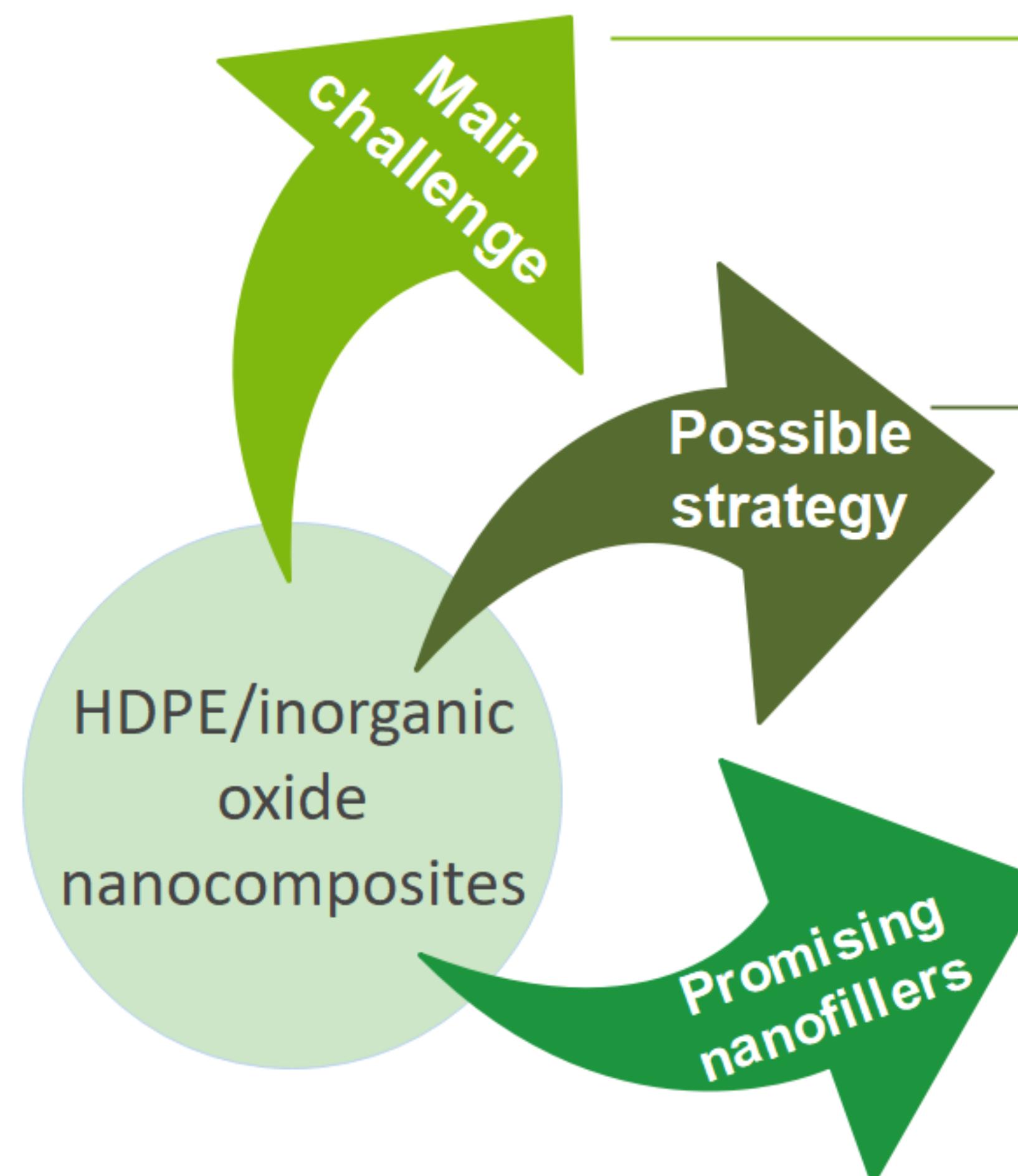


IMPROVING THE MECHANICAL PERFORMANCE OF HDPE EMPLOYING DENDRIMER-LIKE SILICA NANOSPHERES AND HALLOYSITE NATURAL NANOTUBES AS PROMISING NANOFILLERS THROUGH IN-SITU POLYMERIZATION

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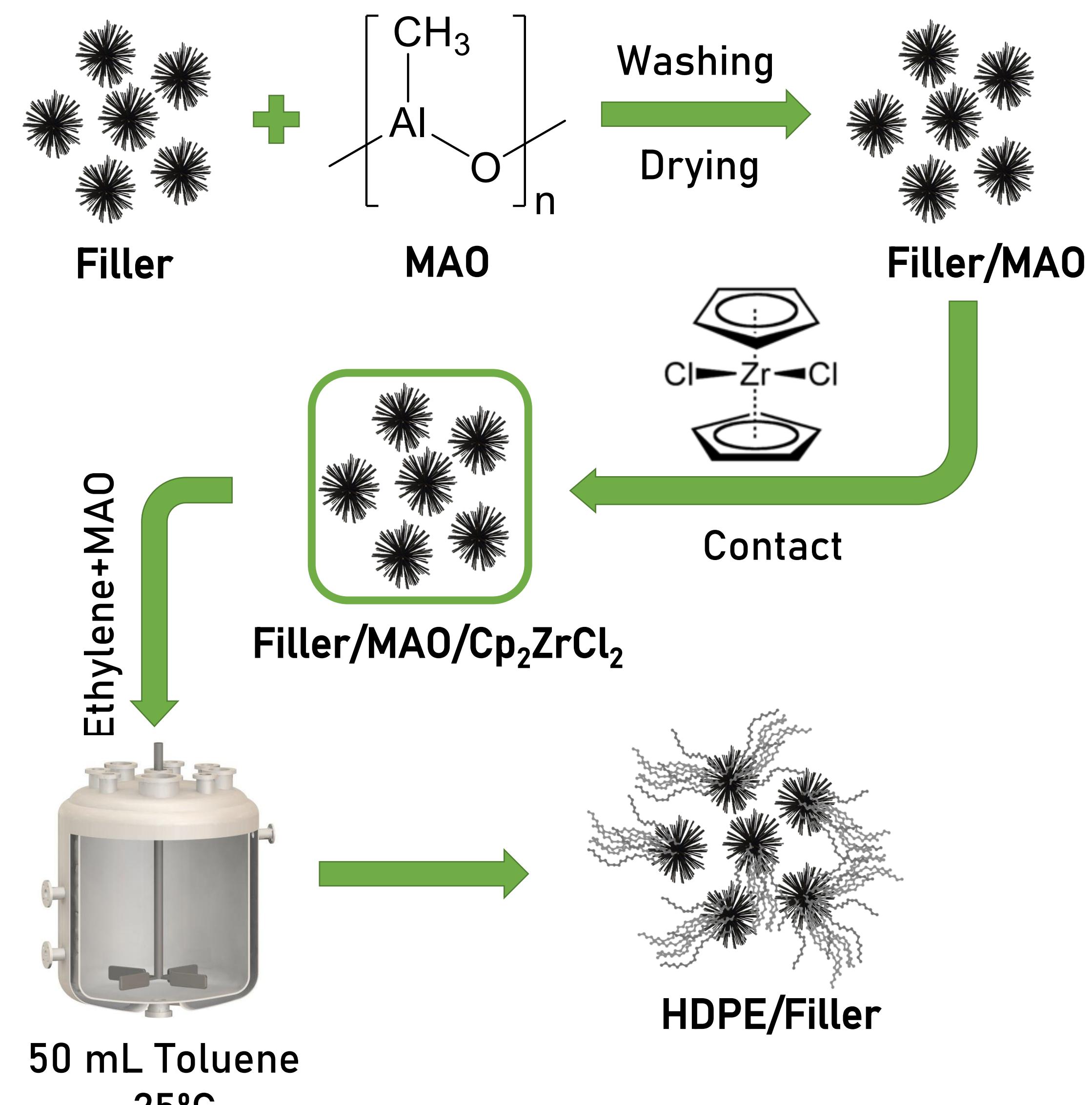


Compatibilize polymer/filler interface
Good compatibilization promotes better filler dispersion, which in turn avoids filler agglomeration and enhances the reinforcement effect.

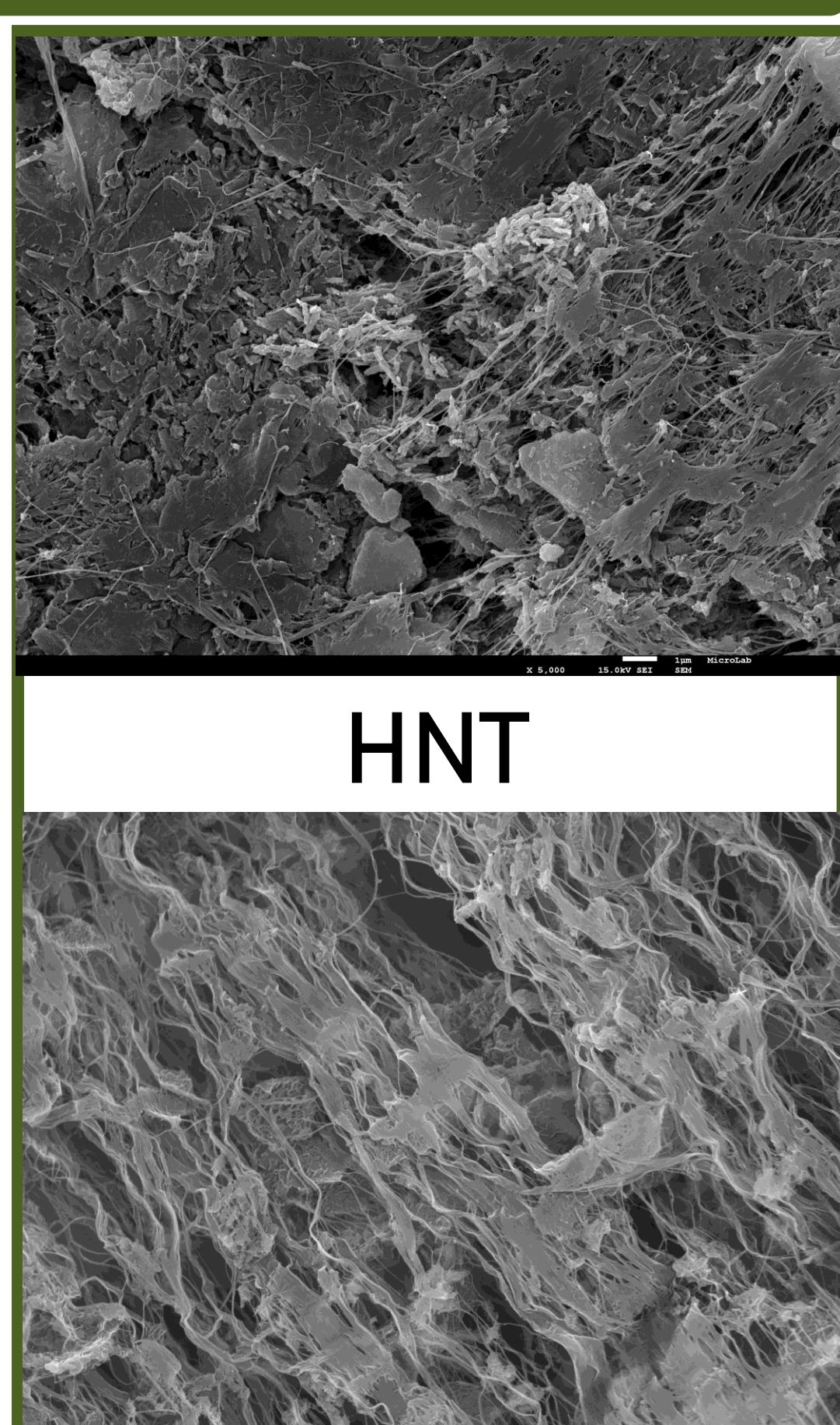
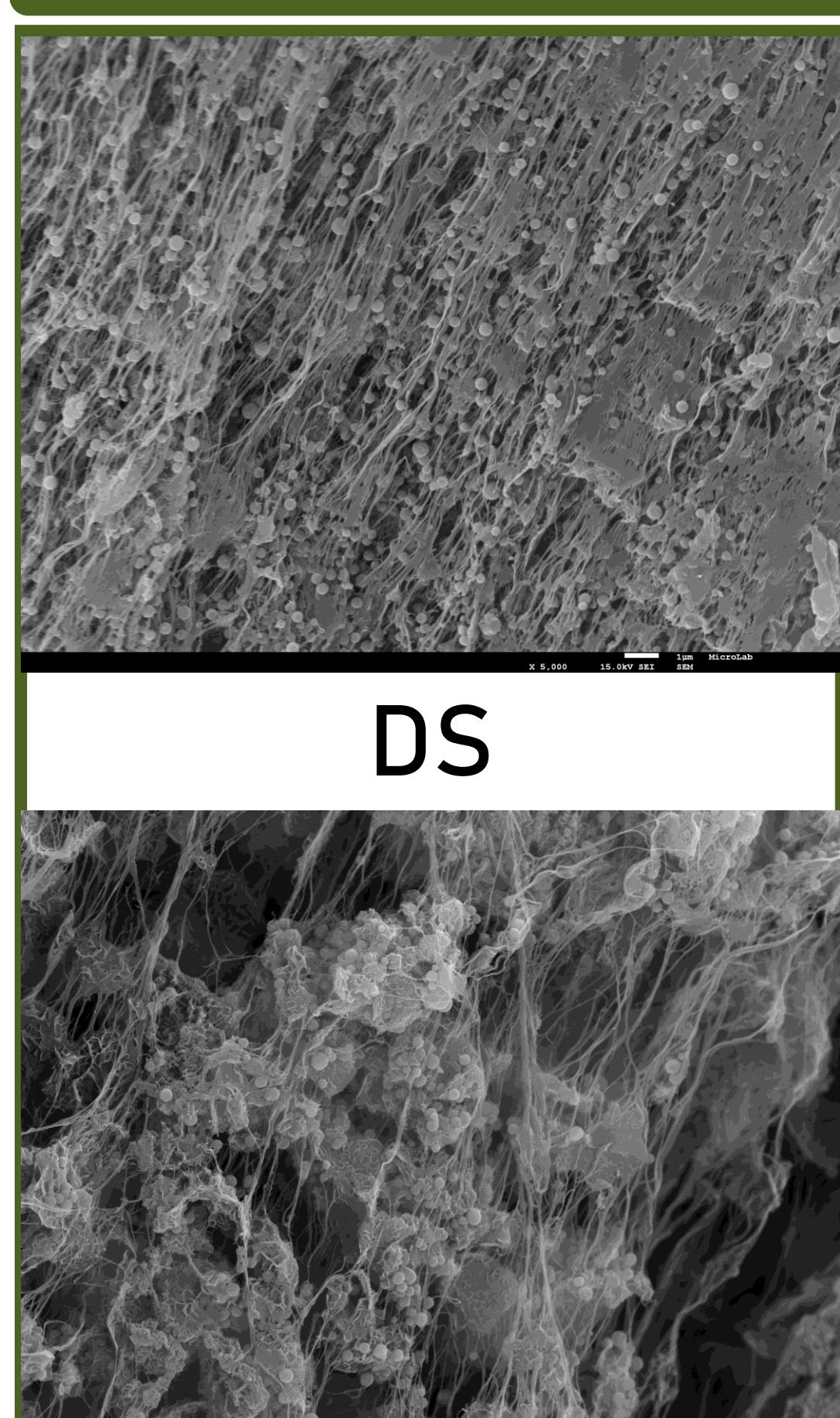
In-situ polymerization
Effective technique for nanocomposite preparation that provides better filler dispersion compared to other techniques and allows for chemical modification of the filler surface to improve compatibilization.

Dendrimeric silica nanospheres (DS)
Dendrimer-like silica nanospheres with open porosity. Has proven a promising support for metallocene catalysts in ethylene polymerization.
Halloysite natural nanotubes (HNT)
Naturally abundant aluminosilicate with a tubular morphology, which can be readily used as nanofiller with existing techniques.

Nanocomposite preparation procedure (DS-MAO/HNT-MAO)

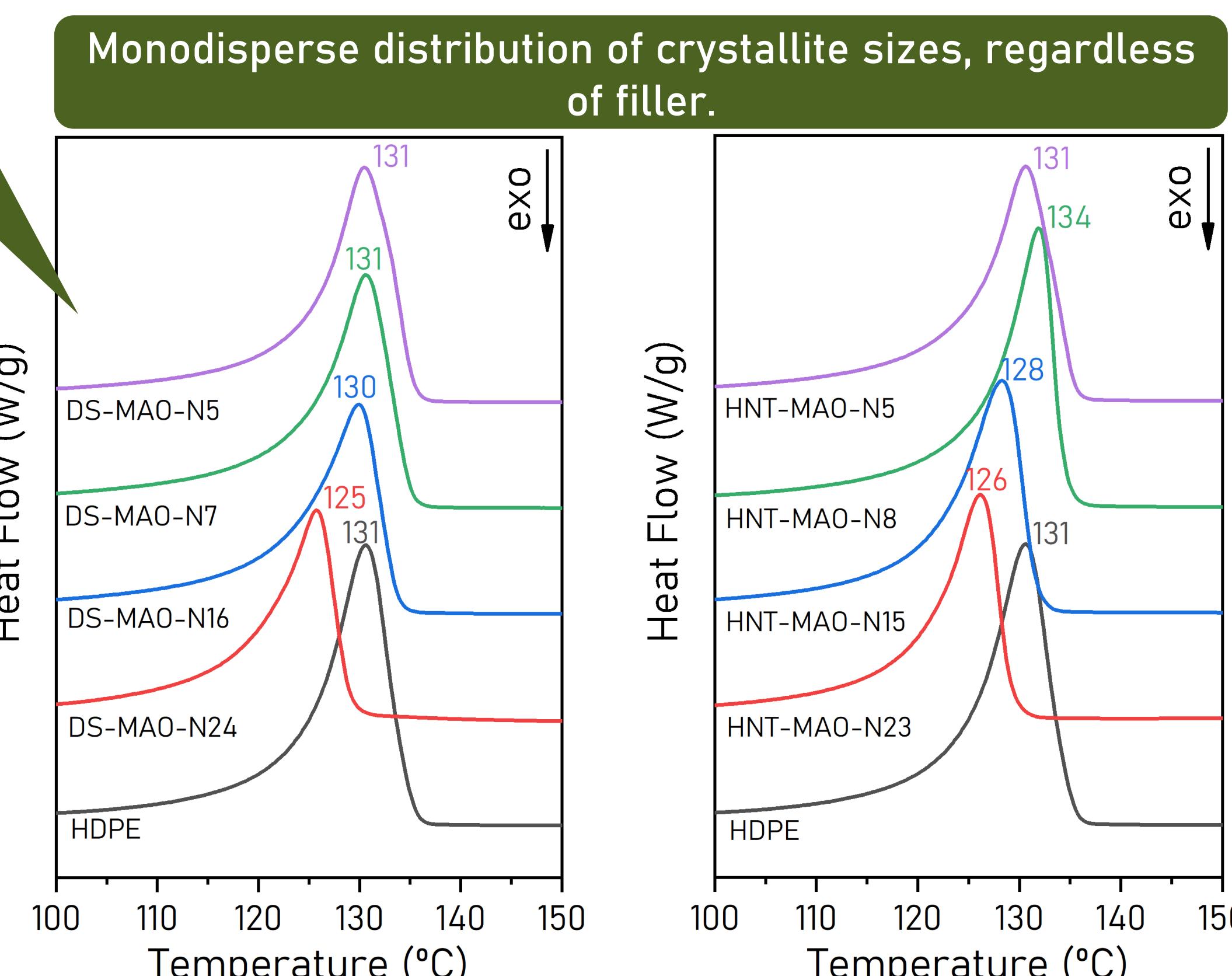


Good dispersion of DS and HNT at the beginning of polymerization.



Melting temperature decreases with higher filler loadings, regardless of filler.

Rapid polymer growth hides the nanofiller particles at the end of polymerization.



Nanocomposite	Total yield (mg)	Filler loading (wt. %) ^[a]	T _m (°C)	Young's Modulus (%) ^[b]	Elongation at break (%)
HDPE	1330	-	131	100	840
DS-MAO-N5	1070	5	131	110	660
DS-MAO-N7	1240	7	131	115	790
DS-MAO-N16	1220	16	130	124	700
DS-MAO-N24	1240	24	125	146	410
HNT-MAO-N5	1050	5	131	105	600
HNT-MAO-N8	1160	8	134	108	740
HNT-MAO-N15	1220	15	128	114	930
HNT-MAO-N23	1190	23	126	123	770

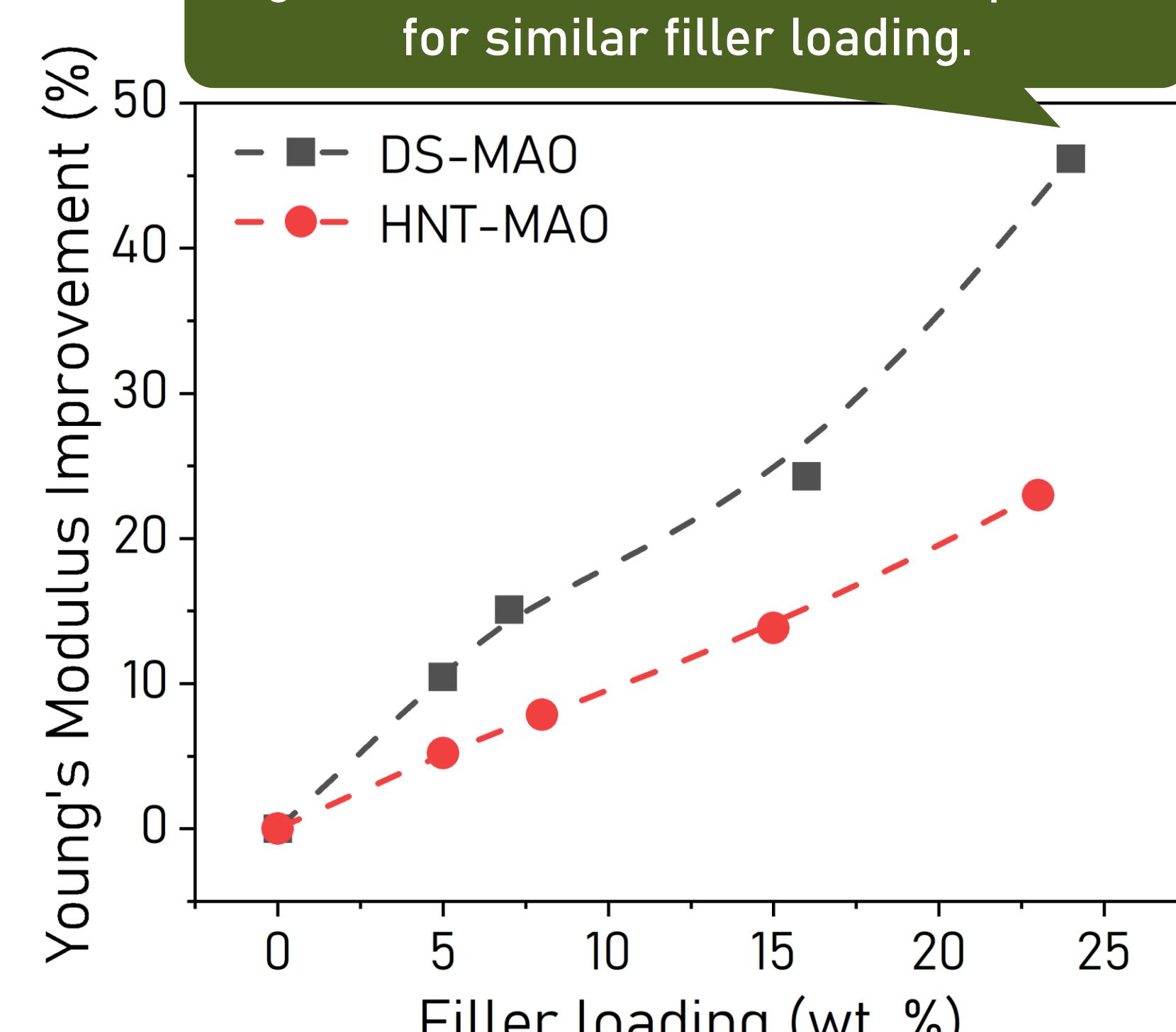
All loading on the support/filler = 4 mmol/g, Zr loading on the support/filler = 35 µmol/g, Al/Zr ≈ 1600 during polymerization

^[a]Determined by TGA. ^[b]Reference Young's Modulus for HDPE = 415 MPa

All composites retain polymer limit stretching ability to a significant degree, confirming good filler dispersion.

HNT nanocomposites retain HDPE ductility better than the DS analogues, at higher filler loading.

Higher stiffness for DS nanocomposites for similar filler loading.



Conclusions

- Nanocomposite were successfully prepared and show good filler dispersion, regardless of the filler.
- DSC shows monodisperse crystallites in the polymer matrix, regardless of filler, with decreasing melting temperature as more filler is included.
- All nanocomposites show stiffness improvement, although DS leads to higher stiffness compared to HNT at similar filler loadings.
- Nanocomposites retain limit stretching ability of HDPE, with HNT reinforced materials presenting higher elongation at break than the DS analogues at higher filler loadings.

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REFERENCES

- [1] João M. Campos, João Paulo Lourenço, Ernesto Perez, Maria L. Cerrada and M. Rosário Ribeiro, Journal of nanoscience and nanotechnology, 6 (2009) 3966
- [2] Duarte M. Cecílio, Auguste Fernandes, João Paulo Lourenço and M. Rosário Ribeiro, ChemCatChem, 10 (2018) 3761
- [3] Katarzyna Szpilka, Krystyna Czaja and Stanisław Kudla, Polimery, 06 (2015) 359

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