)) have been exposed to various APNEPs under a variety of gas, flow rate and geometric conditions. X-ray photoelectron spectroscopy (XPS) has been used to measure the surface chemical composition of standards and plasma modified polymers to a depth of 5-30 nm. The XP-spectra that were recorded indicate that surface oxygen enhancement had occurred in the cases of HDPE, LDPE, PP and PET. In comparison with RF vacuum plasma surface modification, APNEP induced changes have been shown to require less than a tenth of the exposure time to achieve a similar degree of modification. For PMMA, removal of oxygen species was detected indicating the loss of the acrylate side group and surface cross-linking.

By varying the APNEP conditions (source gas, flow rate, substrate position and reactor geometry), the rate and degree of surface modification can be controlled.

Increases in the surface energy of APNEP treated polymers have also been measured. Data in Table 1 summarise a few surface energy measurements.

Substrate	Surface Energy /mN m^{-2}	
	Untreated	APNEP treated
HDPE	26.9 ± 2.5	42.5 ± 6.5
PET	39.9 ± 3.8	49.3 ± 6.6

Table 1. Surface energy measurements.

The change in the chemical structure (as indicated by the XPS data) and surface energies result in enhanced surface properties. For example, the polymer-polymer adhesion of polyolefins (using an epoxy adhesive) has been shown to be enhanced. Other surface property changes include a change in wettability (all five substrates) and increased surface hardness (PMMA).

2.3. APNEP Induced Physical Modification

Both thermally and chemically induced physical changes have been observed for a variety of substrate/APNEP expeperiments. For the case of thermally sensitive materials, for example the polyolefins, thermally driven processes dominate the morphology of APNEP treated substrates. Partial surface melting and subsequent post-exposure cystallisation and solidification tend to result in a smooth surface replacing the originally textured and scatched surface of the untreated material.

Reaction with chemically active species from nitrogen APNEPs generated micron-scale pitting on the surface of PET as detected using laser scanning confocal microscopy. No thermally induced changes were detected for PET. This is unsurprising as this polyester has a substantially higher thermal stablity than the polyolefins.

The combination of the thermal and chemical effects can be used to etch the surface of material. Using atomic force microscopy , it was seen that the surface of PET was etched/ablated to reveal the topography of the underlying crystal phase.

2.5. APNEP Reaction Time Scales

Further XPS studies on the effect of post-exposure time on chemical composition revealed that active species on the surfaces of modified substrates had life-times of many hours and

even days. In addition, rapid transfer experiments indicated that some reactions were complete within a few seconds of being removed from the plasma downstream. Therefore, a combination of rapid in-situ and slow post exposure reactions both contribute to the overall degree of surface chemical modification.

2.5. APNEP Downstream Processing

It is thought that excited but electronically neutral species in the downstream APNEP exhaust impinge on surfaces and induce reaction. As reactions can be induced upto a 1 metre or more away (through an atmospheric pressure gas) from the plasma itself, the authors believe that energy exchange cascade reactions must occur to sustain such long range energy transfer processes.

3. Conclusions

We have demonstrated that Atmospheric Pressure Non-Equilibrium Plasma (APNEP) has the potential to perform surface cleaning, surface chemical and surface physical modification of a variety of commercially important polymers. Further work has shown that APNEP can also act as an atmospheric pressure chemical vapour deposition source when appropriate gases/monomers are used [3].

References

[1] UK EATL patent application 9414561.2, July 1994; International patent application N. PCT/GB95/01628, July 1994.

[2] M.D. Connaughton: “Novel Plasma Processing for Enhanced Surface Engineering.” Materials World **389**, 1996.

[3] *Unpublished results from EA Technology Ltd.*