Evaluating the Impact of Structure and Morphology of Plastomers on the Low Shrinkage Performance TPOs

Sabancı Universitesi

CV & Research Paper

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Ravago

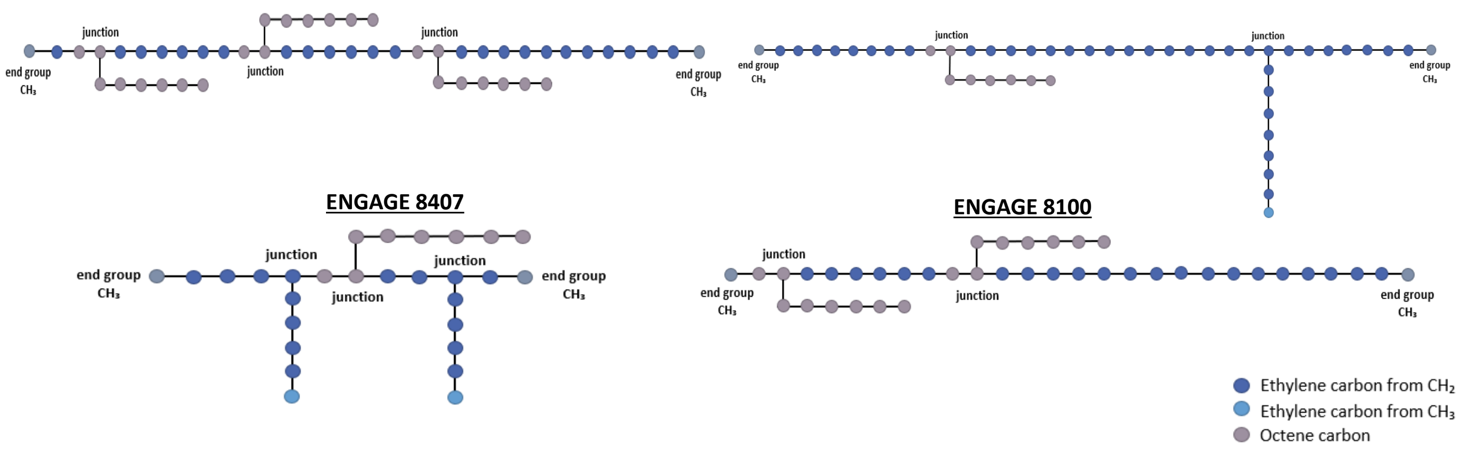
Abstract. Thermoplastic Polyolefins (TPOs) are among the most used polymeric materials in the automotive industry due to their superior elastomeric properties compared to commercial polyolefins. Thermoplastic polyolefins (TPO's) are prepared by mixing a polyolefin, usually copolymer polypropylene, and a plastomer in a certain fraction to improve elastomeric properties. One of the most challenging problems in the automotive industry during the production of these materials is to control the mold shrinkage of TPOs since the parts having very high aspect ratios, such as bumpers, exterior trims, and glass run channels, are produced by those materials. This problem is used to solve by talc addition to TPO formulations. However, talc, having high density, results in high weight and high fuel consumption for vehicles which poses environmental hazards and pollutions. More sustainable and environmentally friendly way to solve the mold shrinkage problem is considered as tuning the crystalline/amorphous region ratio in TPOs by plastomer incorporation. For that purpose, TPO formulations were prepared with plastomers having different crystallinity values and then these TPO samples were investigated under three main criteria, such as the effect of plastomer load, the effect of crystallinity of plastomer, and the effect of flow (MFI) of plastomer. Therefore, the structure analysis of plastomers and their Molecular Dynamics (MD) simulations were conducted to obtain a better understanding of the structural mechanism that affects the plastomer properties and the properties of final products formulated with these plastomers. The complementary results of structural and MD analysis of plastomers and final TPO samples showed that TPO compound named "sample A" contains 70% plastomer with medium crystallinity and 30% copolymer PP. It shows low mold shrinkage values in parallel (0,19%) and perpendicular (0,2%) to flow direction and optimum tensile strength (13,4 MPa), and elongation at break (815%) results. Findings of this study is useful in understanding the micro-events taking place during the compounding of PP with plastomers, and to explain the necessary PP-plastomer ratio with desired mechanical traits.

Plastomers – Structural Characterization – NMR Analysis

Property	Engage 8100	Engage 8540	Engage 8842	Engage 8407
Density (g/cm³)	0,87	0,90	0,85	0,87
MFI (g/10min.)	1	1	1	30
Crystallinity (%)	18	34	13	21
Octene Content (%)	38	17	45	40

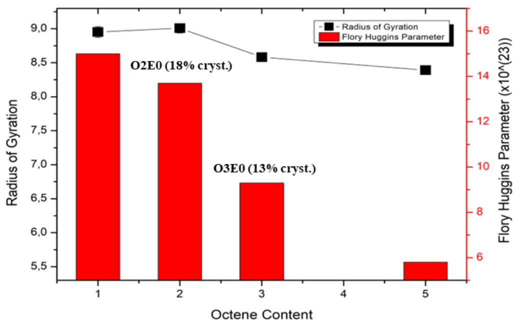
Engage Number	Code	MFI (g/10min.)	Crystallinity (%)	Octene Content (wt%)
8842	O3E0	1	13	47,8
8100	O2E0	1	18	39,8
8407	O1E2	30	21	28,4
8540	O1E1	1	34	26,2

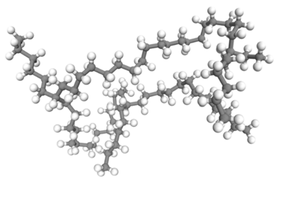
✓ Decreasing octene content increases the crystallinity



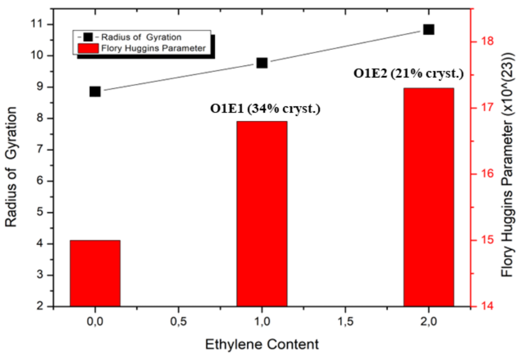
Plastomers – Molecular Dynamics Simulation Analysis

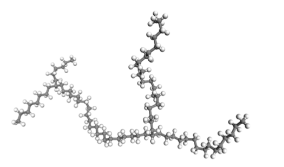
Radii of Gyration (Rg) and Flory-Huggins Parameter values vs octene content & ethylene content





3D chemical structure of plastomer having packed formation (O3E0)



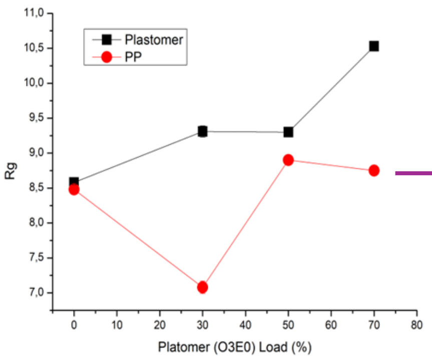


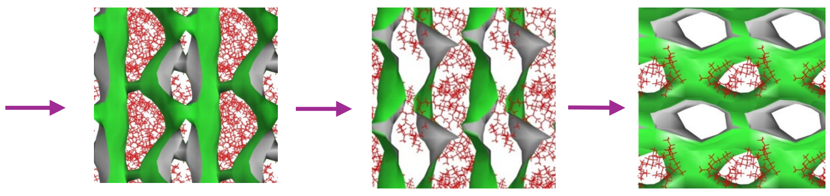
3D chemical structure of plastomer having extended formation (O1E1)

- ✓ **Increasing octene content** in plastomer decreases the Rg value
  - Plastomer chains fold up, get a packed conformation, and generate a cluster of molecule chains, preventing alignment of polymer chains and decreasing the crystallinity
- ✓ Increasing octene content decreases the Flory-Huggins parameter
  - Increasing compatibility
- ✓ **Increasing ethylene content** in plastomer increases the Rg value
  - Plastomer chains extend and become aligned, and increase crystallinity
- ✓ Increasing ethylene content increases Flory Flory-Huggins parameter
  - Decreasing compatibility between PP and plastomers

TPO Sample Preparation & Molecular Dynamics Analysis

Composition	PP	A	B	C	D	E	F	G	H	I	J	K	L
Polypropylene	100	30	30	30	30	50	50	50	50	70	70	70	70
O2E0 (MFI=1, Cryst.=18%)		70				50				30			
O1E1 (MFI=1, Cryst.=34%)			70				50				30		
O3E0 (MFI=1, Cryst.=13%)				70				50				30	
O1E2 (MFI=30, Cryst.=18%)					70				50				30

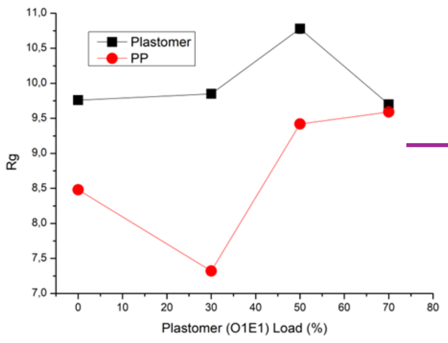


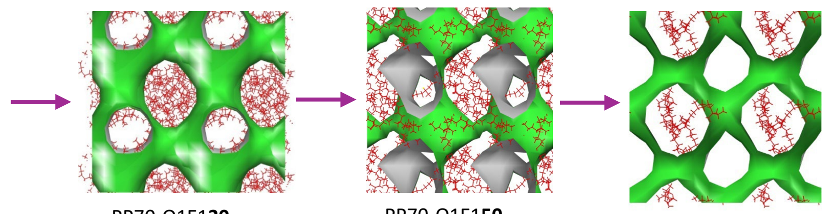


PP70-O3E0**30** (Compound K) | PP70-O3E0**50** (Compound G) | PP70-O3E0**70** (Compound C)

- Increasing Rg value of plastomer
- Decreasing Rg value of PP
- More clustered structure

Interpenetrating structure => packed and clustered forms of plastomer network



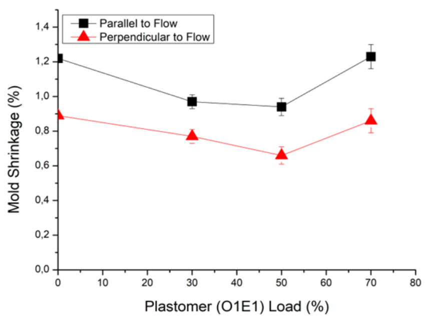


PP70-O1E1**30** (Compound J) | PP70-O1E1**50** (Compound F) | PP70-O1E1**70** (Compound B)

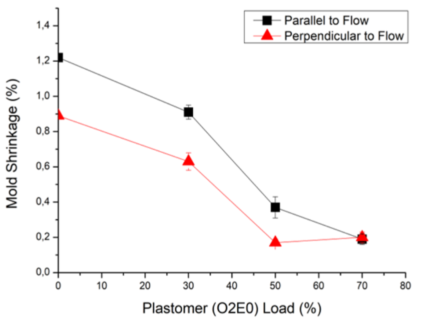
- Decreasing difference between Rg values of plastomer and PP with increasing plastomer load

More interpenetrated structure with increasing plastomer load => more aligned structure and phase separation at highest plastomer load

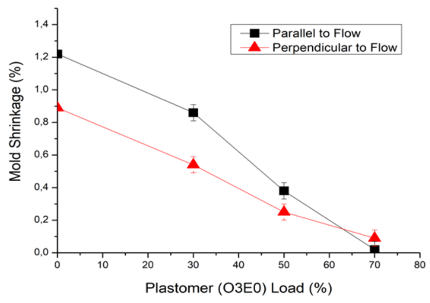
TPO Samples – Mold Shrinkage Results



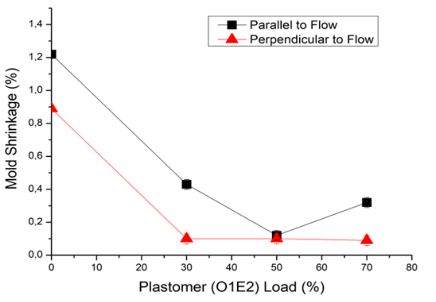
(34% crystallinity and 1 g/10min. MFI)



(18% crystallinity and 1 g/10min. MFI)



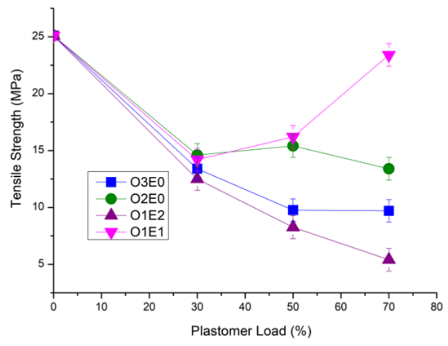
(13% crystallinity and 1 g/10min. MFI)



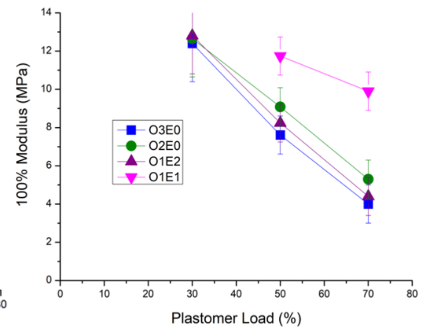
(21% crystallinity and 30 g/10min. MFI)

- ✓ Incorporation of high crystalline plastomer (O1E1) results higher mold shrinkage values
- ✓ Mold shrinkage values decrease as the crystalline phase decreases and amorphous phase increases in the TPO material

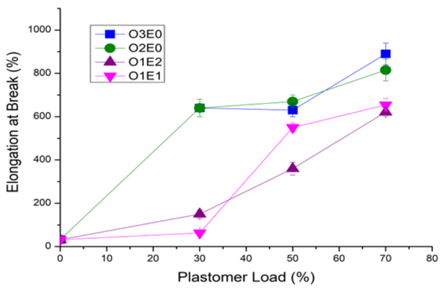
TPO Samples – Mechanical Test Results



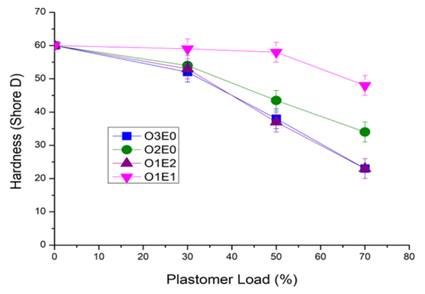
- Highest tensile strength value => Compound containing O1E1 (34% cryst.) at 70% loading level



- Decreasing moduli values with increasing plastomer load



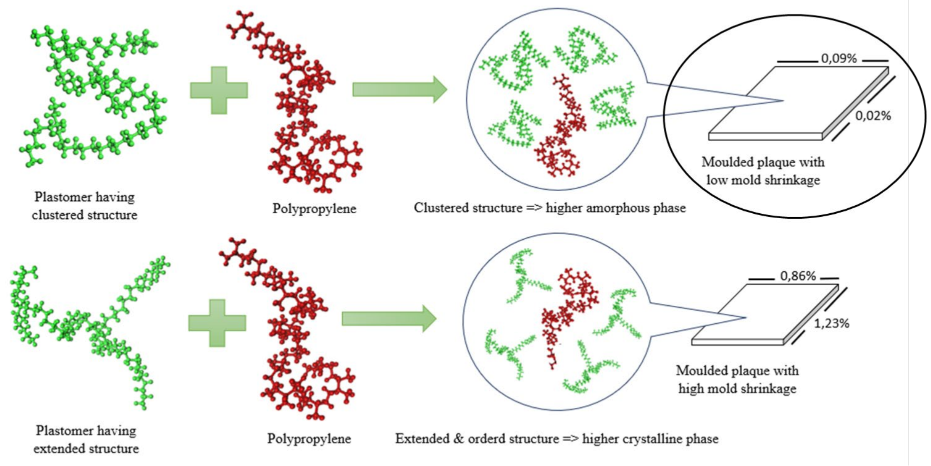
- O3E0 (13%) & O2E0 (18%) => higher elongation
  - Octene chains => low Rg, less ordered
- O1E2 (21%) and O1E1 (34%) => lower Elongation
  - Extended ethylene branching, restricted mobility



- Plastomer addition => decrease in hardness
- Lower crystalline plastomer => lower hardness

Conclusion

Molecular structure, octene/ethylene side chain content, and molecular conformations of plastomers govern their microstructure and the crystallinity => physical and mechanical traits of final TPO products



Best results in terms of low mold shrinkage => Compound C (70% O3E0 & 30% PP) but with insufficient mechanical properties

Optimum TPO Compound => Sample A

(70% O2E0 & 30% PP) => isotropic low mold shrinkage values and high mechanical properties

References

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