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Continuous one-pot melt extrusion approach for high-density polyethylene-based vitrimers

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ACS Green Chemistry Institute
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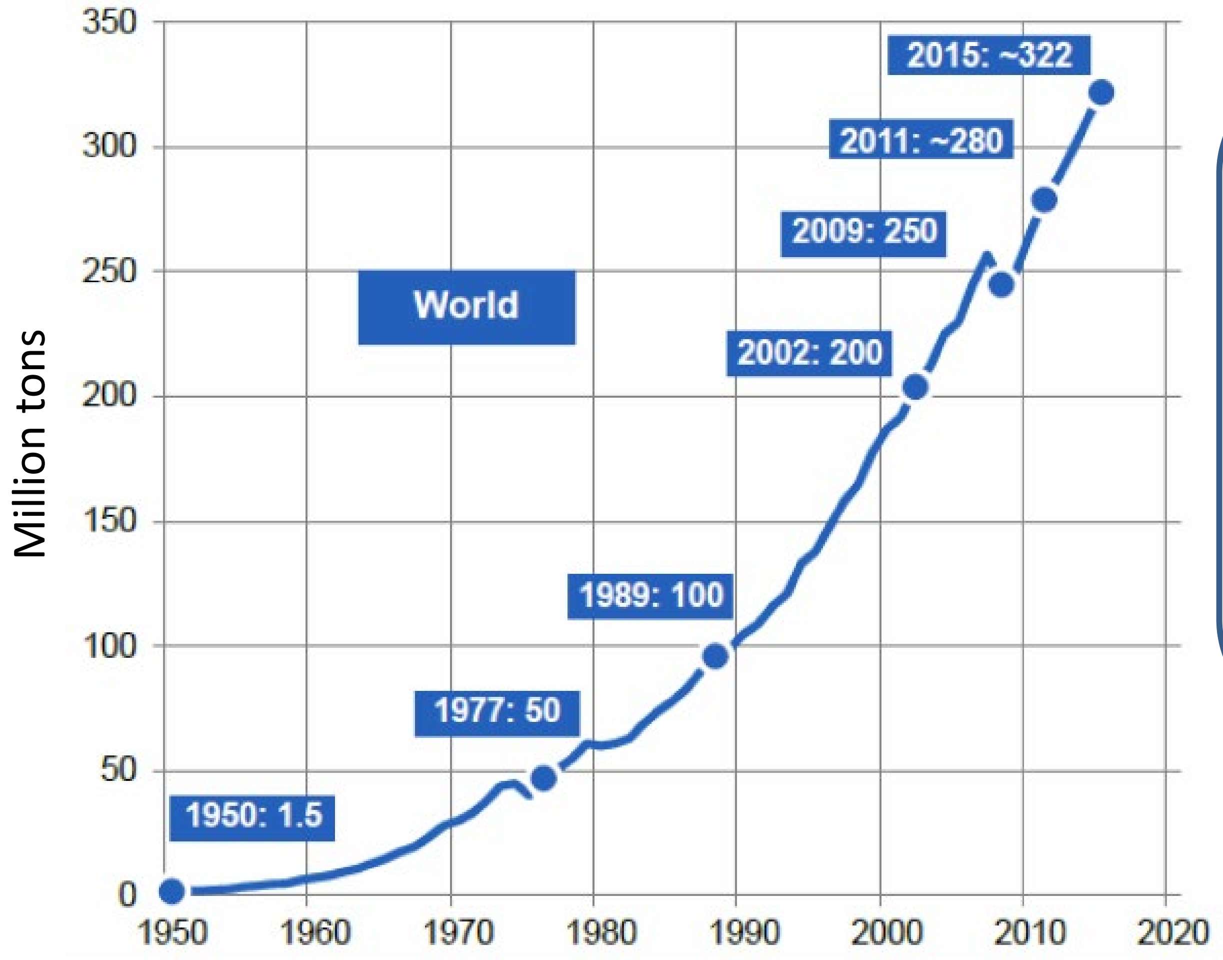
Outline

- Introduction
- Vitrimers
- Data
- Conclusion

Plastic production over the years

Polymers

- Automotive parts
- Synthetic fibers
- Cups
- Bags
- Electronics
- Biomedical products



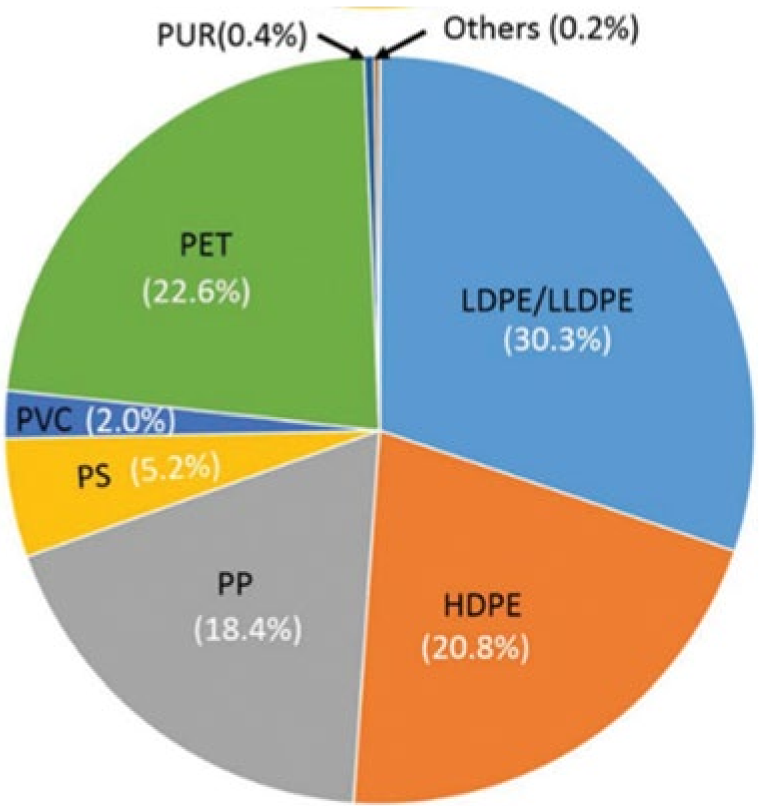
Plastic consumption by 2050

Adapted from: World Economic Forum ‚The New Plastics Economy: Rethinking the Future of Plastics‘, 2016.

Polyolefins – An important feedstock from a recycling perspective

- **Practical Recycling: Key Components**
- **Feedstock Supply in MSW**
  - POs: Predominant component (~ 60% of plastic in MSW)
- **Reprocessing of Recycled Stream**
  - POs: Easy to Process
  - Minimal degradation
  - No drying required
- **Market for Recycled Stream**
  - **Challenge: Need for increased market demand for POs**

Our aim is to find more avenues of use for recycled POs



Plastic use in the packaging industry throughout the world in 2015

Rabnawaz et al, *Green Chem.*, **2017**, *19*, 4737

Vitrimers can bridge the gap among commodity thermoplastics, engineering polymers and thermosets via thermally reversible crosslinking

a) Commodity Thermoplastics

- ✓ melt-(re)processable
- ✓ recyclable
- X solvent resistance
- X mechanical properties

b) Thermosets

- ✓ solvent resistance
- ✓ mechanical properties
- X melt-(re)processable
- X recyclable

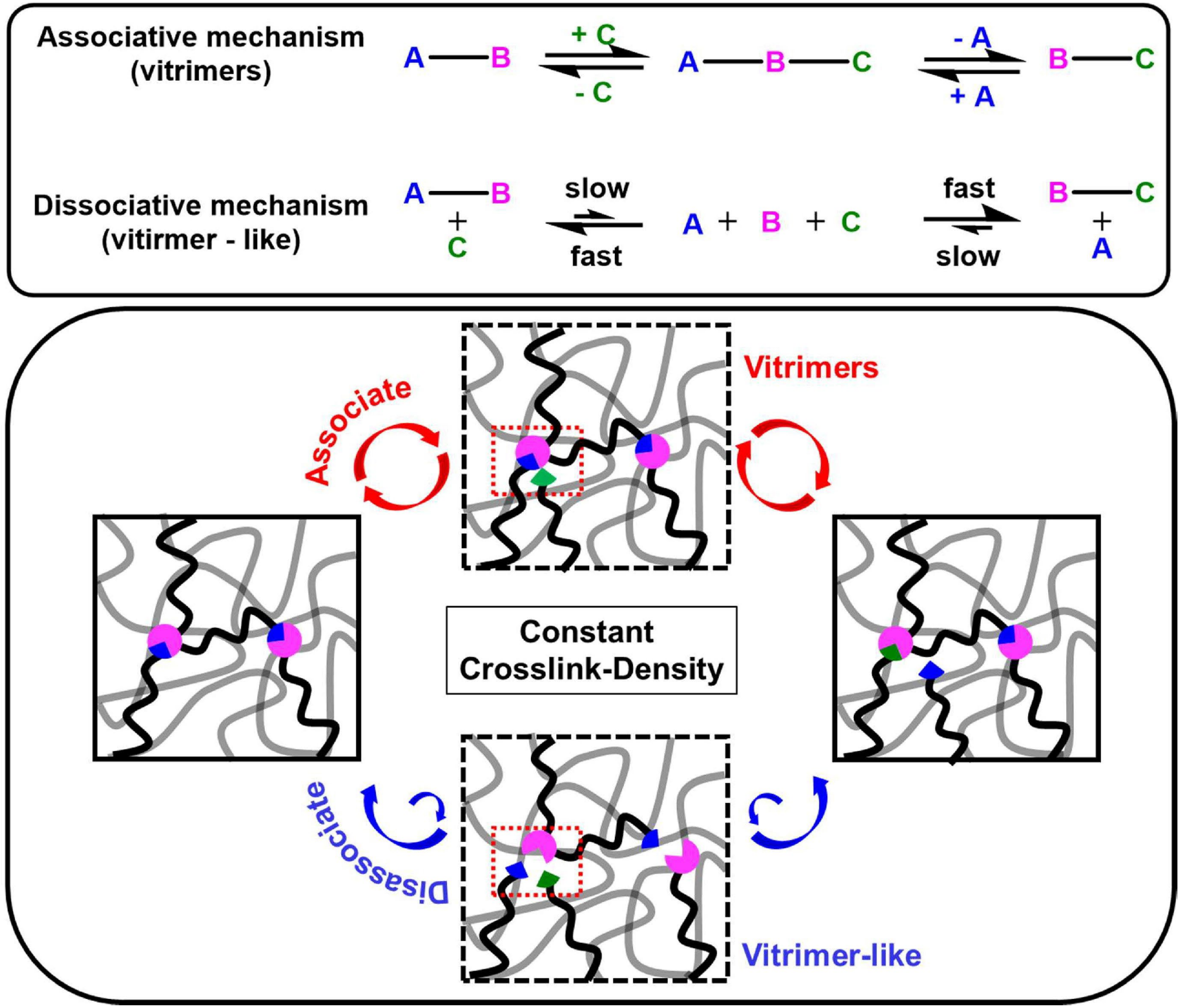
c) Engineering Polymers

- ✓ mechanical properties
- ✓ melt-(re)processable
- X cost
- X recyclability

d) Vitrimers

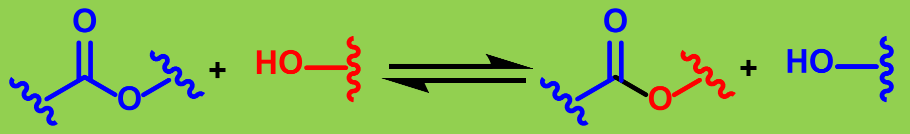
- ✓ solvent resistance
- ✓ mechanical properties
- ✓ melt-(re)processable
- ✓ recyclable

Dynamic Covalent Bonds

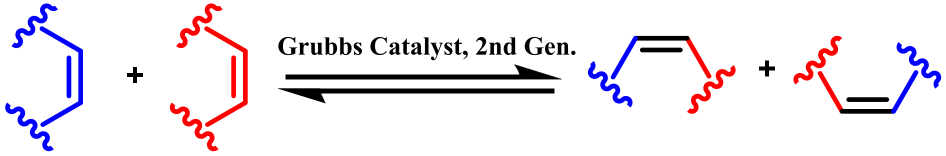


Materials Today, **2021**, *51*, 586-625; *Polymers* **2020**, *12*, 1660.

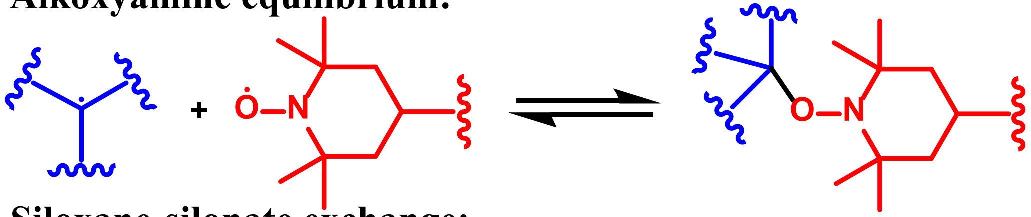
Transesterification:



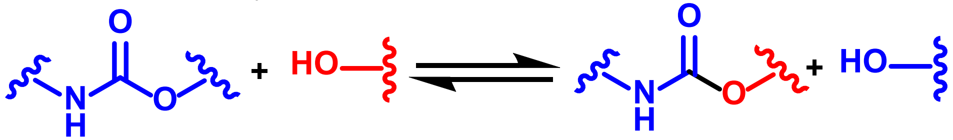
Alkene metathesis:



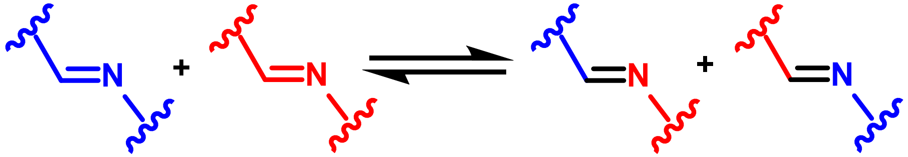
Alkoxyamine equilibrium:



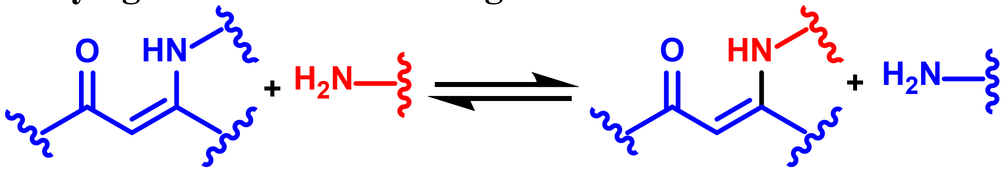
Transcarbamoylation:



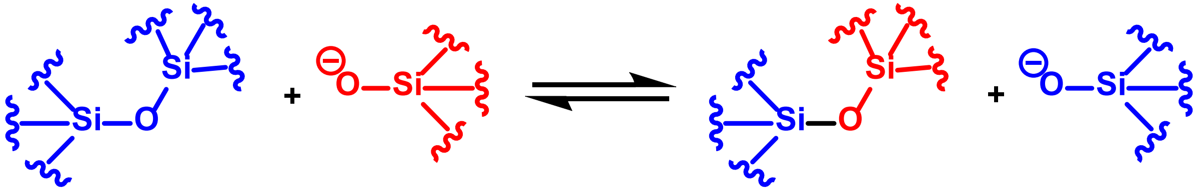
Imine exchange:



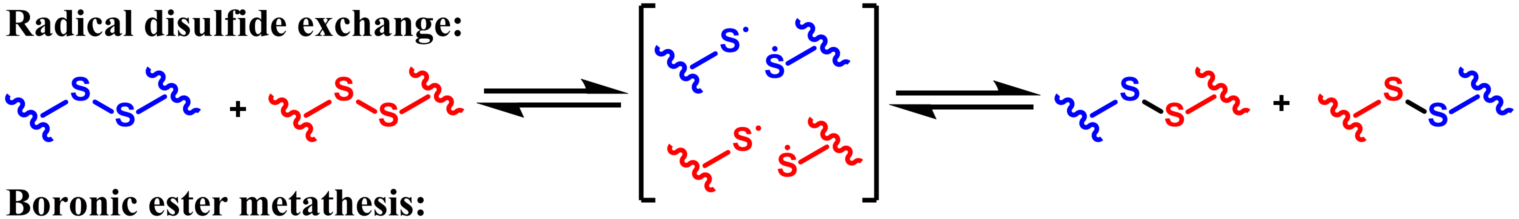
Vinyloguos urethane exchange:



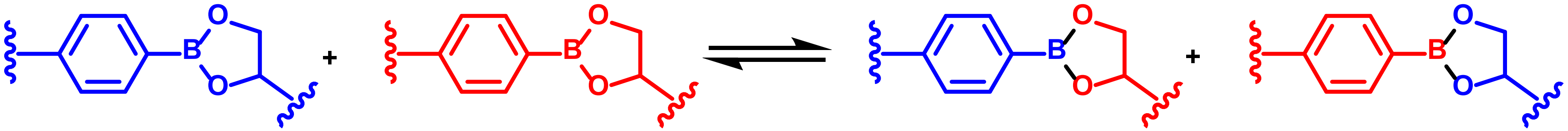
Siloxane-silonate exchange:



Radical disulfide exchange:



Boronic ester metathesis:

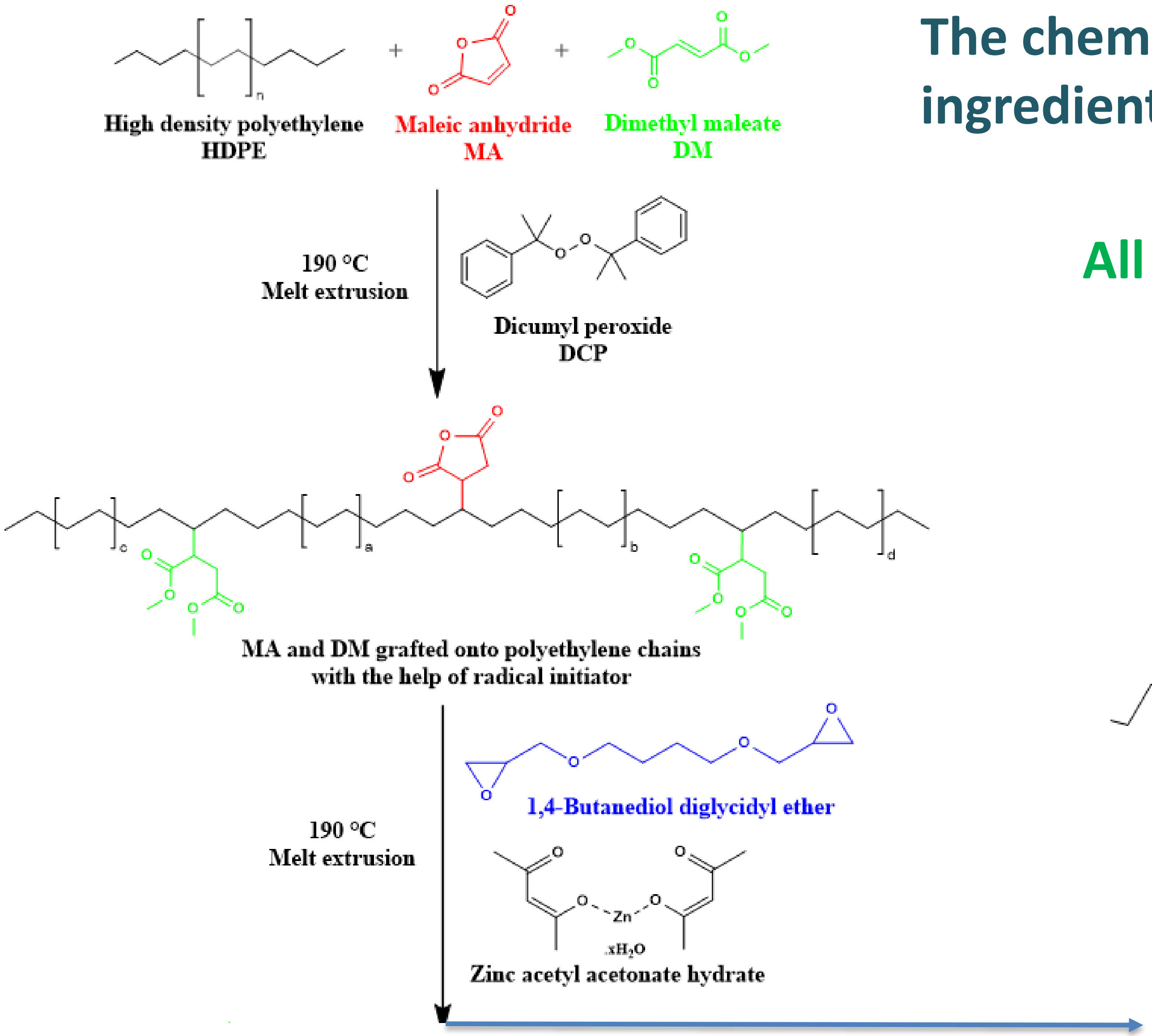


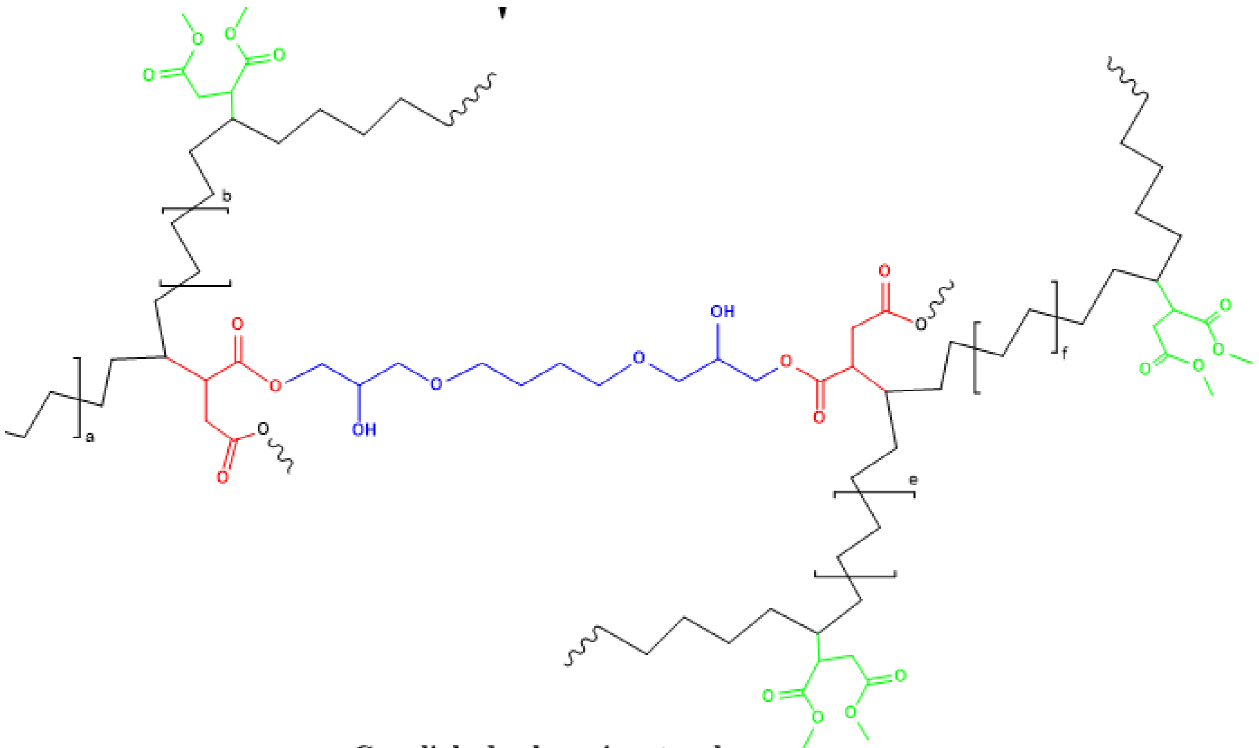
Our approach to vitrimers

Novelty	Tactics
Single-step solvent-free manufacturing of vitrimers	Use of reactive extrusion
Maximize the storage modulus at high temperatures	Use of surface energy modifiers to tailor the grafting density

The chemistry where a low surface energy ingredient is added!!!

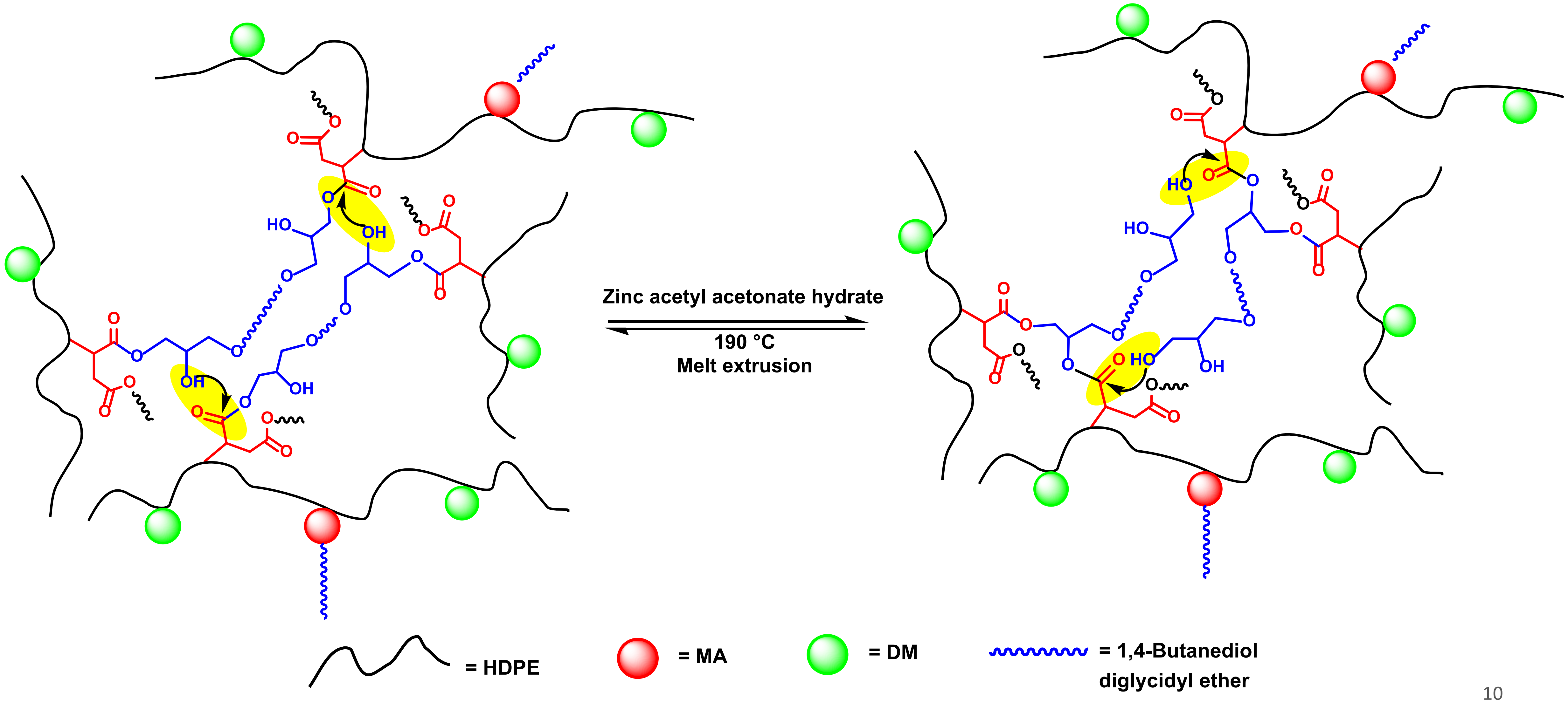
All in one step!!!!!!!



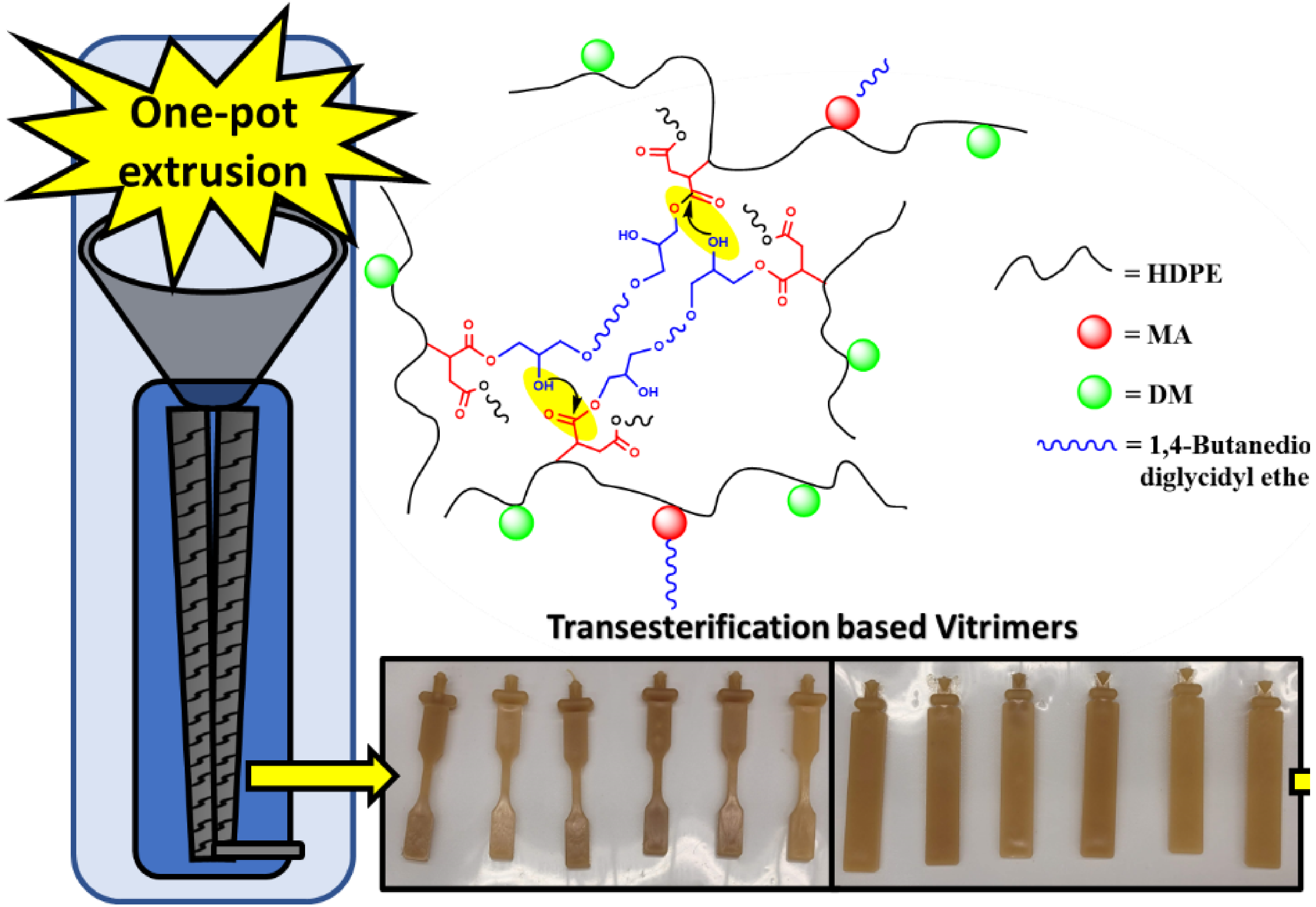


Crosslinked polymeric network

The chemistry chosen - Transesterification



One-pot extrusion with a diepoxy crosslinker



Formulations

Sample	Maleic Anhydride, MA (mol %)	Dimethyl maleate, DM (mol %)	Dicumyl peroxide, DCP (mol %)	Catalyst (mol%)	Crosslinker (mol %)
HDPE	0	0	0	0	0
$MA_{0.5}$	0.14	0.00	0.01	0.21	0.18
$MA_{0.5}$ $DM_{0.5}$	0.14	0.10	0.01	0.21	0.18
$MA_{0.5}$ DM_1	0.14	0.19	0.02	0.21	0.18
MA_1	0.29	0.00	0.01	0.21	0.36
MA_1 DM_1	0.29	0.19	0.01	0.21	0.36
MA_2	0.57	0.00	0.02	0.21	0.71
MA_2 DM_2	0.57	0.39	0.04	0.21	0.71

All the sample names used in this study are designated by the weight percentage of the grafting agent. MA_2 DM_2 denotes a sample of HDPE grafted with 2 wt% maleic anhydride (MA) and 2 wt% dimethyl maleate (DM) crosslinked with diepoxy crosslinker

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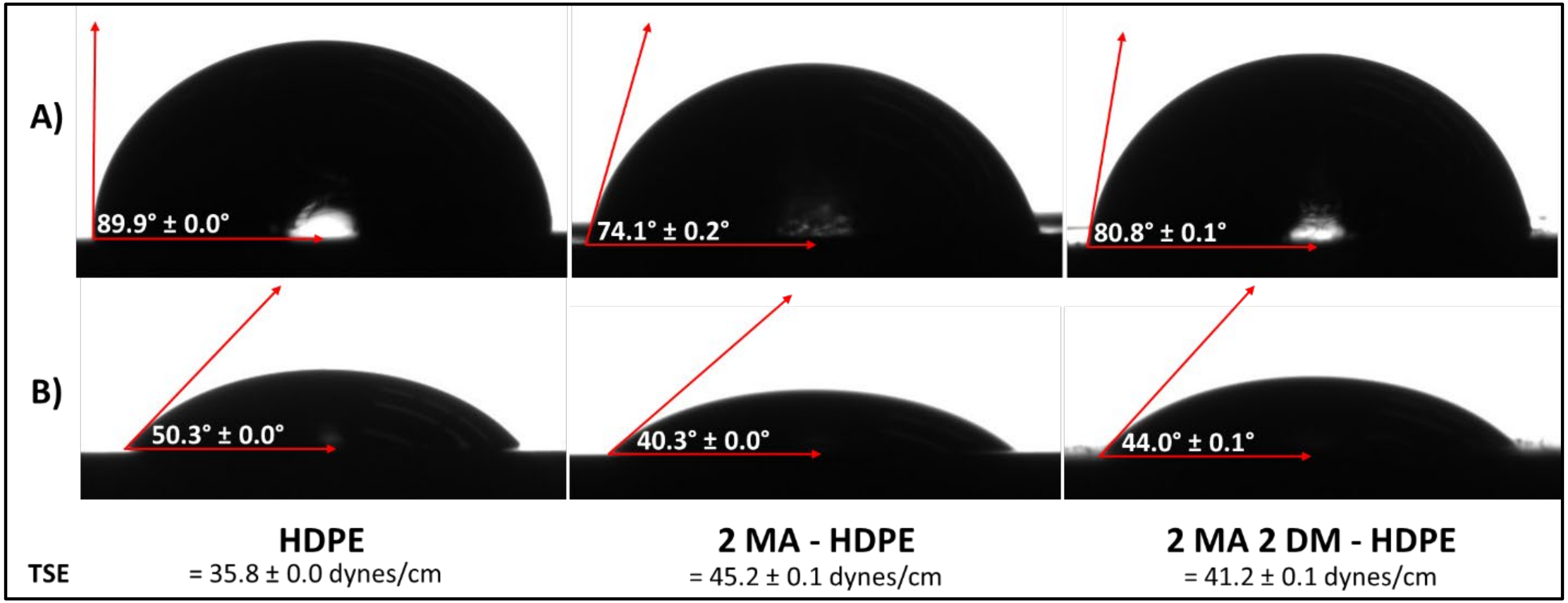
Surface energy of HDPE, 2MA-HDPE, and 2MA2DM-HDPE



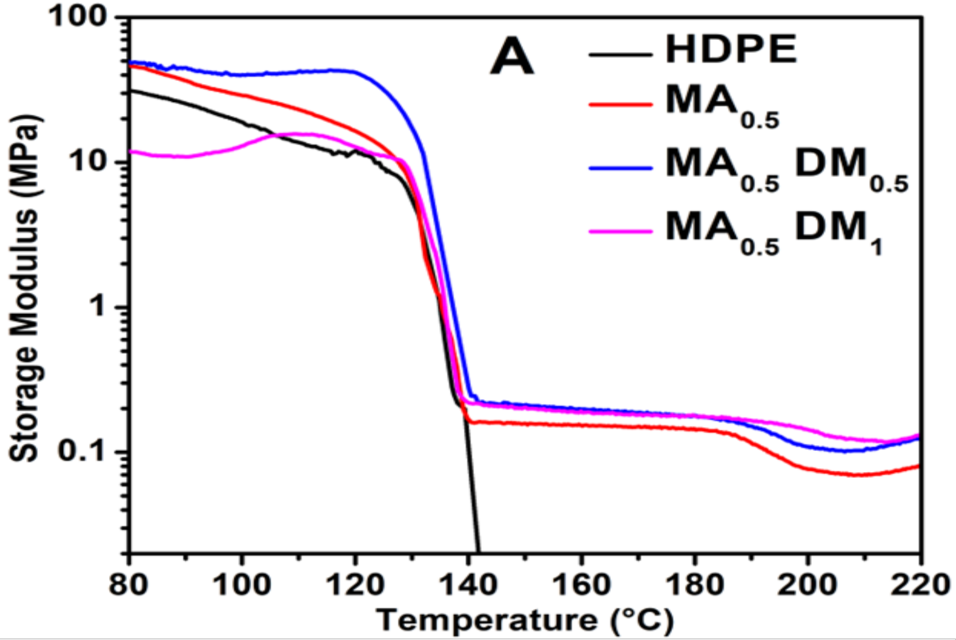
A) Water droplet images and their contact angles on HDPE, 2MA-HDPE, and 2MA2DM-HDPE, respectively.

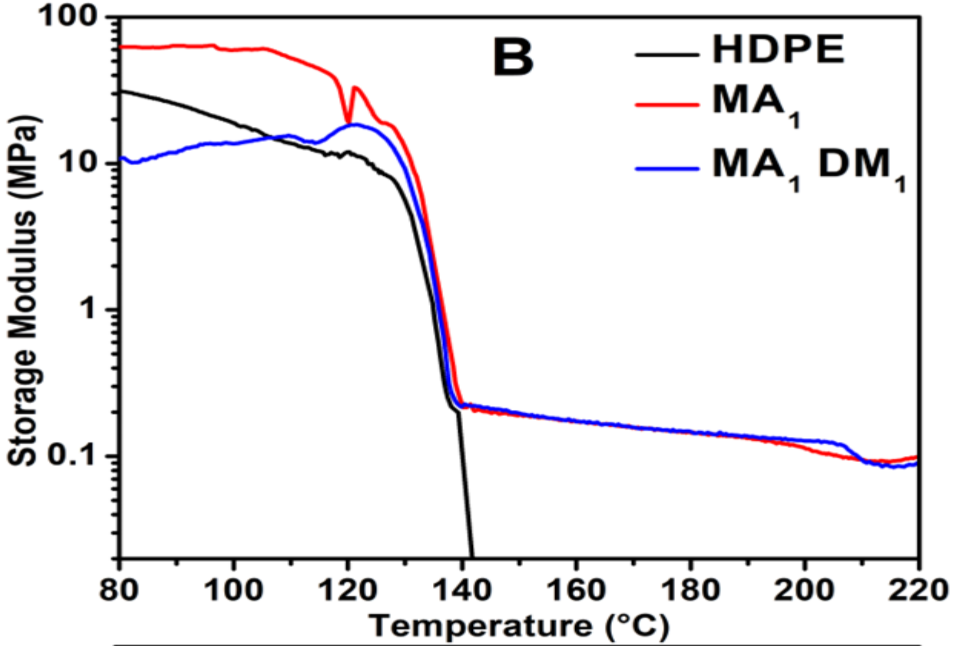
B) Diiodomethane droplet images and their contact angles on HDPE, 2MA-HDPE, and 2MA2DM-HDPE, respectively.

Dynamic Mechanical Analysis

The maximum crosslinking density for MA_2 DM_2 (3.52×10^{-5} mol/cm^3) is almost twice that of MA_2 (1.81×10^{-5} mol/cm^3).

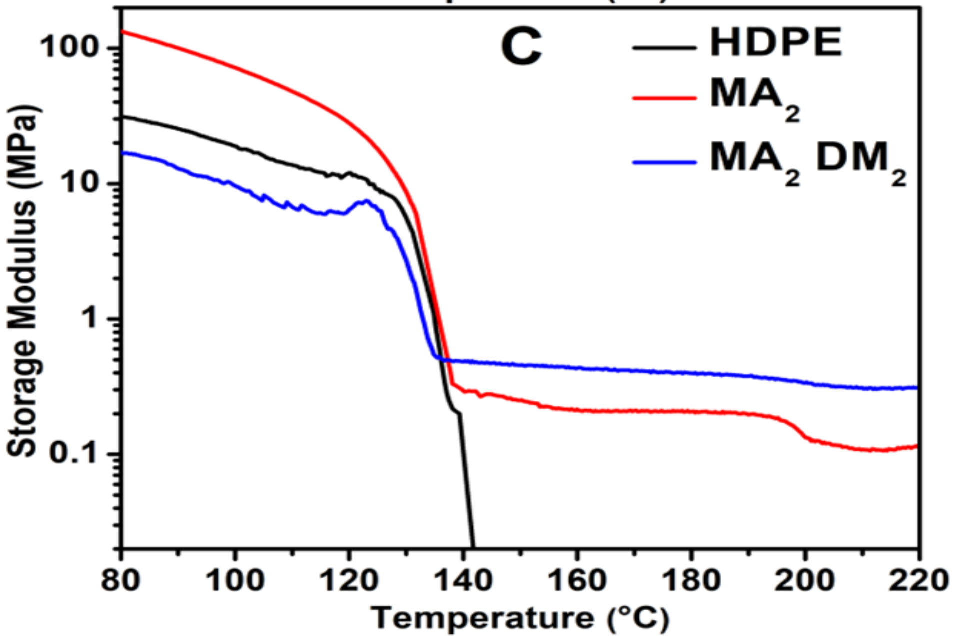
Sample code	E' at 453.15 K (MPa)	Crosslinking density v ($\times 10^{-5}$ mol/cm^3)	Melt Flow Rate (MFR) at 463.15 K (g /10 min)
HDPE	0.00	0.00	9.015 ± 0.470
$MA_{0.5}$	0.15	1.29	0.524 ± 0.028
$MA_{0.5}$ $DM_{0.5}$	0.18	1.59	0.591 ± 0.021
$MA_{0.5}$ DM_1	0.18	1.58	0.619 ± 0.014
MA_1	0.15	1.29	0.535 ± 0.009
MA_1 DM_1	0.15	1.30	0.509 ± 0.008
MA_2	0.21	1.83	0.116 ± 0.007
MA_2 DM_2	0.40	3.52	-



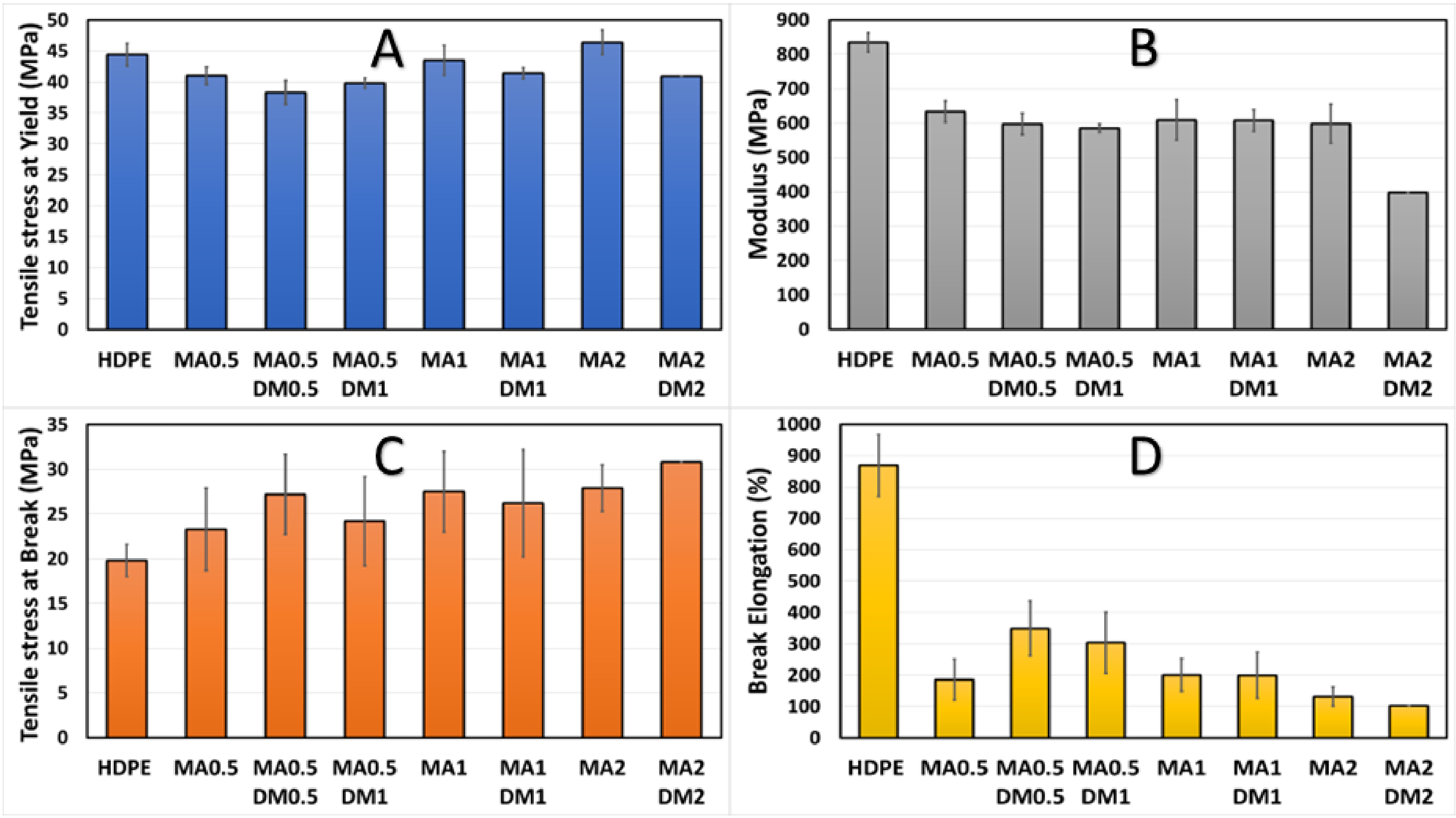


- There is a higher MA grafting density in MA_2DM_2 as compared to the MA_2 system.

- **DM is not a reactive grafting agent and does not take part in the formation of a networked structure.**



Tensile properties



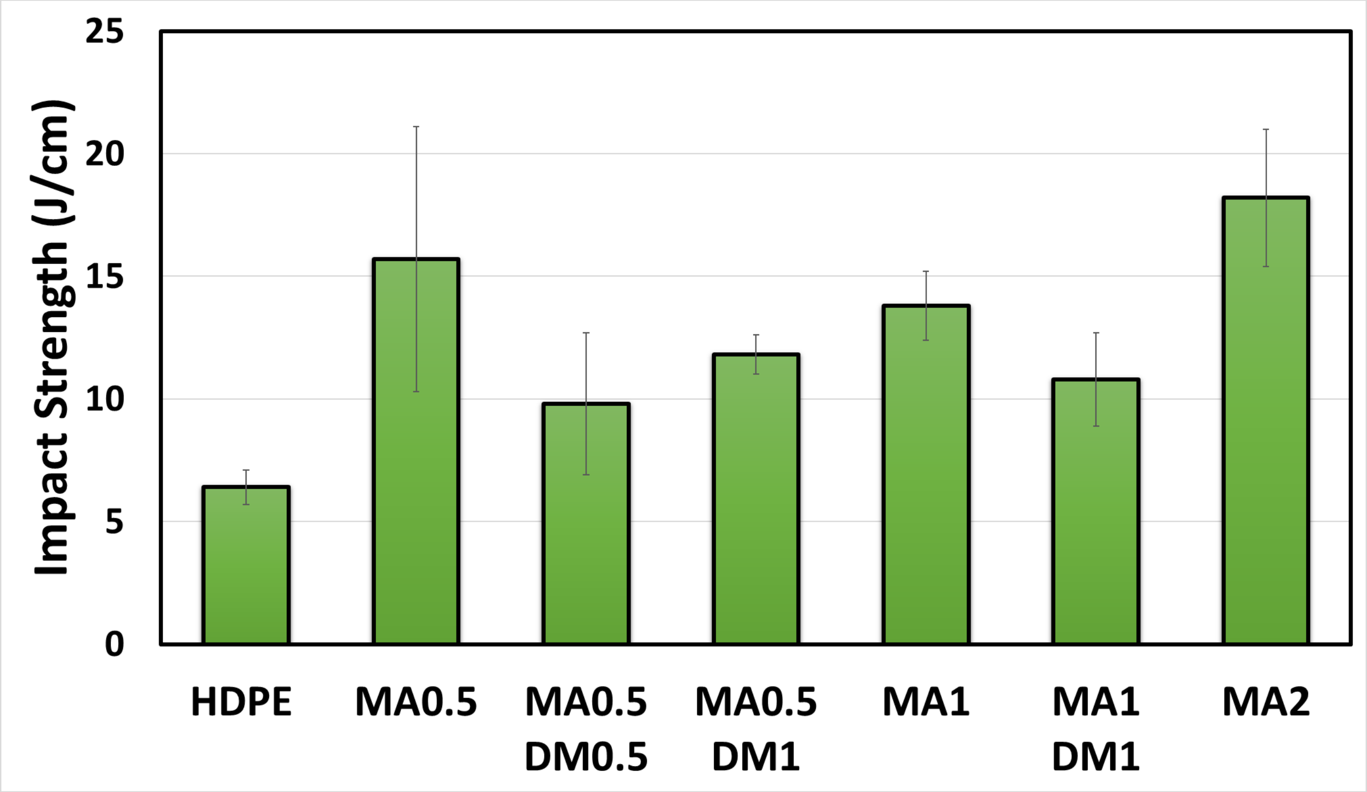
Two important factors that play contrasting roles:

1) **A decrease in the crystallinity of the polymer leads to a decrease in the tensile strength and modulus.**
2) **An increase in the crosslinking density leads to an increase in the tensile strength and modulus.**

HDPE showed much elongation because of the free polymer chain slippage due to its uncrosslinked structure.

In contrast, the vitrimers are crosslinked and their polymer chains cannot slide and thus they break at a lower elongation percentage.

Tensile properties (continued)



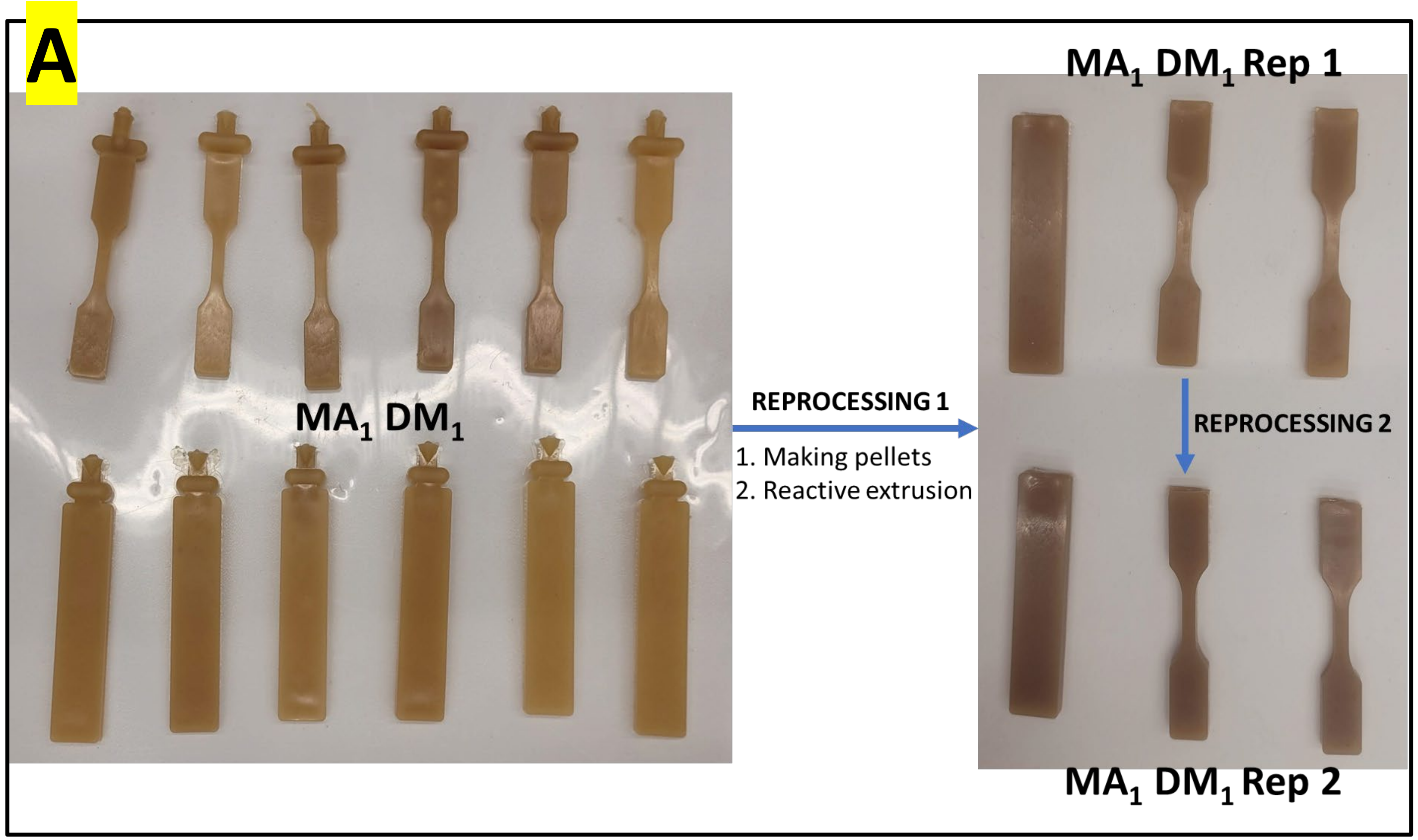
- **Both crosslinking and crystallinity significantly influence the impact strength.**
- **MA_2 which had the lowest crystallinity and highest crosslinking density, exhibited a ~2.8-fold increase relative to the control sample (unmodified HDPE).**

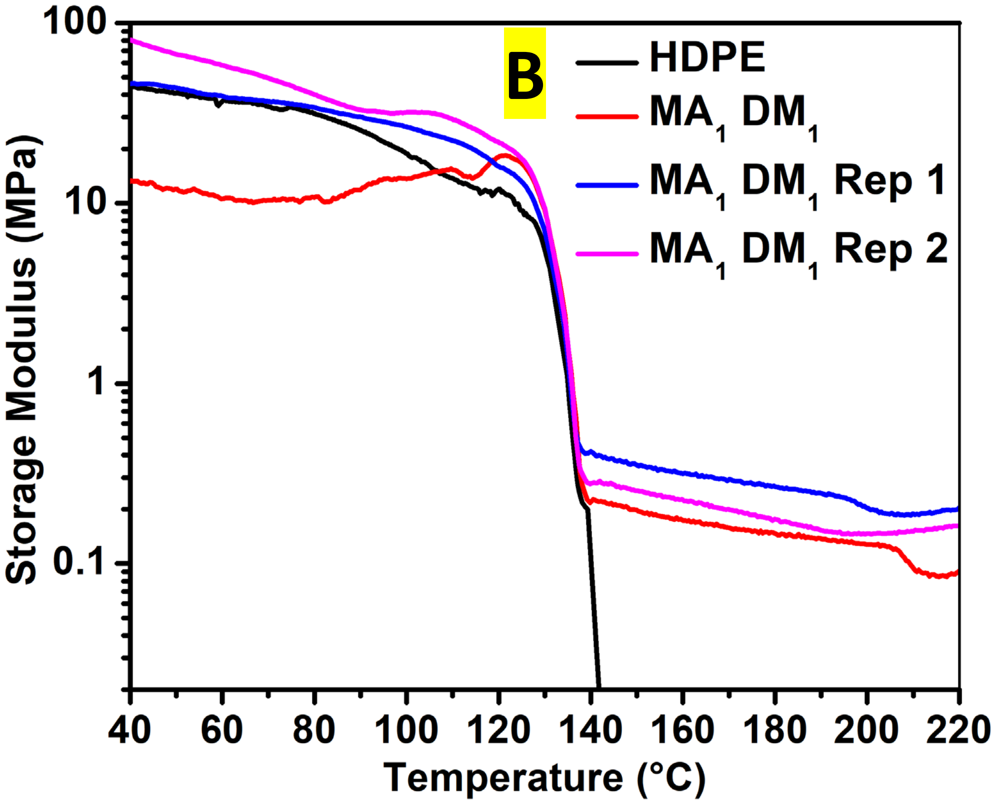
Differential Scanning Calorimetry (DSC)

Sample	ΔH_m (J/g)	ΔH_c (J/g)	χ_c (%)	T_m (°C)	T_c (°C)
HDPE	192.5	205.8	65.6	133.7	112.3
$MA_{0.5}$	189.5	204.0	64.5	133.0	117.6
$MA_{0.5}$ $DM_{0.5}$	186.3	191.6	63.5	133.4	115.1
$MA_{0.5}$ DM_1	179.2	188.6	61.0	132.8	116.3
MA_1	186.8	199.2	63.6	138.2	113.5
MA_1 DM_1	178.4	181.6	60.8	136.2	113.5
MA_2	178.1	185.0	60.7	136.1	114.3
MA_2 DM_2	155.5	159.4	53.0	134.5	110.1

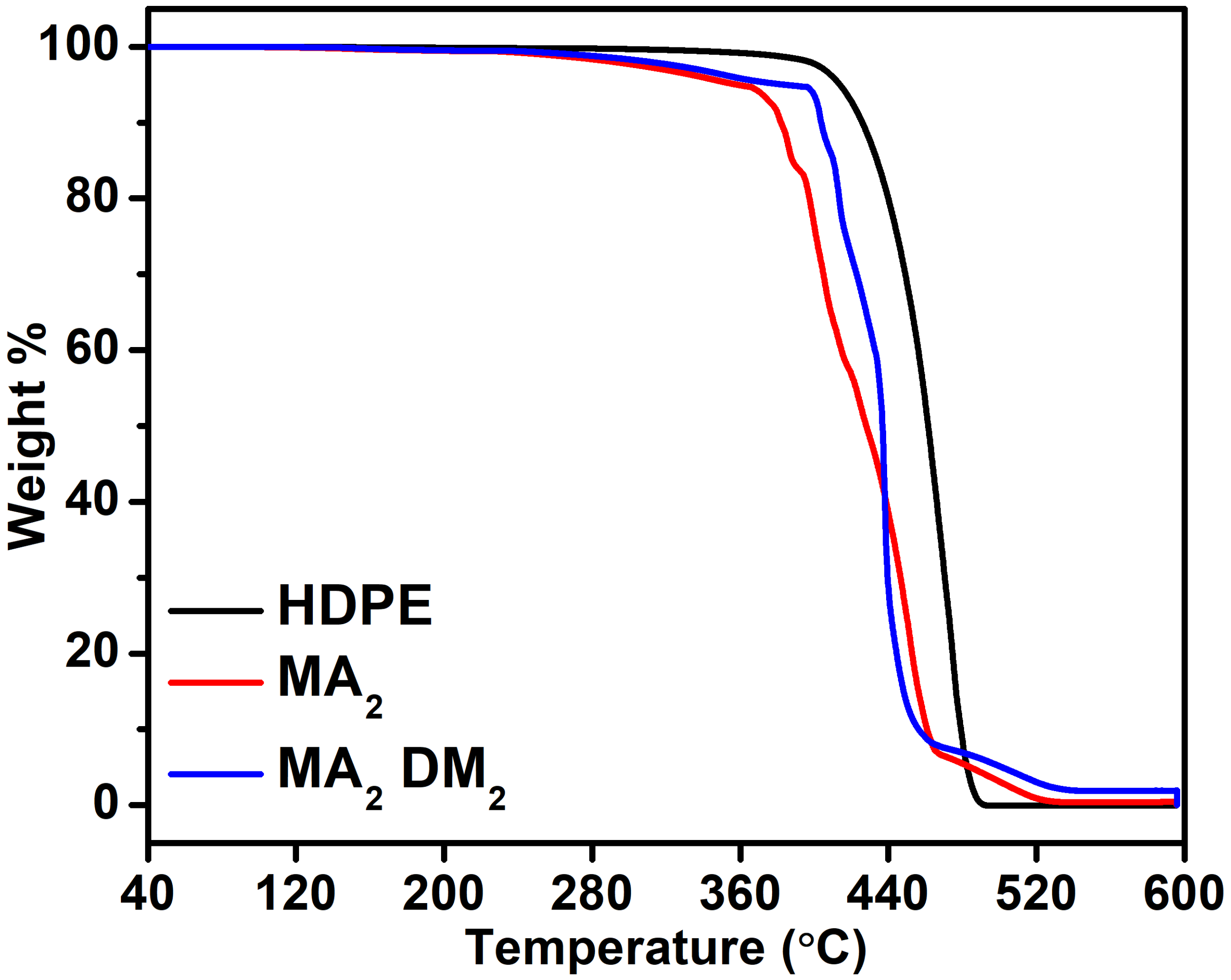
- **Crystallinity decreases as grafting is increased because MA and DM hinder chain packaging.**
- **Crosslinking also reduces crystallinity because it lowers the chain mobility, thereby preventing the chains from packing into ordered crystalline arrangements.**
- **Broad heating and cooling curves indicate that these crosslinks are well-distributed, and that there are differences in crystallite size distribution in the polymer.**

Melt-reprocessing experiments

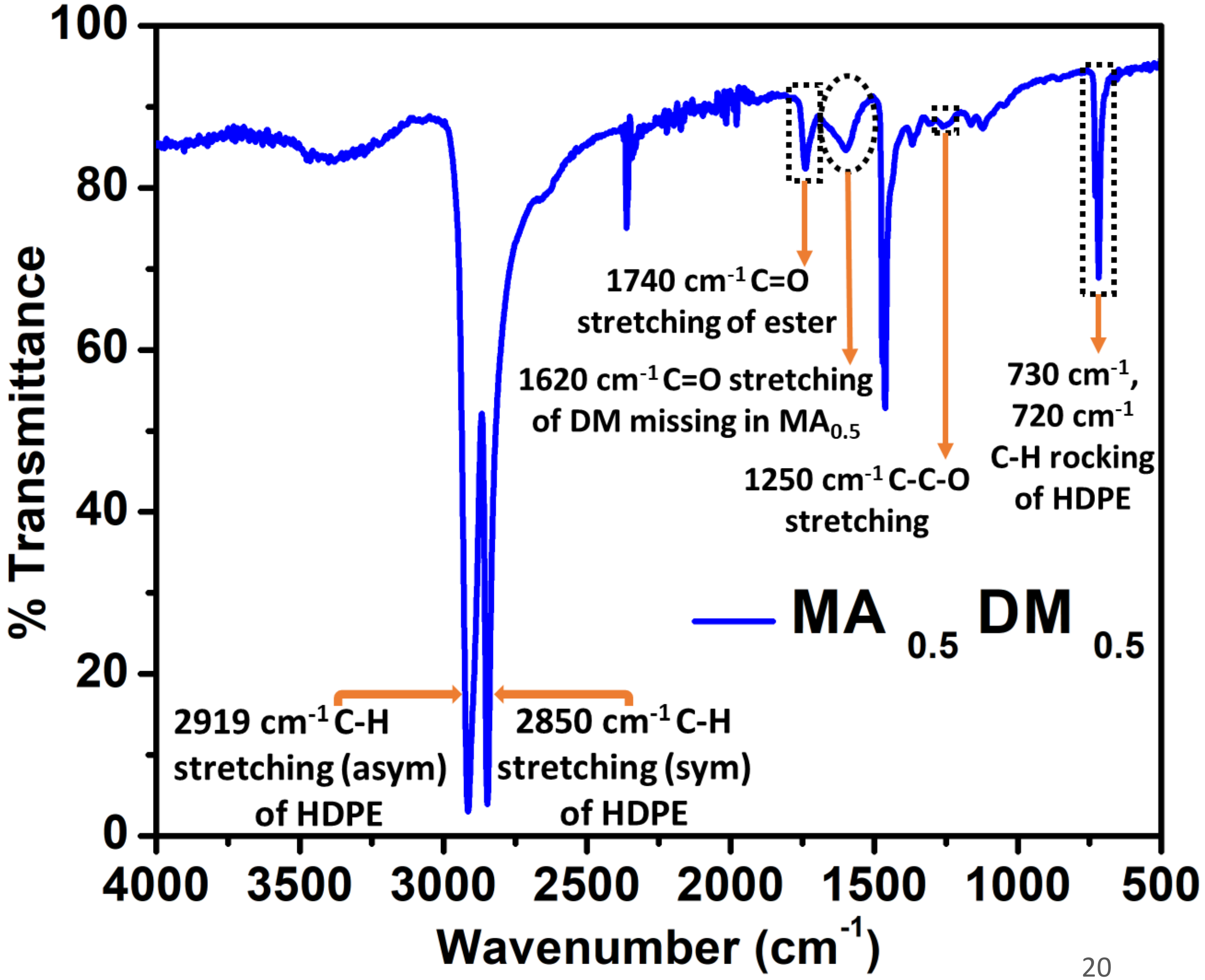




Thermogravimetric Analysis



Fourier-Transform Infrared Spectroscopy



Conclusion

- **Demonstrated a solvent-free and continuous approach to produce HDPE-based vitrimers.**

- **The interplay of the two grafting agents is an important aspect of this study because MA acted as a reactive grafting agent that promoted crosslinking while DM served as a co-agent which helped to lower the surface energy, thereby facilitating the grafting of MA to HDPE.**

- **Significant enhancement in tensile stress at break was observed for our HDPE-based vitrimers, while the tensile stress at yield was similar to that of unmodified HDPE. The impact resistance also improved as the crosslinking density increased and, in some cases, increased by 2.8 times compared that of the neat HDPE.**

- **Storage modulus beyond the T_m confirmed the presence of a crosslinked network. The crosslinking density increased two-fold for MA_2DM_2 as compared to MA_2 because of the better grafting of MA thanks to the lower surface energy provided by DM.**

- **Crystallinity decreased as the crosslinking and grafting increased. The vitrimers showed excellent thermal stability.**

In review - ACS Applied Polymer Materials

Acknowledgments

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