ATMOSPHERIC PRESSURE PLASMA PROCESSING OF POLYPROPYLENE*

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AGENDA

• Introduction to plasma surface modification of polymers
• Description of the model for gas phase and surface kinetics
• Processing of polypropylene in humid air plasmas
• Concluding remarks
PLASMA SURFACE MODIFICATION OF POLYMERS

- Polymers typically require surface activation to improve their wetting and adhesion properties.

- Atmospheric pressure plasmas (typically coronas) are used for the ease of generation of gas-phase radicals which react with and modify the polymer surface.
Most polymers, due to their low surface energies, are hydrophobic.

For good adhesion between a liquid and a polymer, the surface energy of the polymer should exceed the surface tension of the liquid by \( \approx 2-10 \text{ mN m}^{-1} \).
COMMERCIAL CORONA PLASMA EQUIPMENT

(Tantec Inc.)

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POLYMER TREATMENT APPARATUS

- TYPICAL PROCESS CONDITIONS:
  - Web speed: 10 - 200 m/min
  - Residence time: a few s
  - Energy deposition: 0.1 - 1.0 J cm⁻²
  - Applied voltage: 10-20 kV at a few 10s kHz
  - Gas gap: a few mm
HUMID-AIR PLASMA

BOUNDARY LAYER

POLYPROPYLENE

Layer 1

Layer 2

Layer 3

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POLYPROPYLENE (PP) - STRUCTURE

Polypropylene polymer:

- Primary C – attached to only one another carbon;
- Secondary C – attached to two carbon atoms; and
- Tertiary C – attached to three carbon atoms.

The reactivity of an H-atom depends on the type of C bonding.

Reactivity scales as: $H_T > H_S > H_P$ ($H_T$ = tertiary H; $H_S$ = secondary H; $H_P$ = primary H)
FUNCTIONALIZATION OF THE PP SURFACE

• Untreated PP is hydrophobic (repels water).

• The increase in surface energy of PP after corona treatment is attributed to the functionalization of the polymer surface with hydrophilic groups (attract water).

• An air-corona-processed PP film contains hydrophilic functional groups such as:
  - Carbonyl (-C=O)
  - Peroxy (-C-O-O)
  - Alcohols (C-OH)
  - Acids ((OH)C=O)

• The process parameters are energy deposition and relative humidity (RH).

• At sufficiently high energy deposition, erosion of the polymer occurs.
DESCRIPTION OF THE MODEL: GLOBAL_KIN

- Modules in GLOBAL_KIN:
  - Circuit model
  - Homogeneous plasma chemistry
  - Species transport to PP surface
  - Heterogeneous surface chemistry

[Diagram showing the flow of data from Offline Boltzmann Solver to Lookup Table of k vs. T_e, then to Gas-Phase Kinetics, Surface Kinetics, and Circuit Module, leading to N(t+Δt), V, I and VODE ODE Solver.]
• Gas phase products of humid-air corona treatment include $O_3$, $N_2O$, $N_2O_5$, $HNO_2$, $HNO_3$. 

![Chemical reaction diagram]

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SPECIES TRANSPORT TO THE POLYMER SURFACE

- Species in the bulk plasma diffuse to the PP surface through a boundary layer (d \sim \text{a few } \lambda_{\text{mfp}} \approx \mu \text{m}).

- Flux of the radicals reaching the surface is,

\[ \phi = \frac{n v_{th}}{4} , \quad n = \text{density, } v_{th} = \text{thermal speed}. \]

- Radicals react on PP based on a site balance model.
REATIONS AT PP SURFACE

• O and OH abstract H from PP to produce alkyl radicals.

• Reactions of O$_3$ and O$_2$ with alkyl radicals produce peroxy and alkoxy radicals, which further react to form alcohols and carbonyl species.
BASE CASE: \( n_e, T_e \)

- Ionization is dominantly of \( N_2 \) and \( O_2 \),

\[
\begin{align*}
e + N_2 & \rightarrow N_2^+ + e + e, \\
e + O_2 & \rightarrow O_2^+ + e + e.
\end{align*}
\]

- Once the gap voltage decreases below sustaining, electrons decay by attachment (primarily to \( O_2 \)).

- The differences between the 1\(^{st}\) and later pulses are due to the incomplete charging of the dielectrics on the electrodes.

- \( N_2/O_2/H_2O = 79/20/1 \), 300 K, 15 kV at 9.6 kHz.

- \( E_{\text{dep}} = 0.8 \text{ J cm}^{-2}, \) Web speed = 250 cm/s.
GAS-PHASE RADICALS: O, OH

- Electron impact dissociation of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) produces \( \text{O} \) and \( \text{OH} \).

- \( \text{O} \) is consumed in the gas phase primarily to form \( \text{O}_3 \),

  \[
  \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}.
  \]

- After 100s of discharge pulses, the radicals attain a periodic steady state.
• Surface concentrations of alcohols, peroxy radicals achieve near steady state with a few J cm\(^{-2}\).

• Alcohol densities decreased at higher energy deposition due to decomposition by O and OH to regenerate alkoxy radicals.

**MODEL VS. EXPERIMENT**

**Air at 300 K, 1 atm, 30% RH**

\[ \text{PP Peroxy Radicals} = \frac{\text{Energy Deposition (J cm}^{-2}\text{) }}{3.0} \]

\[ \text{PP Alcohol} = \frac{\text{Energy Deposition (J cm}^{-2}\text{) }}{3.0} \]

\[ \text{Experiment}^{*} \]

\[ \text{Model} \]

\[ \text{L-A. Ohare et al., Surf. Interface Anal. 33, 335 (2002).} \]
• $O_3$ is produced by the reaction of $O$ with $O_2$,

$$O + O_2 + M \rightarrow O_3 + M.$$ 

• N-containing products include NO, NO$_2$, HNO$_2$ and N$_2$O$_5$,

$$N_2 + O \rightarrow NO + N,$$

$$NO + O + M \rightarrow NO_2 + M,$$

$$NO + OH + M \rightarrow HNO_2 + M,$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M.$$
EFFECT OF RH: PP FUNCTIONALIZATION

• With increasing RH, more OH is produced.
• Due to the high reactivity of OH, more PP alkyl radicals are generated.
• As a result, the densities of peroxy radicals increase,
  \[ \text{PP-H} + \text{OH}_{(g)} \rightarrow \text{PP}• + \text{H}_2\text{O}_{(g)} \quad \text{PP}• + \text{O}_2(g) \rightarrow \text{PP-O}_2• \]
• Alcohol and carbonyl densities decrease at higher RH due to increased consumption by OH to form alkoxy radicals and acids.

![Graphs showing the change in density and concentration with RH](chart.png)
EFFECT OF RH: GAS-PHASE PRODUCTS

- Higher RH results in decreasing O atom densities and so the production of \( O_3 \) decreases.

- Due to the increased production of OH with RH, larger densities of \( HNO_2 \) and \( HNO_3 \) are produced.

\[
N + OH \rightarrow NO + H, \quad NO + OH \rightarrow HNO_2, \quad NO_2 + OH \rightarrow HNO_3.
\]
EFFECT OF TEMPERATURE: GAS-PHASE PRODUCTS

- With increasing gas temperature, consumption of $O_3$ increases.
- Most of the NO is lost by reduction to $N_2$ and oxidation to $NO_2$,
  \[ NO + N \rightarrow N_2 + O, \quad NO + O_3 \rightarrow NO_2 + O_2. \]
- $N_2O_5$ is a maximum at intermediate temperatures,
  \[ NO_2 + NO_3 + M \rightarrow N_2O_5 + M, \quad N_2O_5 \rightarrow NO_2 + NO_3. \]
With increasing gas temperature, the production of O$_3$ decreases leading to lower alkoxy production,

$$\text{PP} \cdot + O_3(g) \rightarrow \text{PP-O} \cdot + O_2(g).$$

... and decreased production of alcohols, carbonyl, and acids,

$$\text{PP-O} \cdot + \text{PP-H} \rightarrow \text{PP-OH} + \text{PP} \cdot$$

$$\text{PP-O} \cdot \rightarrow \text{PP=O}$$

$$\text{PP=O} \rightarrow \text{PP=O} \cdot$$

$$\text{PP}=O \cdot + \text{OH} \rightarrow \text{(OH)PP}=O \cdot$$

Decreased consumption of alkyl radicals by O$_3$ enables increased consumption by O$_2$ increasing the density of peroxo radicals.
SUMMARY

• A surface reaction mechanism for PP has been developed and validated against experiments.

• With increasing energy deposition the surface concentrations of alcohol, acid, carbonyl, and peroxy groups increase.

• However, significant densities of environmentally sensitive gases such as $O_3$ ($10^{17}$ cm$^{-3}$) and $HNO_3$ ($10^{16}$ cm$^{-3}$) are generated.

• Increasing RH resulted in increased surface concentrations of peroxy and acid groups and decreased alcohols and carbonyls.

• Operating at larger RH resulted in reduced production of $O_3$.

• Surface concentrations of alcohol, carbonyl, and acid groups decreased with temperature while those of peroxy groups increased.