Compatibilisation Efficiency in Polycarbonate Blends – a DPD Study

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Covestro Deutschland AG

Schrödinger Polymer Summit

Covestro – leading in the world of plastics

Strong

- €15.9 bn in sales
- ~17,900 employees[1]

Useful

- Plastics, pre-products and solutions
- For many industries

Global

- 50 production sites globally
- Close to customers and partners

Innovative

- ~1,500 employees in research and development
- 80 years of ideas and inventions

Information is based on financial results for 2021, except amount of employees and amount of global production sites. Those are as of June 30, 2021.
[1]calculated as full-time equivalent (FTE)

Key industries in focus

Automotive and transportation

17%

Construction

15%

Wood and furniture

16%

Electrics and electronics

15%

Chemicals

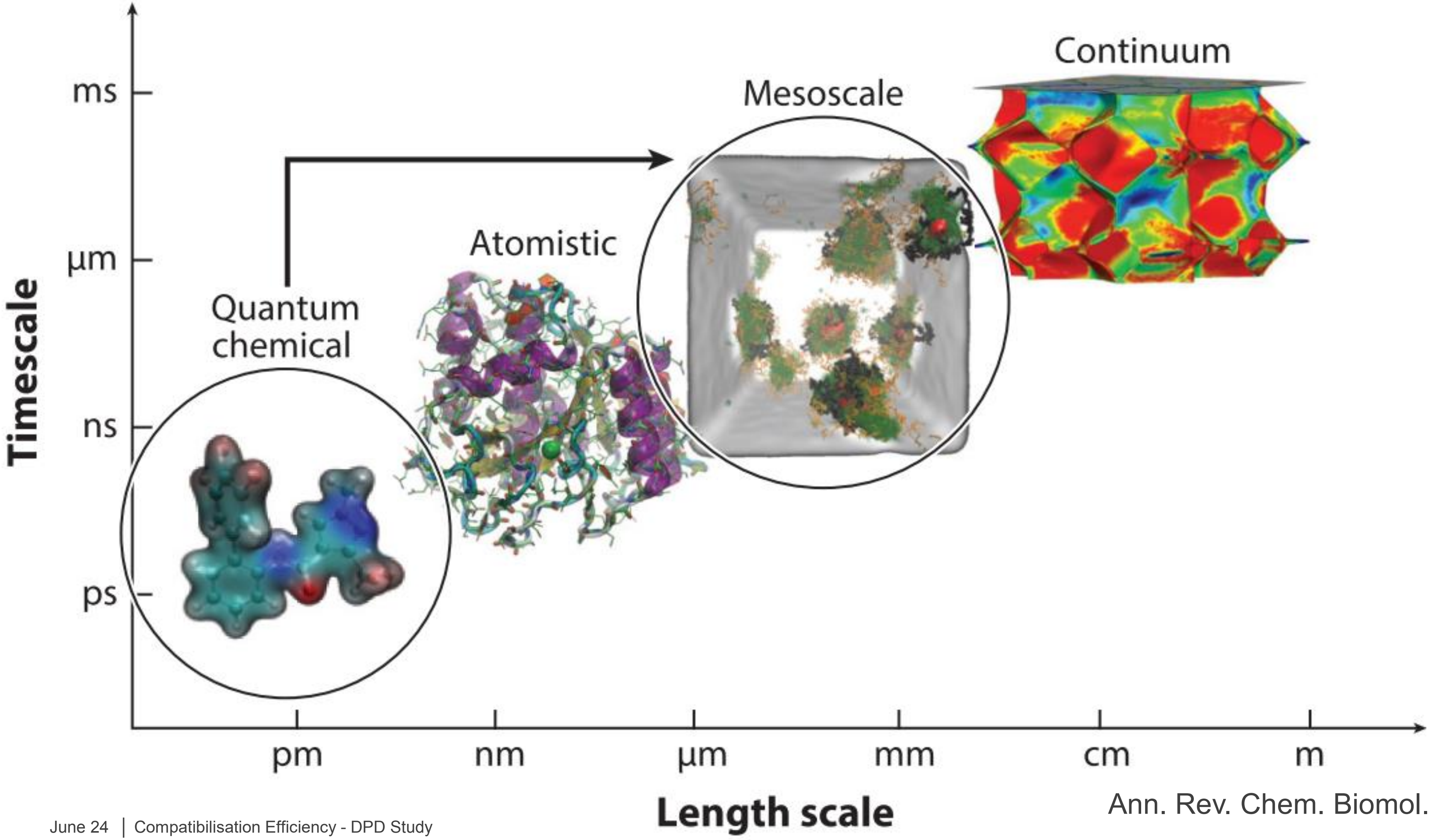
7%

Sports/leisure, cosmetics, health and others

30%

Percentages: Share of total sales in financial year 2021

Modelling is a Key Element in R&D Strategy at Covestro



Ann. Rev. Chem. Biomol. Eng., (2016) **7**, 65

Polymer Blends

- **Blending different polymers as efficient way to improve polymer characteristics**

Makrolon® (Polycarbonate)

Tough

ABS

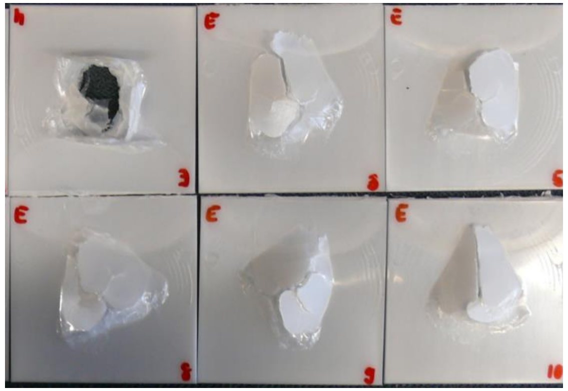
Flame retardant

Bayblend® (PCS + ABS)

Tough + Flame retardant

- **Different polymers tend to be immiscible**

- **Compatibilisers required to hold them together**



Understanding the Mechanism of Compatibilisers

- **Effect of compatibilisers at a fundamental level unclear**
- **More intelligent design of new generation of compatibilisers**
- **Collaboration with the TU Darmstadt (Germany) to gain insight**

TECHNISCHE UNIVERSITÄT DARMSTADT

Tianhang Zhou
Now China University of Petroleum (Beijing)

Prof. Florian Müller-Plathe

Fruitful Collaboration

Macromelecules

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Article

Compatibilization Efficiency of Graft Copolymers in Incompatible Polymer Blends: Dissipative Particle Dynamics Simulations Combined with Machine Learning

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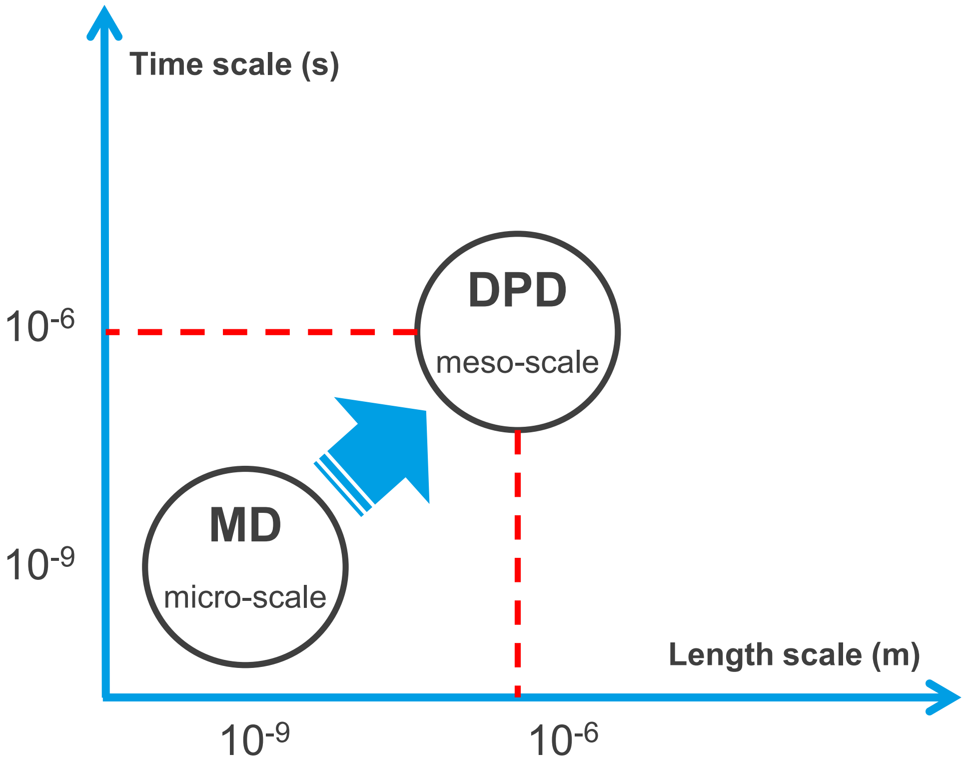
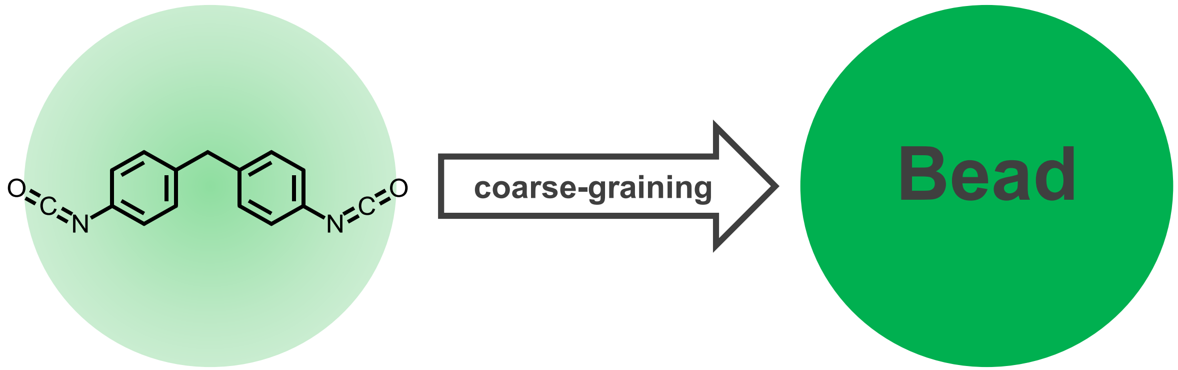
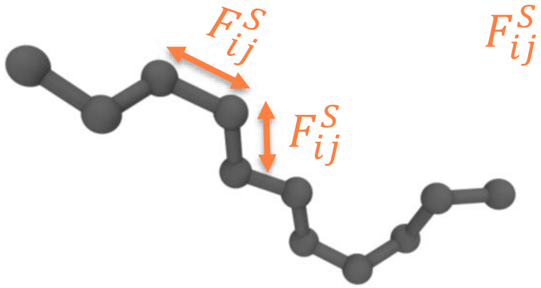
Dissipative Particle Dynamics (I)

- **Interface effects appear at the µm scale**





Harmonic force F_{ij}^{S} between two connected beads



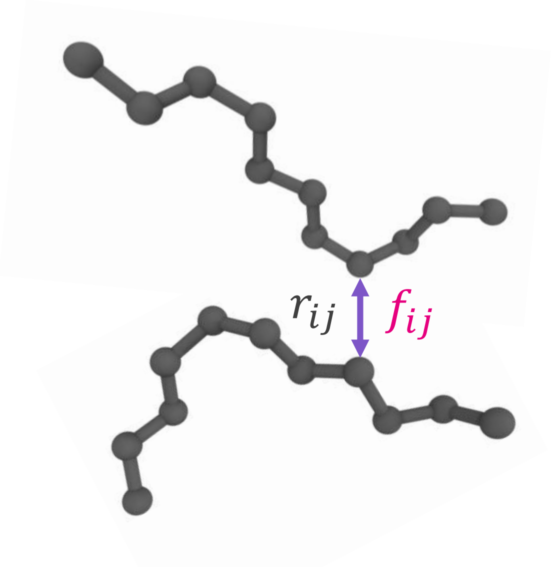
$$F_{ij}^{S} = k(r - r_0)^2$$

$$k = \frac{4k_B}{r_c^2}$$

Dissipative Particle Dynamics (II)

- **The pairwise force f_{ij} acting on two unconnected beads i and j**

$$\hat{\boldsymbol{r}}_{\boldsymbol{ij}} = \frac{\boldsymbol{r}_j - \boldsymbol{r}_i}{|\boldsymbol{r}_j - \boldsymbol{r}_i|}$$



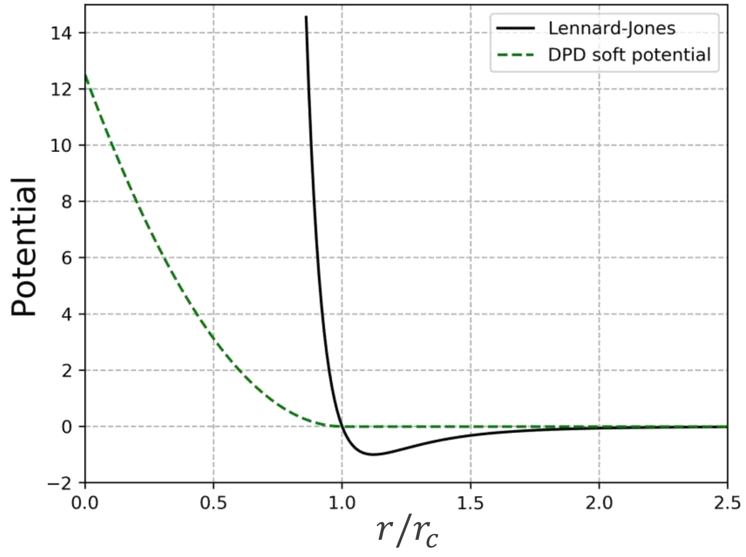
$$f_{ij} = \sum_{i \neq j} \left(F_{ij}^D + F_{ij}^R + F_{ij}^C\right)$$

Dissipative $F_{ij}^D = -\gamma \omega^D(r_{ij})(\hat{\boldsymbol{r}}_{\boldsymbol{ij}} \cdot \mathbf{v}_{\boldsymbol{ij}})\hat{\boldsymbol{r}}_{\boldsymbol{ij}}$

Random $F_{ij}^R = \sigma \omega^R(r_{ij})\xi_{ij}\hat{\boldsymbol{r}}_{\boldsymbol{ij}}$

Thermostat

Conservative F_{ij}^C



$$F_{ij}^C = \begin{cases} \boldsymbol{a_{ij}}\left(1 - \frac{r_{ij}}{r_c}\right)\hat{\boldsymbol{r}}_{\boldsymbol{ij}}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases}$$

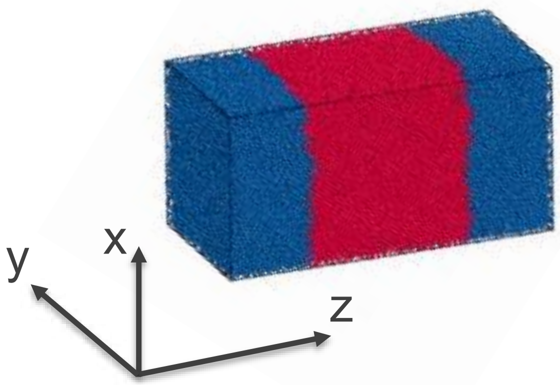
$$a_{ij} = 25\frac{k_B T}{r_c} + 3.27\chi_{ij}$$

- χ_{ij}: Flory-Huggins solubility parameters
- a_{ij} reflects how soluble i is in j
- The larger a_{ij}, the less soluble

JCP, (2017), **146**, 150901

Simulation of Compatibilisation Efficiency

- **162 000 beads are packed in a box 30 x 30 x 60 $r_c{}^3$**
- **Simulation is propagated until equilibration**



- **Further propagation of $2 \cdot 10^6$ timesteps for production of results**

- **Interfacial tension derived from pressure tensor:**

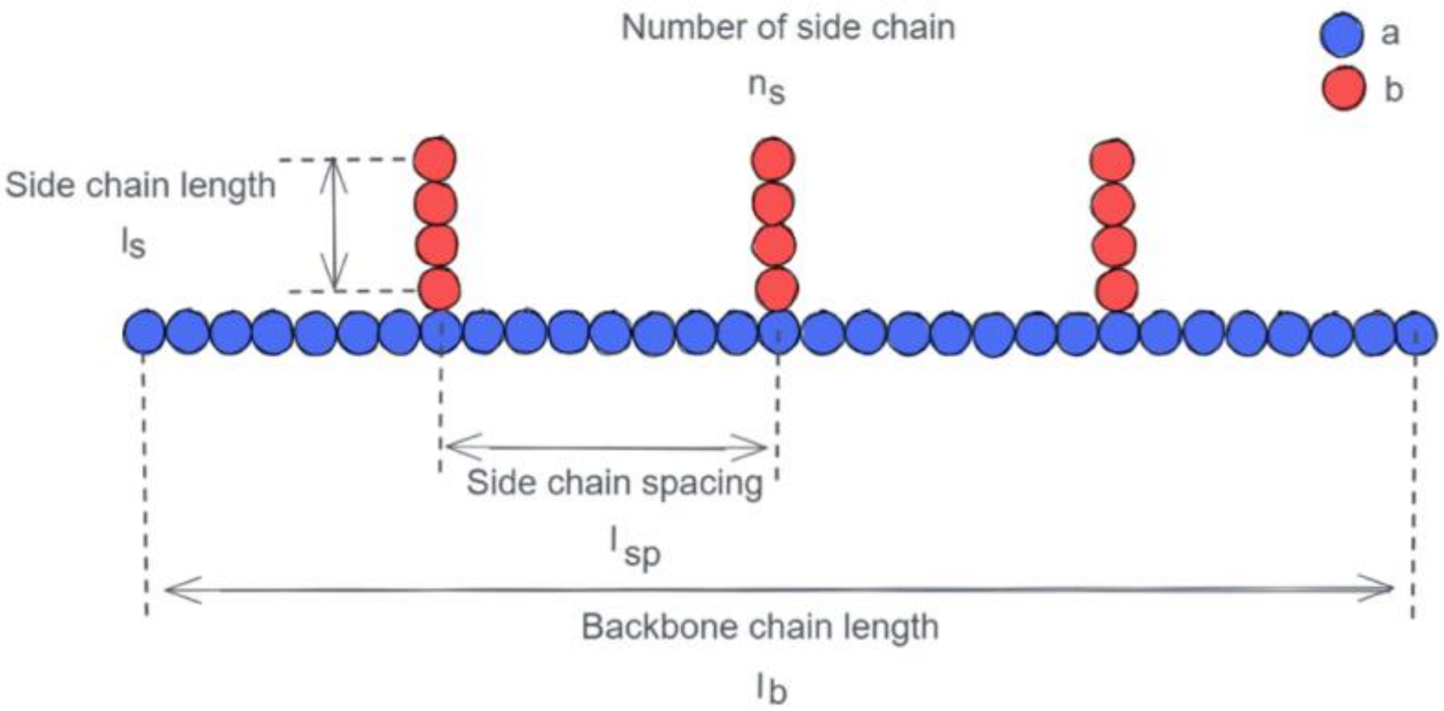
$$\gamma = \frac{L_z}{2}\left[\langle P_{zz}\rangle - \frac{\langle P_{xx}\rangle + \langle P_{yy}\rangle}{2}\right]$$

- **Compatibilisation efficiency as difference between interfacial tension of system with (γ) and without (γ_0) compatibiliser:**

$$1 - \frac{\gamma}{\gamma_0} \in [0, 1]$$

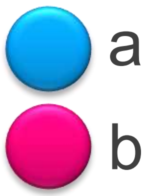
Effect of the Architecture – Graft Coplymer as Example

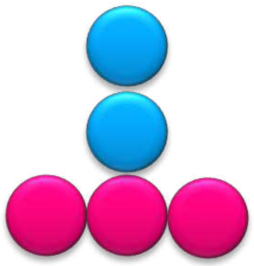
- **Compatibilisers are usually made as a copolymer of the two polymers to blend (A & B)**
- **Graft copolymers are composed of a backbone (of polymer a) and side chains (of polymer b)**
  - A & B are for the polymers to blend, a & b are for the compatibiliser



Regular Grafted Copolymers (I)

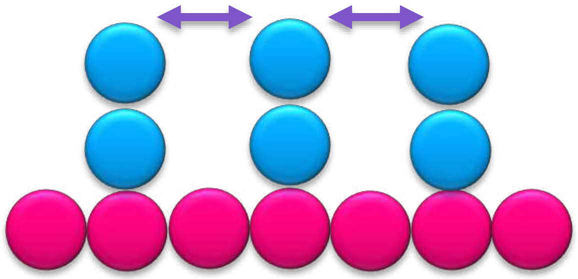
- **Side chains equally spaces along backbone**





a_3b_2

Same spacing between side chains



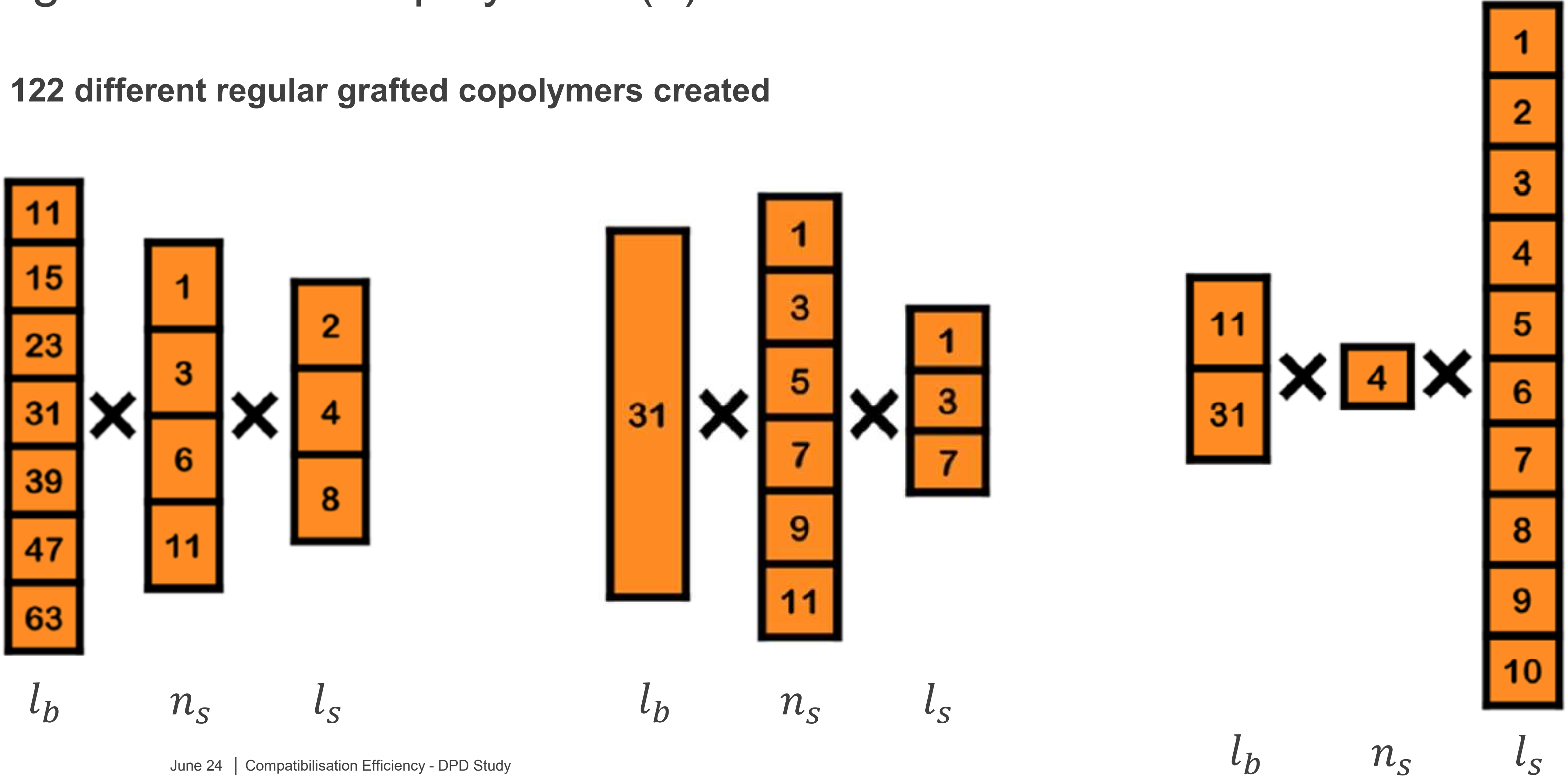
$a_7(b_2)_3$

- l_b: Length of Backbone
- n_s: Number of Side chains
- l_s: Length of Side chain
- **Notation for regular grafted polymers:**

$$\boldsymbol{l_b(l_s)_{n_s}}$$

Regular Grafted Copolymers (II)

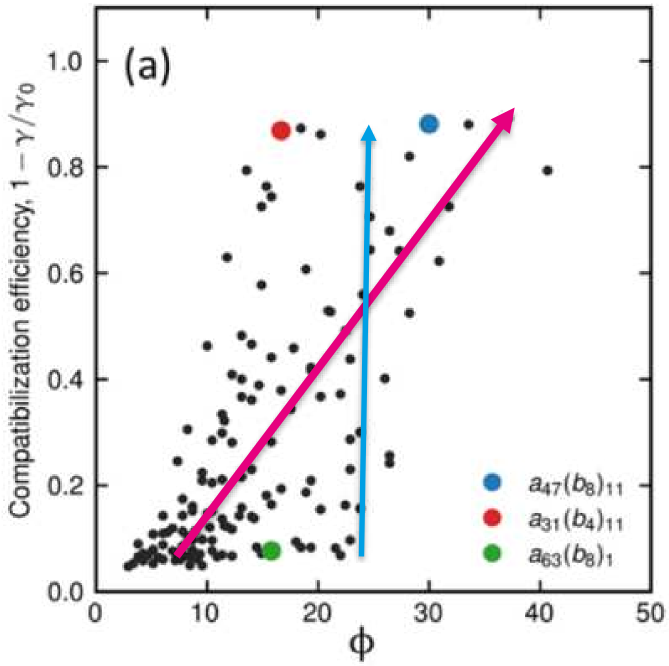
- **122 different regular grafted copolymers created**



Role of the Architecture (I)

- **Previous work, compatibilisation efficiency increase with increasing concentration of compatibiliser at interface area ϕ**

$$\phi = \frac{n_{beads\ of\ compatibiliser}}{I_{cs}} = \frac{n_{compatib}(n_s l_s + l_b)}{L_x L_y}$$



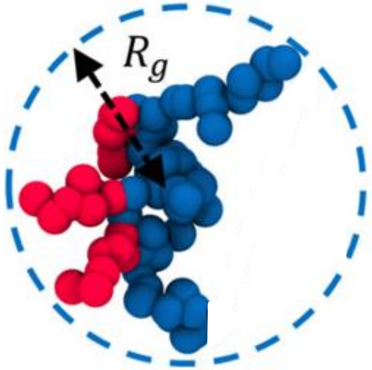
Macromol. (2021), **54**, 9551

- **$a_{AB} = 50$, highly incompatible. Same results for other a_{AB}'s**
- **$1 - \frac{\gamma}{\gamma_0}$ increases with ϕ**
- **A single value of γ shows different compatibilization efficiencies**
- **Architecture of the grafted copolymer plays a critical role**

Role of the Architecture (II)

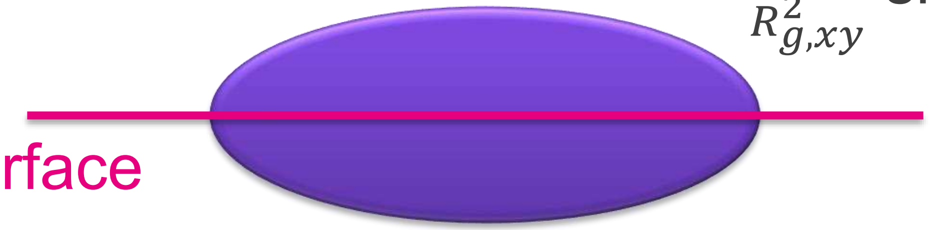
- **Radius of gyration, R_g^2**

$$\langle R_g^2 \rangle = \frac{\sum_i^{n_{molecule}} \sum_{j=1}^{l_{molecule}} \left(r_j^i - r_{cm}^i\right)^2}{n_{molecule} l_{molecule}}$$

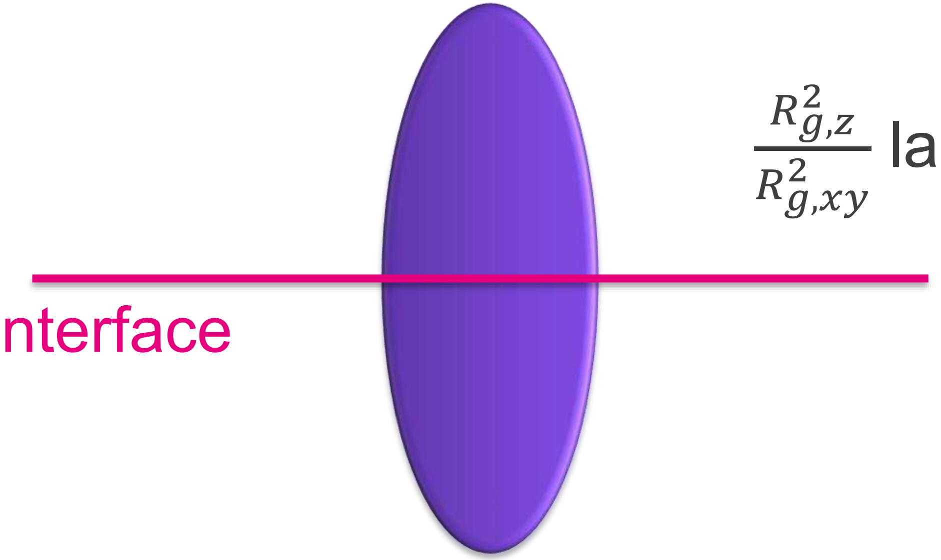


- **$R_{g,z}^2$ represents the extension of the compatibiliser perpendicular to interface**
- **$R_{g,xy}^2 = \left(R_{g,x}^2 + R_{g,y}^2\right)/2$ represents the extension of the compatibiliser along interface**

$\frac{R_{g,z}^2}{R_{g,xy}^2}$ small



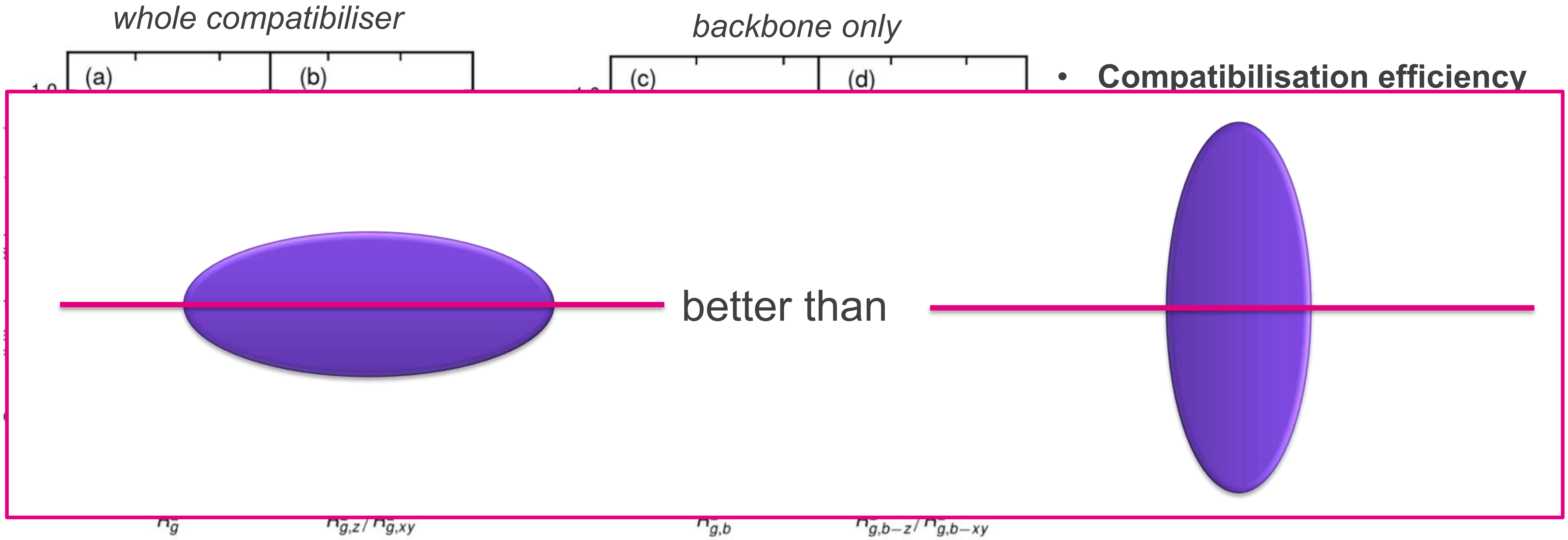
Interface



$\frac{R_{g,z}^2}{R_{g,xy}^2}$ large

Interface

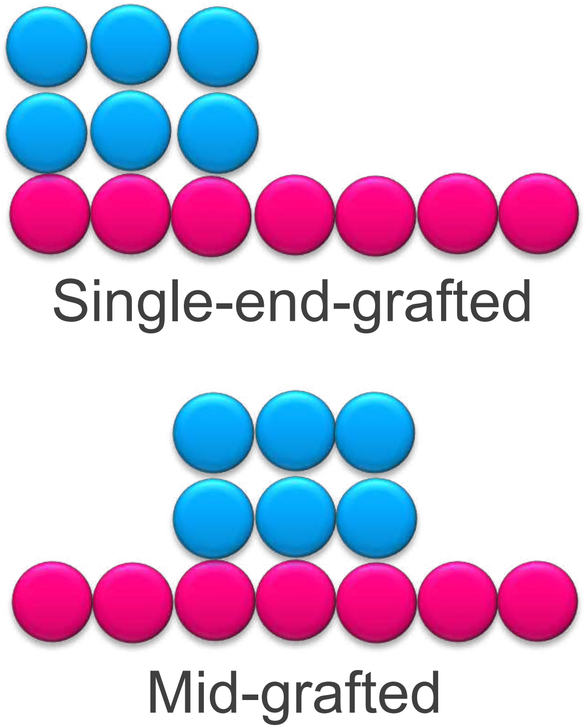
Role of the Architecture (III)

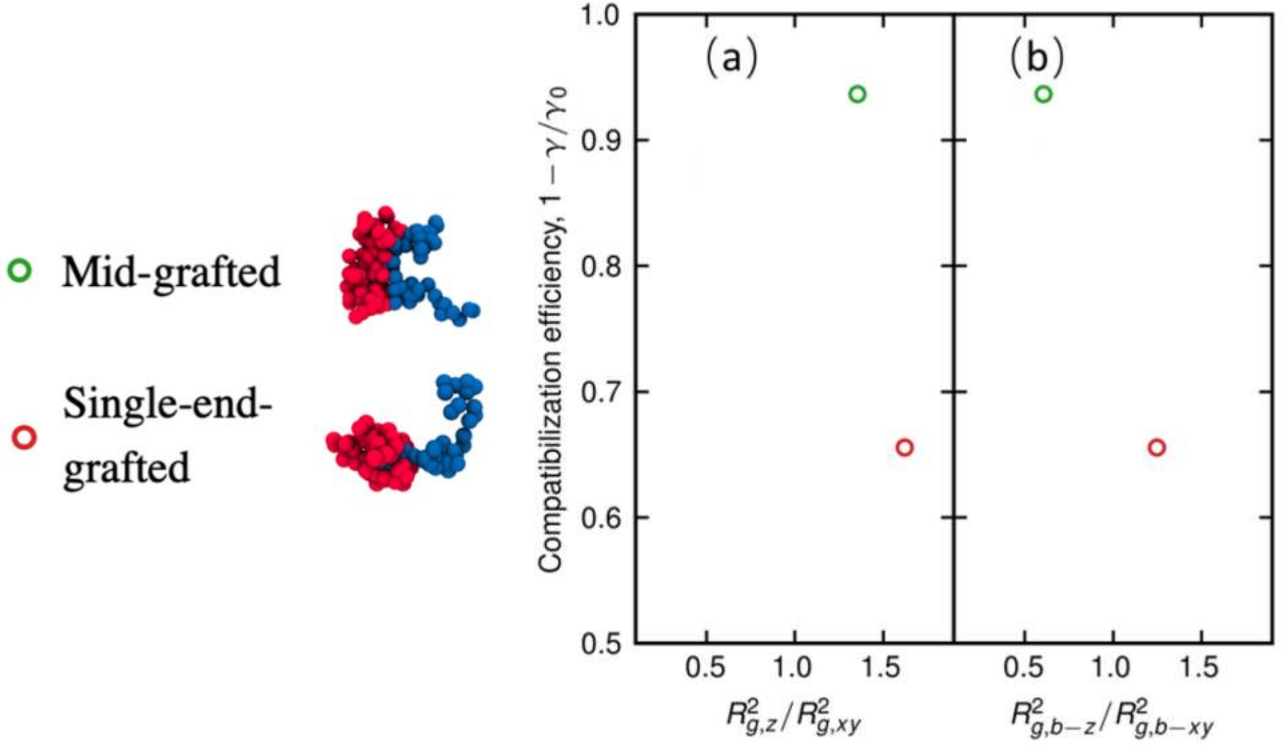


- **Compatibilisation efficiency**

- **Compatibilisation efficiency increase when compatibiliser most spread along the interface**

Beyond Regular Grafted Copolymers





- **Mid-grafted show higher compatibilisation efficiency as, specially backbone, more spread along interface**
- **This principle has been confirmed in the real polymers, a patent being filed**

Conclusions

- **DPD simulations are a useful tool to predict the compatibilisation efficiency of grafted copolymers.**
- **Simulations are a highly valuable tool for R&D in the polymer industry, as they allow to quickly screen many substances which would take too long to repeat in the lab.**
- **Compatibilisation efficiency increases with the areal concentration of the compatibilisator.**
- **The compatibilisation efficiency is maximised when the compatibilisator is most spread along the interface instead of along its perpendicular direction.**
- **This explains why mid-grafted copolymers are better compatibilisers than single-end-grafted ones.**

covestro

Acknowledgments

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LOOKING FORWARD TO QUESTIONS