Synthesis and characterization of biobased biodegradable diisocyanated polyesters to replace LLDPE and LDPE in flexible film packaging

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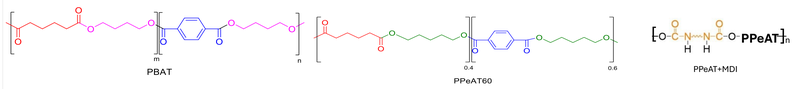
INTRODUCTION

Linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) dominate film packaging applications but pose significant environmental challenges due to their non-biodegradability and contribution to microplastic pollution. Biodegradable alternatives such as poly(butylene adipate-co-terephthalate) (PBAT) have been commercialized; however, their limited stiffness, higher production cost, and reliance on petroleum-based components restrict broader adoption.

Bio-based polyesters such as poly(pentylene adipate-co-terephthalate) (PPeAT), which utilize diols derived from agricultural waste streams, offer a promising pathway toward reducing fossil-fuel dependence. Despite this potential, current PPeAT materials face processing and synthesis limitations that hinder commercialization. In this work, we modify the PPeAT system to achieve the thermal and mechanical properties required for practical film packaging applications.

MATERIALS



PBAT is a commercial copolyester by BASF under the brand name Ecoflex®.

RESULTS AND DISCUSSION

Table 1: *Gel permeation chromatography results for PBAT, PPeAT60 and PPeAT+MDI copolyesters*

Sample	GPC Results			^{1}H NMR Analysis
	Mn	Mw	Đ	Percentage of Terephthalic Acid
	KDa	KDa	-	
PBAT	80	127	1.6	-
PPeAT60	80	226	2.8	74.1
PPeAT60 + MDI	55	136	2.5	62.5
PPeAT65 + MDI	67	152	2.3	68.9
PPeAT70 + MDI	68	188	2.8	72.9
PPeAT75 + MDI	180	466	2.6	78.7

All copolyesters exhibit comparable molecular weights and polydispersities, allowing meaningful comparison of their thermal, mechanical, and crystallization properties.

Thermal properties

Table 2: *Thermal properties LLDPE, PBAT and PPAT60 copolyesters (Scanning rate $10℃/min$)*

Sample	T_g	T_m	T_c	ΔH_m
	℃	℃	℃	J/g
PBAT	-30.0	115.0	38.0	34.0
PPeAT60	-9.0	101.0	-	35.0
PPeAT60 + Na	-12.3	97.2	44.6	31.6
PPeAT60 + MDI	-19.0	73.9	-	21.3
PPeAT65 + MDI	-16.1	82.8	-	24.7
PPeAT70 + MDI	-9.5	93.0	-	24.5
PPeAT70 + MDI + Na	-10.6	93.5	31.6	21.6
PPeAT75 + MDI	-3.5	96.6	-	19.1

Non-isothermal properties

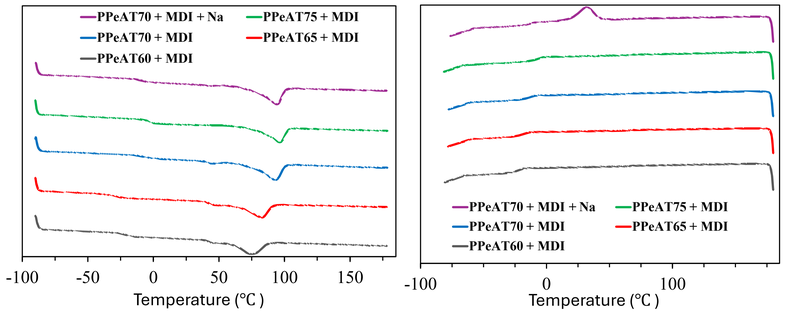


Figure 1: *Differential scanning calorimetry results (left) 1st Heating cycle and (right) cooling cycle.*

Scanning rate for both the heating cycle and the cooling cycle was $10℃/\min$. The slow crystallization rate of PPeAT60 and PPeAT+MDI samples limit the observation of a crystallization peak. The addition of nucleating agent* reduces the half time crystallization (from 40 minutes to 1 minute).

* A patent is pending.

Isothermal Properties

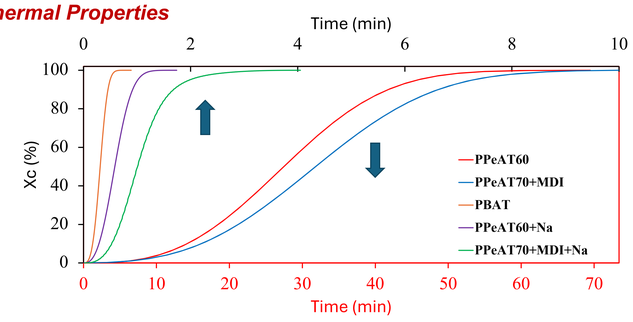


Figure 2: *Isothermal crystallization results for the copolyesters at 40℃*

Mechanical Properties

Table 3: *Mechanical properties of LLDPE, PBAT, PPeAT60 and PPeAT+MDI copolyesters*

Sample	Young's Modulus	Stress at Yield	Strain at Yield	Stress at Break	Elongation at Break
	MPa	MPa	%	MPa	%
LLDPE	251 ± 46	12 ± 0.6	49 ± 14	29 ± 6	637 ± 110
PBAT	78 ± 10	-	-	26 ± 3	815 ± 67
PPeAT60	138 ± 5	10 ± 0.5	16 ± 2	27 ± 2	784 ± 107
PPeAT60 + MDI	93.1 ± 2.1	6.4 ± 0.2	15.1 ± 0.9	16.4 ± 0.8	857.3 ± 25.5
PPeAT65+ MDI	96.8 ± 5.8	6.9 ± 0.5	15.4 ± 1.6	15.7 ± 2.7	710.6 ± 116.0
PPeAT70+ MDI	118.4 ± 3.7	8.6 ± 0.2	15.3 ± 1.0	16.7 ± 2.1	630.5 ± 64.6
PPeAT75+ MDI	144.5 ± 9.0	9.9 ± 0.2	15.4 ± 1.7	28.2 ± 2.7	670.5 ± 37.0

The Young's modulus of PPeAT60 and all PPeAT+MDI copolyesters fall between those of PBAT and LLDPE and increases with terephthalic acid content, while elongation at break decreases accordingly.

Wide and Small Angle X-ray Scattering (WAXS and SAXS)

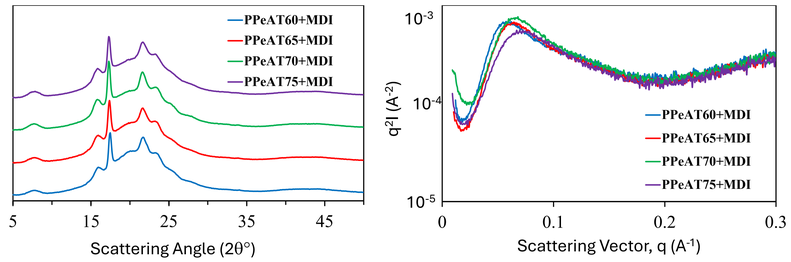


Figure 3: *WAXS and SAXS results for the copolyesters*

Table 4: *Crystalline fraction, q_{max} value, d-spacing, and lamellar thickness values*

Sample	WAXS	SAXS		
	χ_c	q_{max}	d-spacing	Lamellar Thickness
	%	$Å^{-1}$	Å	Å
LLDPE	50.4	0.039	160	80.8
PBAT	19.4	0.051	124	24.1
PPeAT60	18.5	0.061	102	18.9
PPeAT60 + MDI	8.6	0.058	109	9.4
PPeAT65 + MDI	10.2	0.065	96	9.8
PPeAT70 + MDI	13.1	0.068	92	12.1
PPeAT75 + MDI	13.3	0.067	94	12.5

Barrier Properties

Table 5: *Water vapor transmission rate results for LLDPE, PBAT, PPeAT and PPeAT+MDI*

Sample	WVTR
	$g.mm.m^{-2}.d^{-1}$
LLDPE	0.099 ± 0.01
PBAT	6.95 ± 0.21
PPeAT60	1.44 ± 0.12
PPeAT60 + MDI	2.91 ± 0.20
PPeAT65 + MDI	2.31 ± 0.17
PPeAT70 + MDI	1.90 ± 0.10
PPeAT75 + MDI	1.45 ± 0.05

CONCLUSION

- PPeAT70+MDI exhibits thermal properties comparable to PPeAT60 and PBAT while maintaining molecular weight characteristics suitable for film applications.
- Mechanical testing shows that PPeAT-based copolyesters achieve stiffness between PBAT and LLDPE, with elongation tunable through terephthalic acid content.
- The use of a bio-based diol combined with enhanced stiffness relative to PBAT enables thinner films with equivalent performance, suggesting reduced material usage and improved cost efficiency for sustainable film packaging.

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