Influence of ionic cross-linking on polymer interdiffusion in water-borne pressure-sensitive adhesives

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Motivation: Pressure-sensitive adhesives (PSAs)

- Polymer films adhering to substrates upon application of light mechanical pressure

→ Must be viscoelastic to provide for adhesion and cohesion

- Can be based on acrylics

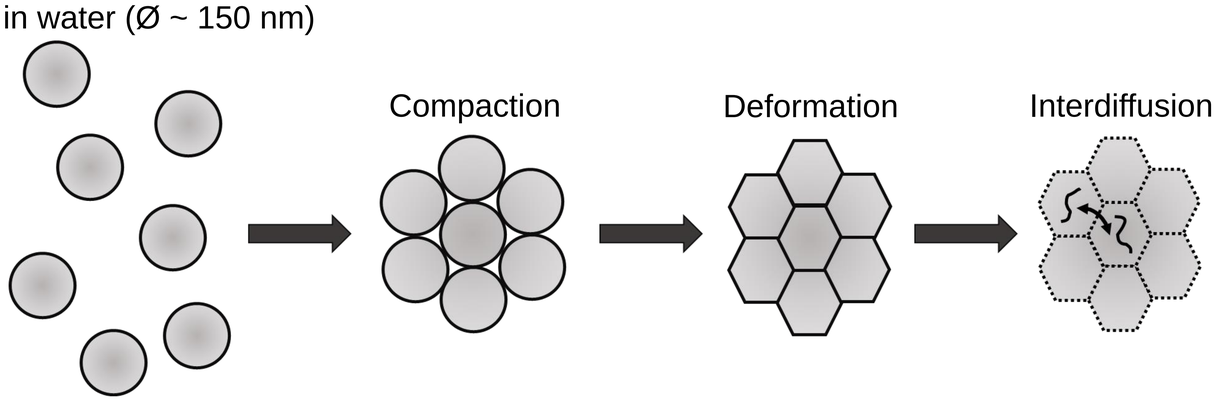
https://www.staples.de/content/images/product/9179143_1_xnl.jpg

→ Acrylic PSA films can be prepared from water-borne polymer dispersions

→ Film formation of dispersions defines properties of the final film

Background: Film formation of polymer dispersions

Polymer particles in water (Ø ~ 150 nm)



Scheme according to Ref. [1]

- Polymer dispersions: Used as coatings, paintings, acrylic PSAs, etc.
- Interdiffusion: Crucial step to obtain a homogeneous film[1]
- Acrylic PSAs → Glass transition temperature below 0°C

→ Interdiffusion fast at room temperature

- Polymer chains in acrylic PSAs usually cross-linked to increase cohesion

→ Cross-linking hinders interdiffusion

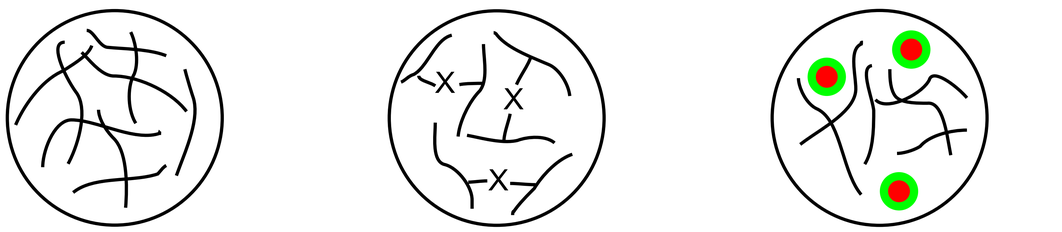
[1] J. L. Keddie, A. F. Routh, *Fundamentals of Latex Film Formation*, **2010**, Springer.

Materials

- Acrylic PSA dispersions provided by BASF SE
- Goal: Obtaining a homogeneous film with cross-linked chains

→ Ionic cross-linking after interdiffusion employing aluminum acetylacetonate

linear | **covalently cross-linked** | **linear + Al(acac)$_3$**

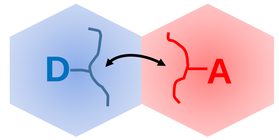


Method: Förster resonance energy transfer (FRET)

$$D \underset{h\nu_{em}}{\overset{h\nu_{exc}}{\rightleftharpoons}} D^* \xrightarrow[r < 1-10\ \text{nm}\ \text{non-radiative energy transfer}]{+\ A} D + A^* \xrightarrow[\text{or } \Delta T]{h\nu'_{em}} A$$

- Study of polymer interdiffusion with FRET:
  - Dispersions with identical properties prepared twice: **donor**- and **acceptor**-labeled
  - Capturing donor fluorescence decays of a film forming blend

Interdiffusion → FRET



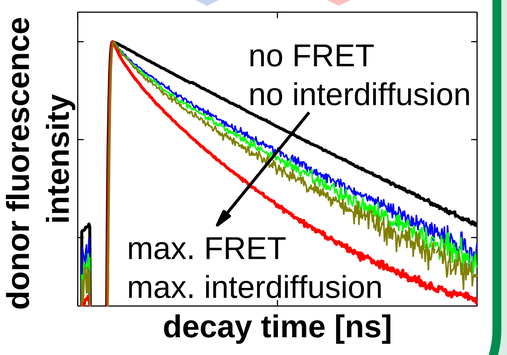
- Fit-function for donor fluorescence decays:[2]

$$I(t') = I_0 \left[A_2 \cdot \exp\left(\left(-\frac{t'}{\tau_D} \right) - 2\gamma \sqrt{\frac{t'}{\tau_D}} \right) + (1 - A_2) \cdot \exp\left(-\frac{t'}{\tau_D} \right) \right]$$

- Conversion of fit-parameter A_2 to fraction of intermixing f_m[2,3]

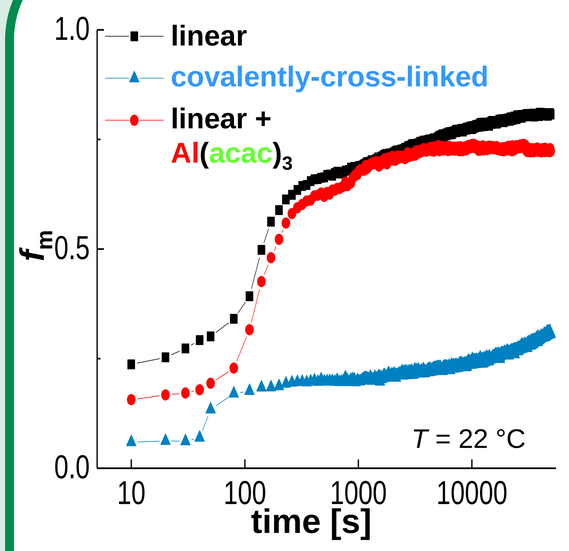
$$f_m(t) = \frac{A_2(t) - A_{2,\min}}{1 - A_{2,\min}}$$

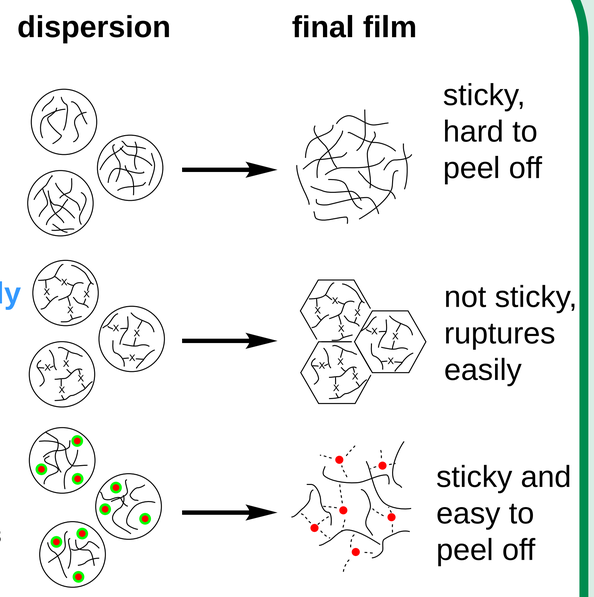
→ f_m increases with interdiffusion



[2] Y. Wang, C.-L. Zhao, M. A. Winnik, *J. Chem. Phys.* 1991, *95*, 2143–2153.
[3] H. Wahdat, C. Hirth, D. Johannsmann, M. Gerst, M. Rückel, J. Adams, *Macromolecules* 2018, *51*, 4718–4726.

Results and Discussion





- linear + Al(acac)$_3$: 75% gel content in final film → Ionic cross-linking
- Cross-linking reaction:[4] 3 Polymer−COOH + Al(acac)$_3$ ⇋ Al^{3+}(⁻OOC−Polymer)$_3$ + 3 acetylacetone

→ Chains in wet dispersion mostly linear

→ Cross-linking mainly occurs when acetylacetone can evaporate

[4] Z. Czech, M. Wojcechowicz, *Eur. Polym. J.* 2006, *42*, 2153–2160.

Outlook

- Investigation of degree of cross-linking in wet dispersion blended with Al(acac)$_3$

Acknowledgements

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