Control of Plasma Polymerization Processes

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Advanced Fibers

- Fiber and Textile Chemistry
  - finishing, wet-chemical treatment

- Fiber Development
  - bi-component fiber spinning device

- Plasma-modified Surfaces
  - cleaning, activation, deposition

Outline

Control of Plasma Polymerization Processes

- Plasma polymerization

- Influence of
  - reactor geometry
  - plasma expansion
  - pressure
  - monomers
  - carrier / reactive gas

- Nanoporous coatings

- Scale-up
**Plasma Polymerization**

Different regimes

- retention of monomer groups
- fragmentation, cross-linking

- hydrogels: e.g. PEO-like
- functional density control: e.g. hydrophobic, -COOH, -NH₂
- permeation control / barrier: e.g. SiOₓ, a-C:H
- hard coatings: e.g. a-C:H

- energy-deficient
- monomer-deficient

![Diagram](image)

**Macrosopic Kinetics**

Concept of chemical quasi-equilibria related to plasma

`gas flow` `dissociation excitation` `recombination relaxation` `stable products`

- e.g. monomer: active zone
- passive zone: e.g. deposition

**Macroscopic kinetics:**

(Behler formula)

\[
S = \frac{W \tau_{act}}{pV_{act}} \propto \frac{W}{F}
\]

\[
\tau_{act} = \frac{pV_{act}}{p_0F}
\]

The similarity parameter \( S \) represents the energy invested per particle of the gas mixture during the flow through the active plasma zone.


Evaluation of deposition rates

For radical-dominated discharges the reaction parameter power input per gas flow $W/F$ within the active plasma zone determines the mass deposition rate $R_m$

$$\frac{R_m}{F} = G \exp\left(-\frac{E_a}{W/F}\right)$$

$E_a$: (apparent) activation energy

$G$: geometrical factor


Evaluation of Deposition Rates

Deposited mass for different reactor geometries

\[ \text{pp-HMDSO} \]

\[ R_m F = \text{[10}^6 \text{ g/min cm}^2 \text{sccm]} \]

\[ E_a: \text{slope of linear fit} \]

\[ (W/F)^1 [(W/sccm)^{-1}] \]

1 Hegemann et al., Plasma Polym. 6, 2001, 221.

Influence of Reactor Geometry

Plasma deposition in a reaction vessel

\[ S = \frac{W}{F} \]

\[ W_{dep} = W \frac{A_{dep} V_{act}}{V_{dis}} \]

\[ F_{dep} = F \frac{A_{dep} d_{gas}}{V_{gas}} \]

\[ S = \frac{W d_{act} V_{gas}}{F d_{gas} V_{dis}} \]

Similarity parameter is related to power and flow that contribute to film deposition.

Influence of Reactor Geometry

**Tubular set-up**

\[ S = \frac{W \cdot d_{act}}{F \cdot l} \]

\[ V_{gas} = A_{dep} \cdot d_{gas} \]

\[ V_{dis} = A_{dep} \cdot l \]

\[ S = \frac{W \cdot \tau_{act}}{p \cdot V_{dis}} \]

\[ \tau = \frac{V}{F} \cdot \frac{p}{p_0} \quad ; \quad T = \text{const.} \]

Similarity parameter changes with position of substrate within the discharge.

→ Fragmentation increases with distance and residence time.


**Symmetric plane parallel set-up**

\[ S = \frac{W \cdot d_{act}}{F \cdot l} \]

\[ l = d_{act} + 2d_{sh} \]

\[ S = \frac{W}{F} \left( 1 - 2 \frac{d_{sh}}{l} \right) \]

Similarity parameter increases with electrode distance.


**Symmetric Reactor**

**Plasma length** $d_{act}$

- well defined geometrical conditions
- known gas flow (vertical flow)
- known power adsorption

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**Variation of temperature, power, flow, and pressure**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_S$</td>
<td>30-90°C</td>
</tr>
<tr>
<td>$W$</td>
<td>50-400 W</td>
</tr>
<tr>
<td>$F$</td>
<td>50-120 sccm</td>
</tr>
<tr>
<td>$p$</td>
<td>10-50 Pa</td>
</tr>
</tbody>
</table>

$S = \frac{W \cdot d_{act}}{F \cdot l}$

$d_{act} \approx const$

$V_{dis} = V_{gas}$

Influence of Plasma Expansion

Plasma polymerization within asymmetric discharges

Different activation energies (slopes) were obtained for different gas flows.


Influence of Plasma Expansion

Light distribution of plasma in front of RF electrode

Influence of Plasma Expansion

Light distribution of plasma in front of RF electrode

Expanding plasma zone depending on power and flow

\[ d_{\text{act}} = 3.7 \left( \frac{W}{F} \right)^{0.33} \]

\[ d_{\text{act}} \approx \sqrt[5]{W^{0.33} / F^{0.33}} \]

\[ d_{\text{act}} = 2.5 \left( \frac{W}{F} \right)^{0.34} \]

\( d_{\text{act}} \) only depends on \( W \) (independent of different monomer flows)

Influence of Plasma Expansion

Consideration of similarity factor

\[ S = \frac{W d_{act} V_{gas}}{F d_{gas} V_{dis}} \]

\[ V_{gas} \approx V_{dis} \]

volume-dominated

Introduction of similarity factor yield same activation energy.

**Influence of Pressure**

Plasma polymerization within asymmetric discharges

Different activation energies (slopes) were obtained for different pressures.

Influence of Pressure

Light distribution of plasma in front of RF electrode

Expanding plasma zone depending on energy input

\[ \text{d}_{\text{act}} \text{ increases with decreasing pressure (and power input)} \]

Influence of Pressure

Consideration of similarity factor

Transition from volume- to corner-dominated discharge at a pressure >8 Pa.

Introduction of similarity factor with decreasing discharge volume yield same activation energy.
Plasma Polymerization

Formation of film-forming radicals

- Same radicals determine film growth (same plasma chemistry) – higher number (due to more fragmentation) with increasing energy input

\[
\frac{R_m}{F} = G \exp\left(-\frac{E_a}{W/F}\right)
\]


Influence of Monomers

- Generalized activation energy
  - Similarity factor enables the finding of a generalized activation energy
  
  \[
  S = \frac{W d_{act} V_{gas}}{F d_{gas} V_{dis}}
  \]

- Comparative graph showing the influence of different monomers on the rate of film formation for symmetric and asymmetric, confined RF discharge.
**Influence of Monomers**

**Generalized activation energy of different monomers**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Formula</th>
<th>Activation energy</th>
<th>Main dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>5.3 ± 0.5 eV</td>
<td>C-H, (H-H)</td>
</tr>
<tr>
<td>acetylene</td>
<td>C₂H₂</td>
<td>9.0 ± 0.7 eV</td>
<td>C≡C</td>
</tr>
<tr>
<td>ethylene</td>
<td>C₂H₄</td>
<td>12 ± 1.2 eV</td>
<td>C=C, C-H (2x)</td>
</tr>
<tr>
<td>pyridine borane</td>
<td></td>
<td>12 ± 1.5 eV</td>
<td>C-N, C-C, N:B, C-H</td>
</tr>
<tr>
<td>TBBD</td>
<td></td>
<td>15 ± 1.5 eV</td>
<td>C-N (3x), C-C, C-H</td>
</tr>
<tr>
<td>HMDSO</td>
<td>(CH₃)₃-Si-O-Si-(CH₃)₃</td>
<td>12.8 ± 0.7 eV</td>
<td>Si-C, C-H, Si-O</td>
</tr>
</tbody>
</table>

HMDSO Discharge

**Initiation of HMDSO plasma polymerization**

\[ E_a = 55 \text{ J/cm}^3 \]
\[ = 7.6 \text{ MJ/kg} \]
\[ = 1230 \text{ kJ/mol (HMDSO)} \]
\[ = 12.8 \text{ eV per molecule} \]

Si-O bond: 452 kJ/mol  
Si-C bond: 360 kJ/mol  
C-H bond: 435 kJ/mol  
\[ \rightarrow 1247 \text{ kJ/mol (12.9 eV)} \]

The activation energy gives the dissociation energy to obtain the radicals that predominantly lead to plasma polymer growth.
Influence of Carrier / Reactive Gases

Oxygen added to HMDSO discharge

\[ F = F_m + a F_c \]

Increasing \( O_2 \) admixture

\( a = 0.6 \)


Design of \( O_2/HMDSO \) Coatings

Control of wetting properties

pdms

SiOC:H films

quartz

The residual C concentration also scales with the crosslinking and thus the permeability.
Influence of Carrier / Reactive Gases

Correction factor for the combined flow $F = F_m + a F_c$

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Added gas</th>
<th>Flow factor $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbons</td>
<td>Ar, He</td>
<td>0.05-0.1</td>
</tr>
<tr>
<td></td>
<td>H$_2$</td>
<td>~0.15</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>~0.15</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>NH$_3$</td>
<td>0.5</td>
</tr>
<tr>
<td>HMDSO</td>
<td>O$_2$</td>
<td>0.6</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>H$_2$</td>
<td>~0.25</td>
</tr>
</tbody>
</table>


Influence of Reactive Gases

Plasma polymerization of hydrocarbon/ammonia

$F = F_m + a F_c$

$\text{a: reaction crosssection}$

$\rightarrow$ energy consumed by carrier gas

Plasma polymerization of asymmetric N$_2$/CH$_4$ discharges

RF plasma, 40 Pa, -650 V$_{bias}$

Deposition rate (μm/h)

\[ \text{Deposition rate} = \frac{\text{N}_2}{(\text{N}_2 + \text{CH}_4)} \]

\[ R = F_m + a F_c \]

\[ a = 0.35 \]


Deposition of Nanoporous Coatings

Rivaling deposition/etching processes

plasma polymerization + chem./phys. etching
Deposition of Nanoporous Coatings

Hydrocarbon/ammonia RF discharges

Amine-functionalized coatings

porous structure: <30 nm
porous structure: <20 nm


Deposition of Nanoporous Coatings

Film density related to porous structure

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Nanoporous Plasma Coatings

Dyeing of plasma coatings on textile fabrics

\[
\text{C}_2\text{H}_2/\text{NH}_3 \text{ discharge}
\]

Dye molecules (~3 nm) are able to diffuse into nanoporous structure.

Dyestuff: C.I. Acid blue 127:1


Nanoporous Plasma Coatings

Dyeability (color intensity K/S) vs. pore sizes

Color intensity correlates with pore sizes, while overall N content is constant for a fixed NH\textsubscript{3}/C\textsubscript{2}H\textsubscript{2} ratio.
Nano-porous Plasma Coatings

Permanence of dyed plasma coatings on textile fabrics

Martindale before testing after 70'000 cycles

PP multifil

PET monofil

dyestuff: C.I. Acid blue 127:1

Hydrophilic treatment – hydrophobic recovery

Aging due to internal and external effects:
- re-organization
- surface reactions
- absorption layers

permanent hydrophilicity
Nanoporous Plasma Coatings

Loading with wet chemicals

UV absorber

Fluorocarbon

UV exposure of aramid fabrics

Martindale abrasion test

Transfer of Plasma Polymerization

Scale-up to Web Coater

Continuous processing of textiles, membranes, foils, bands, and papers

width = 65 cm
velocity = 0.1..100 m/min
\( A_{dep} = 10'000 \text{ cm}^2 \)
Transfer of Plasma Polymerization

Different reactor geometries

Scale-up can be performed successfully using the identified similarity parameter

\[ S = \frac{W \cdot d_{act} \cdot V_{gas}}{F \cdot d_{gas} \cdot V_{dis}} \]

Outlook

Control of Plasma Polymerization Processes

control / design of

- plasma reactors
- nano-scaled coatings
- nanoporous coatings
- multifunctional (textile) surfaces
- transfer into industry
Acknowledgement

Laboratory of Advanced Fibers

- Plasma group

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D. Balazs, M. Hossain, E. Körner, U. Schütz, M. Amberg, S. Guimond

- Chemistry group: M. Heuberger, A. Ritter, F. Reifler

- CTI Bern (funding) KTI/CTI

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