

Balancing free-volume and hydrogen-bond/ion-pair interactions: Plasticisation of cassava starch with glycerol-monoethanolamine deep eutectic solvents

Chien Van Nguyen, Mai Thi Pham, Phuong Thi Hoang*

Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Nghia Do Ward, Hanoi, Vietnam

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Abstract:

Thermoplastic cassava starch was plasticised with deep eutectic solvents (DES) based on choline chloride (ChCl), glycerol (Gly), and monoethanolamine (MEA) to balance free-volume creation and hydrogen-bond/ion-pair junctions. Binary (ChCl:Gly 1:3; ChCl:MEA 1:3) and ternary ChCl:Gly:MEA (1:1:1; 1:1:2; 1:2:1) DES at 25 wt% were melt-compounded and assessed by processing metrics, FTIR-ATR, dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), X-ray diffractometry (XRD), wettability (Owens-Wendt-Rabel-Kaelble (OWRK)), and 56-day ambient aging ($23 \pm 2^\circ\text{C}$, $50 \pm 5\%$ RH). Gly-rich systems enhanced flow but depressed cohesion, whereas MEA-rich systems strengthened interchain junctions. The ternary ChCl:Gly:MEA 1:1:2 delivered the best process-structure-property balance, combining high melt processability with tensile strength (TS) ~ 2.9 MPa and elongation at break (ϵ_b) $\sim 195\%$ ($n=5$) and displaying the lowest 56-day ductility loss ($\Delta\epsilon_b \sim 17\%$) compared with glycerol controls ($\sim 50\%$). FTIR (O-H/N-H red-shift and broadening), together with SEM fracture morphology and OWRK-derived surface energetics, supports a dual-mode plasticisation mechanism in which MEA-enabled junctions counterbalance Gly-induced free volume, thereby stabilising the amorphous phase and is consistent with reduced retrogradation without sacrificing strength. This composition-structure map identifies ChCl:Gly:MEA (1:1:2) as a composition window that stabilises starch-based thermoplastics (TPS) mechanical performance during ambient aging.

Keywords: deep eutectic solvents, dual-mode plasticisation, monoethanolamine, retrogradation, thermoplastic starch.

Classification numbers: 2.2, 2.3

1. Introduction

Starch-based thermoplastics (TPS) are compelling candidates for sustainable packaging and agricultural uses because starch is abundant, renewable, low-cost, and biodegradable [1, 2]. However, native starch is brittle and difficult to process: its semicrystalline framework, stabilised by dense intra- and intermolecular hydrogen bonding between amylose and amylopectin, limits chain mobility, elevates glass transition (T_g), and narrows the melt-processing window [3]. Plasticisation is therefore required to disrupt this network and enable thermoplastic flow. Conventional plasticisers (glycerol, sorbitol, urea) can improve flexibility; among them, glycerol is prevalent owing to its availability and price [4]. Yet glycerol-plasticised TPS commonly exhibits excessive moisture uptake, strong retrogradation, and loss of TS during storage - consequences of a free-volume-dominated mechanism that depresses T_g but weakens cohesive interactions [2, 3, 5]. Binary/ternary mixtures (e.g., glycerol-sorbitol, glycerol-urea) partially mitigate these trade-offs by combining complementary interactions [6, 7].

Deep eutectic solvents (DES) have recently emerged as tuneable, cost-effective “designer” plasticisers for polysaccharides [8]. DES are formed by pairing a hydrogen-bond acceptor (HBA; e.g., choline chloride) with hydrogen-bond donors (HBDs; polyols, amides, or amines), producing eutectic systems with depressed melting points yet strong polarity and H-bonding capacity. Prior studies show that DES such as ChCl:urea and ChCl:glycerol can plasticise starch, reduce crystallinity, and increase extensibility; DES have also been explored in TPS-lignin systems [9], improving interfacial interactions and processability under melt conditions. Despite this progress, component-level roles remain under-resolved. Polyols (e.g., glycerol) primarily generate free volume, strongly lowering T_g but compromising strength, whereas amines such as monoethanolamine (MEA) can act as both HBD and (to a degree) HBA, forming H-bond/ion-pair junctions with choline chloride and starch hydroxyls that may temper T_g depression and recover load-bearing [8, 10]. Systematic, side-by-side comparisons of glycerol-rich, MEA-rich, and ternary glycerol-MEA DES at fixed content and identical processing are scarce. Moreover, quantitative links among

*Corresponding author: Email: hoangphuong15@gmail.com

spectroscopic H-bond signatures (FTIR), rheology (torque, MFI), morphology (SEM), and macroscopic properties (TS, ϵ_b , T_g) remain limited.

In this study, these gaps are addressed by fixing DES at 25 wt% and implementing standardised compounding (internal mixing, twin-screw extrusion, hot pressing) to compare ChCl:Gly, ChCl:MEA, and ChCl:Gly:MEA ternaries across controlled compositions. We test the hypothesis that glycerol-rich DES maximise extensibility but reduce strength (free-volume dominance), MEA-rich DES partially recover strength via reversible -OH/-NH H-bond/ion-pair junctions, and ternary formulations provide a balanced window of ductility, strength, and processability. By integrating FTIR, DMA, mixing/MFI/SME, SEM, and tensile metrics, we establish a composition-structure-property map that clarifies how DES chemistry governs mobility versus supramolecular association in TPS. The resulting guidelines support rational selection of multifunctional, sustainable plasticisers for next-generation starch-based bioplastics.

2. Experimental section

2.1. Chemicals

Cassava starch (CS) with an amylose content of 22–28%, a moisture content of approximately 13%, and an ash content of 0.2% was obtained from NEO Nam Vietnam Co., Ltd. Glycerol ($\geq 99.5\%$ purity) was purchased from Sigma-Aldrich and used as received. Monoethanolamine (MEA, Sigma-Aldrich), glycerol and DES were used as plasticisers in this investigation. To make the DES, choline chloride (ChCl), glycerol and MEA were mixed together in respective molar ratios of 1:3:0, 1:0:3, 1:1:1, 1:2:1, 1:1:2 and then heated to 80–90°C until the combination turned into a clear, smooth liquid; subsequently, the mixture was sealed and stored at ambient conditions.

2.2. Preparation of thermoplastic starch samples

Thermoplastic starch samples were prepared via twin-screw melt compounding (HAAKE Rheomex PTW16/25 OS, Thermo Scientific, Germany) located at the Institute of Chemistry. CS powder was dried at 60°C for 8 h before quantification and fed into the extruder by a feeder. The plasticisers (DES) with specified content (Table 1), were fed into the extruder by a liquid feeder pump. Synthetic mixing was carried out at the following temperatures of the mixing zones: feeder zone: 110°C, melt zone: 120–125°C, mixing and conveying: 115–120°C, die temperature: 110°C, and at a screw speed of 150 rpm. The extruded samples were cooled to room temperature and then dried for 24 h after pelletising. The TPS-DES samples obtained were then moulded into sheets of 3.00 mm in thickness by hot pressing at 120°C for 2 min under a nominal press load of 20 tons, followed by cooling to room temperature. The sheets were used for further characterisation.

Table 1. Formulation of starch-based thermoplastics samples with varying deep eutectic solvents.

Samples	Composition (g)		DES			
			Plasticiser type		Ratio	
	Cassava starch	Plasticiser		ChCl	Glycerol	MEA
TPS-Gly	75	25	Glycerol	-	-	-
C.G: 1:3	75	25	DES	1	3	-
C.M: 1:3	75	25	DES	1	-	3
C.G.M: 1:1:1	75	25	DES	1	1	1
C.G.M: 1:1:2	75	25	DES	1	1	2
C.G.M: 1:2:1	75	25	DES	1	2	1

DES: deep eutectic solvent, G and Gly: glycerol, M: monoethanolamine, C: choline chloride.

2.3. Analytical methods

2.3.1. Processing rheology

Compounding behaviour was monitored on a HAAKE Rheomex 600 closed mixer (Haake, Germany) at 120°C, 100 rpm, for 10 min. Torque-time and stock temperature-time traces were recorded (PolySoft OS). The steady-state torque was calculated as the average over the final 3 min. Specific mechanical energy (SME) was obtained by integrating the torque-time curve multiplied by angular speed and normalising by sample mass ($n=3$) and is displayed in the energy-time plots.

2.3.2. Tensile properties

Compression-moulded plaques were die-cut into ASTM D638 Type IV dumbbell specimens (gauge length 25 mm; neck width 6.00 ± 0.05 mm; thickness 3.00 ± 0.10 mm). Tests were performed on a 10 kN universal testing machine at a crosshead speed of 20 mm/min at ambient conditions. TS and ϵ_b were extracted from engineering stress-strain curves, following ASTM D638 using an AGX-V Testing Machine (Japan). Values were averaged over five specimens ($n=5$).

2.3.3. Dynamic mechanical analysis

Rectangular strips were tested in single-cantilever mode at 1 Hz with a strain amplitude of 0.1%, which lies within the linear viscoelastic regime (LVR) as verified by preliminary strain-sweep checks on representative samples (no time-dependent drift of E' during isothermal holds). Specimens were pre-conditioned at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ RH for at least 48 h, sealed prior to testing, and scanned under dry N_2 purge. Thermal scans were run from -40 to $+120^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$ under dry N_2 purge. Because the materials are plasticised systems, data interpretation is restricted to the low-temperature window around the primary T_g where plasticiser mobility dominates; the upper part of the scan is reported for completeness but is not used to infer plasticiser-

controlled behaviour. Reported T_g corresponds to the $\tan \delta$ peak temperature ($\pm$ SD, $n=5$), and E' values were taken at the indicated temperatures after baseline stabilisation.

2.3.4. FTIR-ATR spectroscopy

FTIR-ATR spectra were recorded using a Nicolet™ iS50 spectrometer equipped with a diamond ATR accessory over the wavenumber range of 4000–500 cm^{-1} , at a resolution of 4 cm^{-1} , with 16 scans accumulated for each spectrum.

2.3.5. Morphology

Scanning electron microscopy (SEM) was performed using an SM-6510LV microscope (JEOL, Japan) at the Institute for Tropical Technology. The samples were cryo-fractured in liquid nitrogen and subsequently sputter-coated with a thin layer of platinum prior to SEM observation.

2.3.6. Surface wetting properties

Surface wettability was assessed by static contact-angle goniometry (DSA25, KRÜSS GmbH, Germany) under ambient conditions ($25 \pm 2^\circ\text{C}$). Three probe liquids - distilled water, diiodomethane, and formamide - were used to determine the surface free energy (SFE) according to the Owens-Wendt-Rabel-Kaelble (OWRK) model. Samples were secured on glass slides, and a 10- μl microsyringe was used to gently dispense five droplets (5 μl each) of every liquid onto separate regions of the film before imaging. For each specimen, measurements were taken at three distinct locations and averaged. The total SFE and its dispersive and polar components were computed using ADVANCE software (KRÜSS GmbH, Germany).

2.3.7. Aging protocol

After initial testing (day 0), specimens were stored in a controlled chamber at $23 \pm 2^\circ\text{C}$, $50 \pm 5\%$ RH and retrieved at 7, 28, and 56 days for tensile re-evaluation under identical conditions. Each timepoint included re-conditioning per ASTM D618 and ISO 291. Aging analysis focused on retention of σ_t and ϵ_b relative to day 0 ($n=5$).

2.3.8. X-ray diffractometry

Diffractograms were collected on a Bruker D8 ADVANCE (Germany) with Cu K α radiation ($\lambda=0.154$ nm) at 40 kV/30 mA, scanning $2\theta=0-70^\circ$ at $2^\circ/\text{min}$ (step 0.02°). Aged specimens were re-conditioned (ASTM D618/ISO 291) and measured under identical XRD settings. To qualitatively track short-range ordering upon storage, we computed a shoulder-to-halo index $I_{22.7}/I_{am'}$, defined as the maximum intensity within $2\theta=22.3-23.1^\circ$ divided by a local amorphous baseline estimated from a linear fit over $2\theta=21.0-24.0^\circ$.

2.3.9. Melt-flow index

Melt-flow index (MFI) was measured according to ASTM D1238 Procedure A at 130°C with a 2.16 kg load using a 2.095×8 mm die. The reported value (g/10 min) is the average of $n=3$ replicates ($\pm$ SD). The chosen temperature equals (or is below) the melt-processing setpoint used during compounding, so MFI reflects the processing-relevant flow state rather than thermal degradation.

Note on neat-DES thermal signatures. DSC was not performed on the neat DES because the primary objective of this study was to evaluate the processing and thermomechanical responses of the final starch-based materials rather than to establish the phase-transition behaviour of the isolated plasticisers. Previous work has shown that water content affects the supramolecular structure and physicochemical properties of ChCl:MEA-based DESs [14]. Accordingly, the plasticisation response was evaluated at the composite level using DMA-derived $T_g/\tan \delta$ and processing-rheology measurements obtained under identical sample-conditioning conditions.

3. Results and discussion

3.1. Processing behaviour and rheological response

The torque-time profiles and melt flow indices provide the first insight into the plasticisation efficiency of different DES formulations. By comparing Gly-rich,

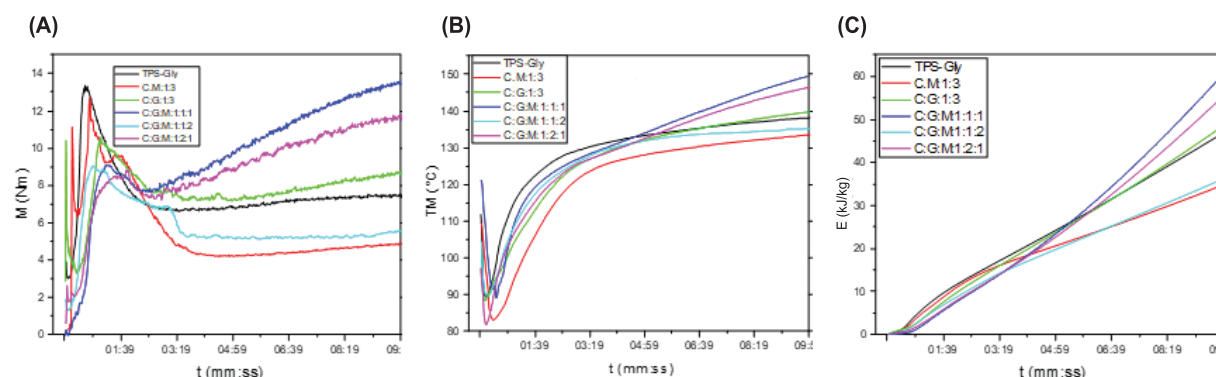


Fig. 1. Melt-processing response of cassava thermoplastic starch plasticised with glycerol and choline-chloride-based deep eutectic solvents. (A) Torque-time profiles; (B) Stock temperature-time profiles; (C) Cumulative mechanical energy-time profiles.

MEA-rich, and ternary compositions, the variations in peak torque, time to plateau, and flowability reveal how the nature of the hydrogen-bond donor influences starch chain mobility during melt processing.

Table 2. Processing and rheological properties of samples: Steady torque at plateau (N·m), terminal melt temperature (°C), melt-flow index (g/10 min), mean±SD (n=3).

Samples	Steady torque (N·m)	Terminal melt temperature (°C)	Melt-flow index (g/10 min)
TPS-Gly	7.4±0.53	138.2±7.8	1.02±0.08
C.G: 1:3	8.7±0.6	139.7±11.3	1.01±0.07
C.M: 1:3	4.8±0.34	133.2±7.7	2.15±0.13
C.G.M: 1:1:1	13.5±0.82	149.0±9.2	0.87±0.07
C.G.M: 1:1:2	5.5±0.43	135.3±9.1	2.45±0.2
C.G.M: 1:2:1	11.6±0.91	146.4±8.5	0.92±0.06

The results in Fig. 1 and Table 2 show that, in comparison to TPS-Gly (MFI 1.02±0.08 g/10 min; torque 7.4±0.53 N·m; final temperature 138.2±7.8°C); ChCl:Gly (1:3) shows similar flow (1.01±0.07) but higher torque (8.7±0.6 N·m) and slightly higher final temperature (139.7±11.3°C); ChCl:MEA (1:3) markedly improves flow (MFI 2.15±0.13 g/10 min) while lowering torque (4.8±0.34 N·m) and final temperature (133.2±7.7°C); The ternary ChCl:Gly:MEA (1:1:2) gives the best trade-off: MFI 2.45±0.2 g/10 min, torque 5.5±0.43 N·m, final temperature 135.3±9.1°C, indicative of a low-viscosity yet cohesive melt. In contrast, ChCl:Gly:MEA (1:1:1) (MFI 0.87±0.07 g/10 min; torque 13.5±0.82 N·m; final temperature 149.0±9.2°C) and 1:2:1 (MFI 0.92±0.06 g/10 min; torque 11.6±0.91 N·m; final temperature 146.4±8.5°C) exhibit over-associated melts and narrower windows.

At fixed geometry and speed, steady torque grows with melt viscosity; conversely, MFI inversely scales with viscosity (and molecular weight), so high-MFI/low-torque pairs signify better flow at processing shear rates [13]. Glycerol supplies free volume (increased mobility), while MEA (-OH/-NH) forms directional H-bond/ion-pair junctions with ChCl and starch -OH, adding reversible network cohesion without over-penalising, consistent with DES literature and water-modulated amine-DES associations [14, 15]. Consequently, Gly-rich blends maximise mobility (high MFI) but risk low melt strength; increasing MEA raises transient associations and stabilises extensional flow.

ChCl:Gly:MEA (1:1:2) balances these countervailing effects (high, stable MFI; moderate torque/temperature), whereas 1:1:1/1:2:1 enter an over-associated regime (high torque, thermal dissipation). Importantly, lower torque and final melt temperature at comparable MFI reduce SME and widen the extrusion/injection window; ChCl:MEA (1:3) and especially ChCl:Gly:MEA (1:1:2) are thus expected to minimise energy input while preserving melt cohesiveness [16, 17].

3.2. FTIR spectroscopy: Hydrogen-bonding interactions

Figure 2 compares the FTIR spectra of native CS, glycerol-plasticised cassava starch (TPS-Gly), TPS plasticised with the binary DESs ChCl:Gly (1:3) and ChCl:MEA (1:3), and TPS plasticised with the ternary ChCl:Gly:MEA DESs (1:1:1, 1:1:2, and 1:2:1). In all plasticised samples, the broad O-H stretching vibrations (in the 3600-3000 cm⁻¹ wavenumber region) shifted to lower wavenumbers and became broader compared to CS. These changes were more evident in the DES-plasticised samples, particularly in the MEA-rich formulation, indicating a redistribution of the hydrogen-bonding environment upon plasticisation. Changes in the O-H stretching region associated with plasticiser-starch hydrogen bonding have also been reported for glycerol/isosorbide-co-plasticised cassava starch [18]. The ν(N-H) (~3350-3300 cm⁻¹) and δ(NH₂) (~1600 cm⁻¹) assignments are in line with recent MEA infrared studies [19]. Together with the HBA character of ChCl, these signatures point to dual-mode plasticisation: glycerol predominantly increases free volume and chain mobility, while MEA furnishes directional H-bond/ion-pair associations with ChCl and starch hydroxyl groups (AGU-OH), yielding a more cohesive yet processable matrix. This spectroscopic picture aligns with processing/DMA trends (enhanced flow,

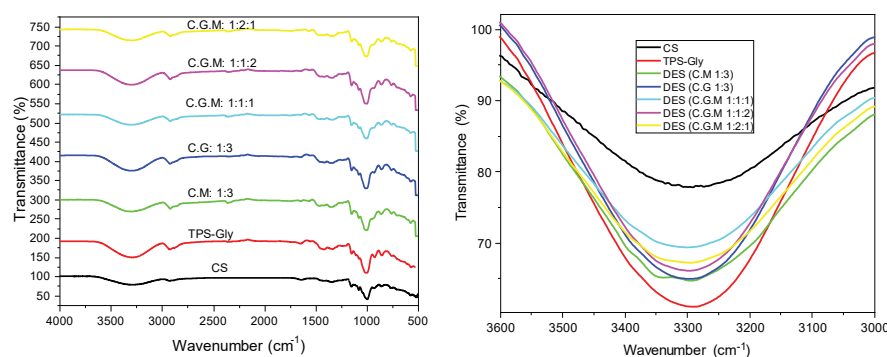


Fig. 2. ATR-FTIR spectra (4000-500 cm⁻¹) of starch-based thermoplastics samples with different plasticisers. O-H envelope: red-shift and broadening diagnose networked H-bonding.

moderated T_g decrease) and rationalises the broader processing window and improved anti-retrogradation of the ternary DES relative to TPS-Gly.

In the fingerprint region (~ 1200 - 900 cm^{-1}), all DES-plasticised TPS displayed subtle (few- cm^{-1}) red-shifts and intensity redistribution within the C-O-C/C-O stretching envelope (~ 1155 - 995 cm^{-1}). Relative to TPS-Gly, MEA-containing and the 1:1:2 ternary systems showed a qualitatively lower 1047/1022 band ratio, together with a modest enhancement near ~ 995 - 1010 cm^{-1} , consistent with reduced short-range order and higher amorphicity. These trends are coherent with the O-H red-shift/broadening discussed above (Fig. 2).

3.3. X-ray diffraction patterns

The X-ray diffraction (XRD) patterns reveal the degree of structural ordering introduced by different DES systems. Immediately after melt-processing, all DES-plasticised TPS exhibit a dominant amorphous halo at ~ 19 - 20° (2θ) with marked attenuation of native A-type reflections near $\sim 15^\circ$, 17 - 18° , and 22 - 23° , indicating extensive amorphisation. This response - loss or attenuation of A-type peaks and dominance of an $\sim 20^\circ$ halo - matches established assignments of starch polymorphs and typical TPS behaviour following plasticisation and shear/thermal treatment [20].

Across formulations, the Gly-rich systems retained the most order (discernible shoulders near ~ 17 - 18° and $\sim 23^\circ$), whereas MEA-containing DES (binary ChCl:MEA and the ternary ChCl:Gly:MEA) produced more featureless halos with lower relative peak intensities-consistent with deeper disruption of inter- and intramolecular packing. Mechanistically, polyol-dominant plasticisation Gly increases free volume and segmental mobility, which facilitates helix re-association upon cooling, while MEA-containing DES introduce stronger, directional H-bond/ion-pair interactions that better “lock” chains in disordered states during quench, delaying recrystallisation. These trends align with contemporary reports that DESs (particularly amide/amine-bearing systems) penetrate/crack ordered lamellae and suppress immediate recrystallisation in starch matrices [10, 21].

Under the melt-processing conditions applied (short residence time, low water content), ChCl:MEA acts as a plasticising/destructuring medium rather than a molecular solvent for starch; the XRD amorphisation and FTIR O-H broadening therefore reflect destructure/gelatinisation rather than complete dissolution.

3.4. Thermal-viscoelastic properties

Dynamic mechanical analysis (DMA) in single-cantilever mode (1 Hz, from -40 to 120°C , within the LVR) resolves the temperature-dependent storage modulus (E') and the main relaxation ($\tan \delta$) associated with starch-chain segmental mobility. T_g is taken at the $\tan \delta$ maximum.

Interpretive note: In polymer-plasticiser systems, the relevant glass transition for mechanics and processing is that of the polymer-rich (starch-rich) phase, which we quantify by DMA, rather than the T_g/T_m of the neat plasticiser. This view is consistent with mixing-rule descriptions (e.g., Gordon-Taylor/Fox) widely applied to plasticised amorphous solids [11, 12]. Together with the pronounced water-sensitivity of neat-DES thermal signatures reported in the literature, which limits cross-laboratory comparability without rigorous water control, neat-DES DSC would add limited interpretive value here. Accordingly, our discussion of mobility relies on DMA $T_g/\tan \delta$ and processing rheology (torque/MFI), which directly govern performance [22-24].

Table 3. Thermoviscoelastic and mechanical properties of the samples: DMA T_g ($^\circ\text{C}$), storage modulus E' (MPa) (Mean $\pm$ SD, $n=3$), tensile strength (MPa), elongation at break ϵ_b (%) (Mean $\pm$ SD, $n=5$).

Samples	Glass-transition temperature ($^\circ\text{C}$)	E' (MPa)	Tensile strength (MPa)	Elongation at break (%)
TPS-Gly	72.4 $\pm$ 3.7	871.1 $\pm$ 56.6	1.54 $\pm$ 0.1	169.9 $\pm$ 14.8
C.G: 1:3	31.9 $\pm$ 2.3	430.2 $\pm$ 27.5	0.97 $\pm$ 0.08	183.9 $\pm$ 15.3
C.M: 1:3	48.2 $\pm$ 2.9	639.5 $\pm$ 46.0	2.27 $\pm$ 0.19	228.9 $\pm$ 21.1
C.G.M: 1:1:1	49.7 $\pm$ 4.0	506.1 $\pm$ 39.5	3.33 $\pm$ 0.27	126.9 $\pm$ 14.2
C.G.M: 1:1:2	42.5 $\pm$ 2.6	875.8 $\pm$ 71.8	2.91 $\pm$ 0.27	195.1 $\pm$ 15.4
C.G.M: 1:2:1	57.9 $\pm$ 3.3	827.2 $\pm$ 51.3	2.31 $\pm$ 0.19	107.7 $\pm$ 9.6

The analysis results (Table 3) show that, replacing neat glycerol with choline-based DES depresses T_g , with the magnitude governed by the Gly/MEA balance: ChCl:Gly (1:3) gives the lowest T_g ($\sim 32^\circ\text{C}$; $\Delta T_g \sim -40^\circ\text{C}$ vs TPS-Gly $\sim 72^\circ\text{C}$), whereas ChCl:MEA (1:3) partially recovers T_g to $\sim 48^\circ\text{C}$ ($\Delta T_g \sim -24^\circ\text{C}$). Ternary systems are non-monotonic: 1:1:2 $\sim 42.5^\circ\text{C}$, 1:1:1 $\sim 49.7^\circ\text{C}$, 1:2:1 $\sim 57.9^\circ\text{C}$ - indicating a tuneable mobility-association balance.

The E' values reported in Table 3 were highest and statistically overlapping for TPS-Gly (871.1 $\pm$ 56.6 MPa) and ChCl:Gly:MEA (1:1:2) (875.8 $\pm$ 71.8 MPa); the other DES-plasticised samples ranged from 430.2 to 827.2 MPa. Relative to ChCl:Gly (1:3), the higher E' retained

by the 1:1:2 ternary is consistent with MEA-enabled, reversible H-bond/ion-pair junctions that increase cohesion without eliminating segmental mobility. The Gly-rich DES (e.g., ChCl:Gly) maximise free-volume creation and thus shift T_g downwards more strongly, whereas MEA-containing systems (e.g., ChCl:MEA or ternaries containing MEA) partially recover T_g due to additional directional -OH/-NH hydrogen-bond/ion-pair junctions that “anchor” segments and moderate mobility. These trends align with the established roles of DES components in TPS-polyols acting as efficient plasticisers and amine-containing HBDs introducing stronger associations [6, 8, 22]. The specific influence of MEA-based DES and of water traces on their supramolecular structure further supports this dual-mode picture [14].

Collectively, the DMA trends support a dual-mode plasticisation: glycerol predominantly supplies free volume (strong T_g depression, higher $\tan \delta$), whereas MEA introduces directional associations with ChCl and starch -OH that modestly raise T_g and damp $\tan \delta$. These outcomes align with torque/MFI (MEA-containing DES combine good flow with adequate melt strength) and FTIR signatures (O-H red-shift; emergent ν (N-H)/ δ (NH₂)) [8, 21, 22]. Notably, the 1:1:2 ternary offers the most favourable trade-off between mobility and supramolecular association.

In this study, free-volume changes are inferred rather than assumed, by combining multiple measured proxies with well-established theoretical frameworks. First, the T_g depression and concomitant reduction of storage modulus E' (DMA) reflect increased segmental mobility; together with the $\tan \delta$ peak shift and broadening, these responses are consistent with a larger fractional free volume and a broader distribution of local environments. Second, the lower melt viscosity/processing torque (i.e., higher MFI under matched conditions) conforms to the Doolittle/Cohen-Turnbull view that viscosity decreases exponentially with increasing free volume. Third, FTIR evidence - O-H red-shift/broadening and intensity redistribution within the 1155-995 cm⁻¹ envelope with a qualitatively lower 1047/1022 ratio - indicates disruption of short-range order in the AGU network, cohering with added interstitial volume. In aggregate, these signatures align with WLF and Gordon-Taylor/Kelley-Bueche relations for plasticised amorphous matrices, and they underpin the glycerol<MEA<DES(ChCl:MEA) ranking observed here. We therefore attribute the stronger plasticisation by DES to cooperative hydrogen-bonding plus ion-pair interactions that both weaken native starch-starch cohesion and act as effective spacers, increasing the accessible free volume without invoking any unmeasured assumptions.

3.5. Morphology and mechanical performance

SEM imaging coupled with tensile testing was conducted to assess how DES composition affects microstructural homogeneity and macroscopic mechanical behaviour. Differences in domain size, fracture morphology, and stress-strain responses illustrate the trade-off between elongation and TS in Gly- and MEA-dominated systems.

Cryo-fractured specimens were sputter-coated with Pt and imaged by SEM (SM-6510LV). Fig. 3 displays the fracture surfaces for TPS-Gly, ChCl:Gly (1:3), and the ternaries ChCl:Gly:MEA (1:1:1; 1:1:2; 1:2:1). MEA-based DES (ChCl:Gly:MEA) yields smoother, more homogeneous planes with fewer voids, indicating a higher density of reversible -OH/-NH hydrogen-bond/ion-pair junctions between MEA, ChCl, and starch, aligning with moderated T_g and partial strength recovery reported for amine-containing DES [24]. Ternaries (ChCl:Gly:MEA) exhibit a composition-dependent balance: 1:1:1 shows flatter, feature-poor facets (over-association); 1:2:1 presents locally rougher regions and occasional voids (insufficient junction density); 1:1:2 displays the most uniform, defect-sparse surface, evidencing efficient stress transfer without brittle cleavage. Collectively, the micrographs support dual-mode plasticisation: glycerol promotes mobility and cavitation, whereas MEA introduces reversible junctions that homogenise the microstructure; 1:1:2 best balances these effects, mirroring the strength-elongation trade-off in this series [25].

Under identical conditions (ASTM-type specimens; $n=5$, Mean $\pm$ SD), DES composition dictates the strength-ductility envelope via dual-mode plasticisation. Glycerol-dominated systems prioritise mobility: TPS-Gly (TS=1.54 $\pm$ 0.10 MPa; ϵ_b =169.9 $\pm$ 14.8%) and ChCl:Gly (1:3) (TS=0.97 $\pm$ 0.08 MPa; ϵ_b =183.9 $\pm$ 15.3%) show ductile flow at low stress. In contrast, ChCl:MEA (1:3) simultaneously increases strength and extensibility (TS=2.27 $\pm$ 0.19 MPa; ϵ_b =228.9 $\pm$ 21.1%), consistent with reversible -OH/-NH H-bond/ion-pair junctions that restore load bearing without over-constraining chains. The ternaries map a tuneable compromise: 1:1:1 maximises cohesion (TS=3.33 $\pm$ 0.27 MPa; ϵ_b =126.9 $\pm$ 14.2%), 1:2:1 limits extensibility (TS=2.31 $\pm$ 0.19 MPa; ϵ_b =107.7 $\pm$ 9.6%), whereas 1:1:2 offers the best balance (TS 2.91 $\pm$ 0.27 MPa; ϵ_b 195.1 $\pm$ 15.4%). These trends align with SEM (rough, voided surfaces in Gly-rich vs. uniform, defect-sparse in MEA-containing/1:1:2) and support a composition-structure-property framework: glycerol supplies free

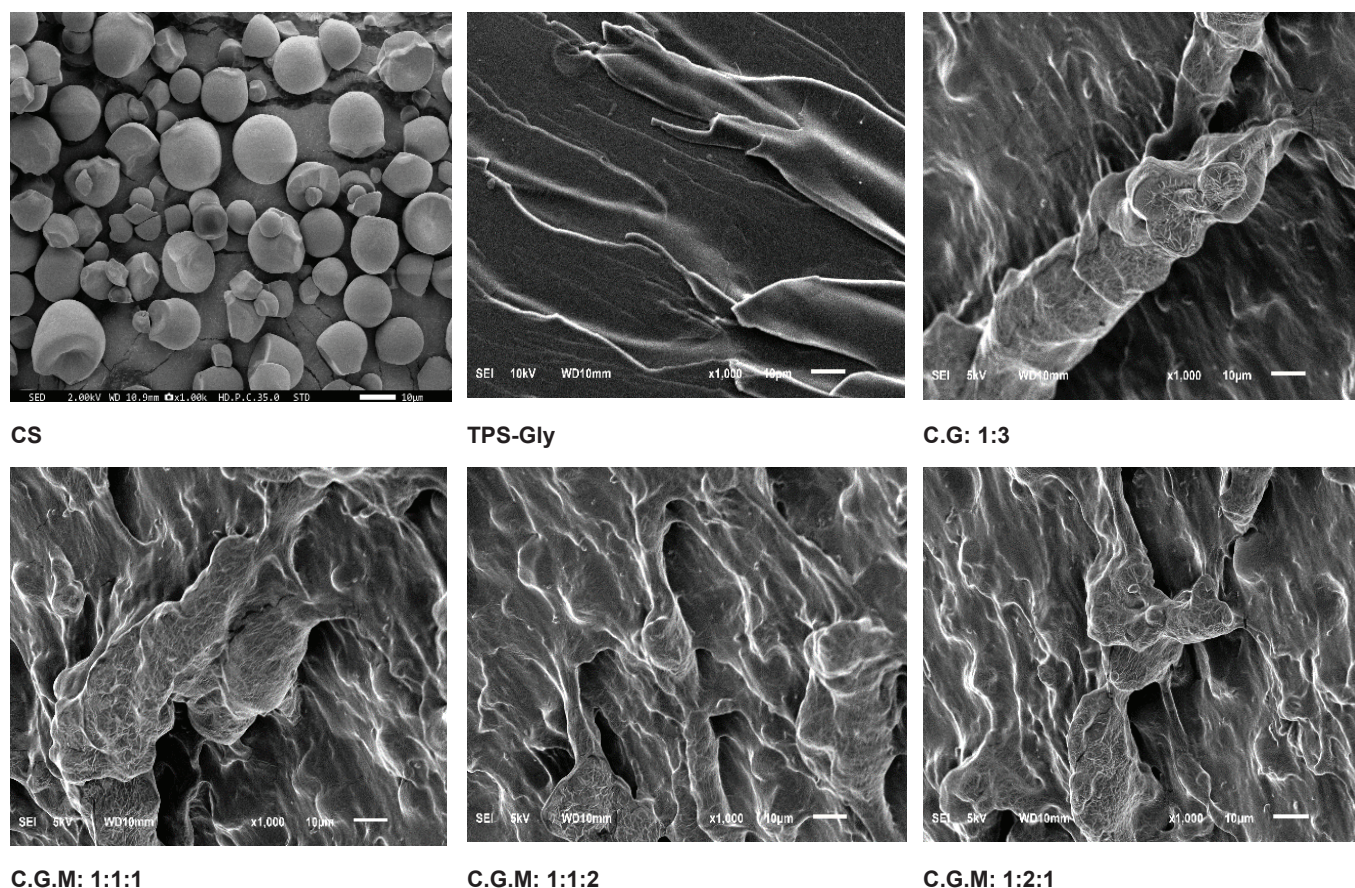


Fig. 3. Scanning electron microscopy images of cassava starch and starch-based thermoplastics samples.

volume; MEA provides supramolecular junctions; 1:1:2 balances both to deliver high strength at sustained ductility. Overall, the results indicate a non-monotonic dependence on composition rather than a simple Gly-to-MEA trend, with the 1:1:2 formulation exhibiting the most favourable strength-ductility balance among the formulations tested.

3.6. Wettability and surface free energy by contact angle

Table 4. Surface free energy components and contact angle of starch-based thermoplastics samples (mean $\pm$ SD, n=3).

Samples	Water (θ , $^{\circ}$)	Formamide (θ , $^{\circ}$)	Diiodomethane (θ , $^{\circ}$)	Dispersive part, γ^d (mN.m $^{-1}$)	Polar part, γ^p (mN.m $^{-1}$)	Surface free energy, γ (mN.m $^{-1}$)
TPS-Gly	42.1 $\pm$ 3.4	36.3 $\pm$ 3.2	28.7 $\pm$ 2.5	32.2 $\pm$ 2.9	22.5 $\pm$ 2.0	54.7 $\pm$ 4.9
C.G. 1:3	45.0 $\pm$ 3.8	39.5 $\pm$ 3.3	30.5 $\pm$ 2.6	31.5 $\pm$ 2.6	20.0 $\pm$ 1.8	51.5 $\pm$ 4.1
C.M. 1:3	71.5 $\pm$ 6.8	63.0 $\pm$ 5.5	44.0 $\pm$ 3.8	31.4 $\pm$ 2.4	7.4 $\pm$ 0.6	38.8 $\pm$ 3.0
C.G.M. 1:1:1	56.0 $\pm$ 4.6	50.0 $\pm$ 4.1	38.0 $\pm$ 3.2	30.6 $\pm$ 2.3	14.8 $\pm$ 1.2	45.4 $\pm$ 3.5
C.G.M. 1:1:2	61.0 $\pm$ 5.0	55.0 $\pm$ 4.4	40.0 $\pm$ 3.3	30.0 $\pm$ 2.2	12.0 $\pm$ 1.1	42.0 $\pm$ 3.0
C.G.M. 1:2:1	50.0 $\pm$ 4.2	44.5 $\pm$ 3.8	34.0 $\pm$ 2.9	31.0 $\pm$ 2.4	17.5 $\pm$ 1.5	48.5 $\pm$ 3.8

The contact-angle and OWRK surface-energy results are summarised in Table 4. They show that replacing glycerol with MEA lowers surface polarity while γ^d remains $\sim$ 30-32 mN.m $^{-1}$; diiodomethane angles change little, confirming polarity-controlled wettability. Versus TPS-Gly ($\theta_{\text{water}}=42.1\pm3.4^{\circ}$, $\gamma^d=32.2\pm2.9$ mN.m $^{-1}$, $\gamma^p=22.5\pm2.0$ mN.m $^{-1}$, $\gamma=54.7\pm4.9$ mN.m $^{-1}$), ChCl:Gly (1:3) shows a small γ drop ($\gamma=51.5\pm4.1$ mN.m $^{-1}$) from modest γ^p loss (20.0 $\pm$ 1.8 mN.m $^{-1}$). ChCl:MEA (1:3) yields much higher contact angles ($\theta_{\text{water}}=71.5\pm6.8^{\circ}$; $\theta_{\text{formamide}}=63.0\pm5.5^{\circ}$) and the lowest γ (38.8 $\pm$ 3.0 mN.m $^{-1}$) due to a sharp γ^p decline (7.4 $\pm$ 0.6 mN.m $^{-1}$) at nearly unchanged γ^d (31.4 $\pm$ 2.4 mN.m $^{-1}$). Ternaries interpolate non-monotonically: 1:2:1 (48.5 $\pm$ 3.8 mN.m $^{-1}$)>1:1:1 (45.4 $\pm$ 3.5 mN.m $^{-1}$)>1:1:2 (42.0 $\pm$ 3.0 mN.m $^{-1}$), tracking a monotonic γ^p decrease (17.5 $\rightarrow$ 12.0 mN.m $^{-1}$) at near-constant γ^d (30-31 mN.m $^{-1}$). Diiodomethane angles change little, confirming polarity, not dispersion, governs wettability. Methodologically, water+diiodomethane+formamide enable Owens-Wendt-Rabel-Kaelble resolution of γ into γ^d and γ^p with an improved robustness [26, 27]. The MEA-containing DES reorient/engage surface -OH via reversible -OH/-NH H-bond/ion-pair junctions, reducing accessible polar groups at the air/solid interface; glycerol-rich

surfaces retain higher γ^p . For applications, ChCl:MEA (1:3) and 1:1:2 offer lower γ and higher water contact angle (moisture resistance), whereas glycerol-dominant formulations favour printability/adhesion. Notably, 1:1:2 couples moderate γ ($42.0 \text{ mN}\cdot\text{m}^{-1}$) with balanced mechanics, marking a practical design window [28].

Although barrier properties (WVTR/OTR) were not measured here, lower γ and γ^p together with higher θ_{water} for MEA-containing systems qualitatively suggest reduced water uptake and potentially lower WVTR relative to TPS-Gly. Nevertheless, gas transport also depends on bulk free volume and crystallinity; our XRD indicates substantial amorphisation in DES systems, which may increase OTR. We therefore anticipate moderate improvement in water-vapor resistance for 1:1:2 and a neutral-to-mixed effect on oxygen transport - an aspect prioritised for future validation.

3.7. Retrogradation

We focus aging assessments on mechanical endpoints because they provide a sensitive, application-level integration of microstructural changes under standardised humidity. These results are interpreted on top of the baseline structure-dynamics fingerprint established immediately after processing (XRD amorphisation; FTIR O-H red-shift/broadening and fingerprint-region redistribution; DMA T_g/E' depression). Under $23\pm 2^\circ\text{C}$ and $50\pm 5\%$ RH re-conditioning prior to each time point, the systematic loss of ductility at near-constant TS is a classical signature of physical retrogradation and reflects performance-relevant consequences of structural re-organisation.

Accordingly, physical retrogradation is inferred from the systematic loss of ductility at near-constant TS under standardised humidity, together with composition-dependent T_g/E' responses. Baseline diffractograms of freshly processed samples confirm extensive amorphisation (with Gly-rich systems retaining the most residual order), which coheres with the larger ϵ_b loss upon storage.

Table 5. Summary of mechanical properties and % change of starch-based thermoplastic samples stored at 0 and 56 days.

Samples	Storage time, days: 0		Storage time, days: 56		$\Delta TS \text{ vs } 0 (\%)$	$\Delta \epsilon_b \text{ vs } 0 (\%)$
	TS (MPa)	$\epsilon_b (\%)$	TS (MPa)	$\epsilon_b (\%)$		
TPS-Gly	1.54±0.1	169.9±14.8	0.79±0.07	85.49±8.6	-48.7±3.5	-49.7±5.3
C.G: 1:3	0.97±0.08	183.9±15.3	0.90±0.08	88.0±9.0	-7.2±0.6	-52.2±6.1
C.M: 1:3	2.27±0.19	228.9±21.1	2.0±0.1	149.49±10.2	-11.9±1.0	-34.7±4.3
C.G.M: 1:1:1	3.33±0.27	126.9±14.2	3.02±0.27	88.0±10.0	-9.2±0.7	-30.7±3.1
C.G.M: 1:1:2	2.91±0.27	195.1±15.4	2.7±0.24	162.0±12.0	-7.2±0.7	-17.0±1.6
C.G.M: 1:2:1	2.31±0.19	107.7±9.6	2.01±0.18	84.0±8.0	-13.0±0.9	-22.0±2.1

After 56 days of aging at $23\pm 2^\circ\text{C}$ and $50\pm 5\%$ RH, all formulations exhibited decreases in ϵ_b , whereas the retention of TS was composition-dependent (Table 5). TPS-Gly showed the largest loss in TS, decreasing from 1.54 to 0.79 MPa (-48.7%), accompanied by a decrease in ϵ_b from 169.9 to 85.49% (-49.7%). ChCl:Gly (1:3) largely retained its TS (0.97 to 0.90 MPa; -7.2%) but exhibited the largest loss in ϵ_b (183.9 to 88.0%; -52.2%). For ChCl:MEA (1:3), TS decreased from 2.27 to 2.00 MPa (-11.9%), while ϵ_b decreased from 228.9 to 149.49% (-34.7%). Among the ternary formulations, 1:1:2 exhibited the highest ϵ_b retention, with ϵ_b decreasing from 195.1 to 162.0% (-17.0%); its TS was also largely retained, decreasing from 2.91 to 2.70 MPa (-7.2%). This was followed by 1:2:1 and 1:1:1, with ϵ_b losses of 22.0 and 30.7%, respectively. Accordingly, the ϵ_b -retention order was 1:1:2>1:2:1>1:1:1>ChCl:MEA (1:3)>TPS-Gly>ChCl:Gly (1:3). These mechanical-property trends were consistent with the XRD results after aging: $I_{22.7}/I_{\text{am}}$ increased from 0.053 to 0.369 for TPS-Gly and from 0.055 to 0.737 for ChCl:Gly (1:3), compared with smaller increases from 0.092 to 0.262 for ChCl:MEA (1:3) and from 0.079 to 0.130 for 1:1:2. The comparatively smaller XRD change and greater ϵ_b retention observed for 1:1:2 are consistent with less extensive structural reorganization during storage.

Polyol-rich networks generate free volume and mobile H-bond bridges, boosting initial ϵ_b but facilitating moisture uptake, chain rearrangement, and recrystallisation, hence embrittlement (classically $\epsilon_b \downarrow$ with modest TS change) [7, 29, 30]. Plasticiser migration can further stiffen the amorphous phase [31]. In contrast, amine/amide plasticisers (e.g., MEA, urea) form stronger, more specific H-bond/ion-pair junctions that suppress retrogradation and better preserve ϵ_b over time; dense HB networks in DES can even impart long-term resistance [29, 30]. Consistently, higher water contact angle and lower OWRK γ^p correlate with slower aging, explaining the superior retention of MEA-containing and especially 1:1:2 systems.

Across formulations, reductions in the polar component of surface free energy (γ) correlate with improved ϵ_b -retention during 56-day storage. Replacing glycerol with MEA-containing DES lowers γ^p while maintaining γ^d ; this coincides with markedly smaller ductility loss (e.g., $\Delta \epsilon \sim -17\%$ for 1:1:2 vs $\sim -50\%$ for TPS-Gly). We ascribe this trend to reduced availability of accessible surface -OH groups (lower γ^p), which diminishes moisture sorption and water-mediated chain rearrangements that typically accelerate retrogradation. Thus, γ^p serves as a convenient proxy for the propensity to undergo water-facilitated secondary crystallisation.

Plasticiser migration was not quantified; nevertheless, the combination of a relatively stable TS with a monotonic ϵ_b decrease, the XRD, and the wettability trends indicates that retrogradation is the primary driver of embrittlement under our storage conditions, although minor migration, particularly in glycerol-rich systems, cannot be entirely ruled out.

While humidity-controlled, time-resolved XRD/DMTA can map crystallite-regrowth kinetics, under the present standardised conditioning, they would serve as confirmatory probes; the convergence of baseline XRD/FTIR/DMA with the aged mechanical response already substantiates our conclusions. Such measurements are therefore deferred to future work.

4. Conclusions

This study maps the composition-structure-property space of cassava TPS plasticised with choline-based DES at 25 wt% (ChCl:Gly, ChCl:MEA, and ChCl:Gly:MEA) and evidences a dual-mode plasticisation: glycerol supplies free volume, whereas MEA introduces reversible -OH/-NH hydrogen-bond/ion-pair junctions. Convergent data from mixing/MFI/SME, FTIR-ATR, DMA, SEM, OWRK, and 56-day aging show that mobility and supramolecular association can be co-tuned by DES composition to achieve processability without forfeiting cohesion. Quantitatively, Gly-only/Gly-rich systems enhance flow but depress cohesion; MEA-based DES lower torque and melt temperature, increase MFI, and simultaneously strengthen the stress-strain response. The ternary 1:1:2 delivers the best balance: MFI 2.45 ± 0.2 g/10 min, torque 5.5 ± 0.43 N·m, TS 2.91 ± 0.27 MPa, $\epsilon_b \sim 195\%$, and the lowest 56-day ductility loss ($\Delta\epsilon_b \sim -17\%$), far outperforming glycerol controls ($\sim -50\%$). Mechanistic signatures (O-H red-shift/broadening with emergent $\nu(\text{N-H})/\delta(\text{NH}_2)$; moderated T_g with sustained E' ; $\gamma^p \downarrow$ at $\gamma^d \sim 30\text{--}32$ mN·m⁻¹; increased amorphisation/delayed recrystallisation) support that MEA-enabled junctions counterbalance Gly-induced free volume, stabilising the amorphous phase and decoupling viscosity reduction from melt-strength loss. Mechanistically, glycerol-dominant DES increase free volume and chain mobility, whereas MEA-containing DES introduce reversible H-bond/ion-pair junctions; tuning their ratio yields viscosity reduction without loss of melt strength and improves aging resistance. These principles should extend to other HBD/HBA pairs beyond ChCl:Gly:MEA. Future work should quantify barrier properties (WVTR/OTR), assess plasticiser migration across humidity/

temperature, and validate the map across processing platforms.

Although plasticiser migration was not quantified, the weight of evidence, stable TS alongside a monotonic decrease in ϵ_b , XRD, and lower polar surface-energy, supports retrogradation as the primary cause of aging-induced embrittlement under the storage conditions employed here. Beyond MEA, the dual-mode plasticisation concept advanced in this work (polyol-driven free volume plus amine/amide-mediated H-bond/ion-pair junctions with ChCl) is expected to extend to other amine-containing DES with composition-dependent trade-offs between stiffness retention and mobility. Collectively, the composition-structure-property map clarifies how HBA-HBD balance governs mobility versus supramolecular association in TPS; these relationships are general and not tied to a specific processing line.

Mechanistic signatures: While DSC gelatinisation and granule-scale microscopy are valuable confirmatory tools, the present XRD/FTIR/DMA/SEM set already captures the structural consequences (loss of A-type order, increased amorphicity and segmental mobility) that DSC/microscopy would diagnose; further calorimetry/imaging is therefore deferred to future work.

5. Limitations

While we provide literature context for neat-DES thermal behaviour, our conclusions do not rely on any absolute T_g/T_m of the neat DES; they rest on composite-level DMA and rheology, which are the controlling parameters for TPS performance.

CRediT author statement

Chien Van Nguyen, Mai Thi Pham: Conceptualisation, Literature review, Data analysis, Writing - Original draft preparation; Phuong Thi Hoang: Supervision, Reviewing and Editing.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] L. Avérous (2004), "Biodegradable multiphase systems based on plasticized starch: A review", *Journal of Macromolecular Science, Part C: Polymer Reviews*, **44**(3), pp.231-274, DOI: 10.1081/MC-200029326.
- [2] M.I.J. Ibrahim, S.M. Sapuan, E.S. Zainudin, et al. (2019), "Physical, thermal, morphological, and tensile properties of cornstarch-based films as affected by different plasticizers", *International Journal of Food Properties*, **22**(1), pp.925-941, DOI: 10.1080/10942912.2019.1618324.
- [3] D. Lourdin, L. Coignard, H. Bizot, et al. (1997), "Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials", *Polymer*, **38**(21), pp.5401-5406, DOI: 10.1016/S0032-3861(97)00082-7.
- [4] A.P. Mathew, A. Dufresne (2002), "Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties", *Biomacromolecules*, **3**(5), pp.1101-1108, DOI: 10.1021/bm020065p.
- [5] M. Paluch, J. Ostrowska, P. Tyński, et al. (2022), "Structural and thermal properties of starch plasticized with glycerol/urea mixture", *Journal of Polymers and The Environment*, **30**, pp.728-740, DOI: 10.1007/s10924-021-02235-x.
- [6] X.F. Ma, J. Yu, J.F. Kennedy (2005), "Studies on the properties of natural fibers-reinforced thermoplastic starch composites", *Carbohydrate Polymers*, **62**(1), pp.19-24, DOI: 10.1016/j.carbpol.2005.07.015.
- [7] X.F. Ma, J.J. Yu, J.G. Wan (2006), "Urea and ethanolamine as a mixed plasticizer for thermoplastic starch", *Carbohydrate Polymers*, **64**(2), pp.267-273, DOI: 10.1016/j.carbpol.2005.11.042.
- [8] M. Zdanowicz, K. Wilpiszewska, T. Spychaj (2018), "Deep eutectic solvents for polysaccharides processing: A review", *Carbohydrate Polymers*, **200**, pp.361-380, DOI: 10.1016/j.carbpol.2018.07.078.
- [9] M. Zdanowicz, K. Sałasińska, K. Lewandowski, et al. (2022), "Thermoplastic starch/ternary deep eutectic solvent/lignin materials: Study of physicochemical properties and fire behavior", *ACS Sustainable Chemistry & Engineering*, **10**(14), pp.4579-4587, DOI: 10.1021/acssuschemeng.1c08542.
- [10] D. Skowrońska, K. Wilpiszewska (2022), "Deep eutectic solvents for starch treatment", *Polymers*, **14**(2), DOI: 10.3390/polym14020220.
- [11] B.C. Hancock, G. Zografi (1994), "The relationship between the glass transition temperature and the water content of amorphous pharmaceutical solids", *Pharmaceutical Research*, **11**(4), pp.471-477, DOI: 10.1023/A:1018941810744.
- [12] D.S. Chaudhary, B.P. Adhikari, S. Kasapis (2011), "Glass-transition behaviour of plasticised starch biopolymer system: A modified Gordon-Taylor approach", *Food Hydrocolloids*, **25**(1), pp.114-121, DOI: 10.1016/j.foodhyd.2010.06.002.
- [13] B. Cheng, C. Zhou, W. Yu, et al. (2001), "Evaluation of rheological parameters of polymer melts in torque rheometers", *Polymer Testing*, **20**(7), pp.811-818, DOI: 10.1016/S0142-9418(01)00008-3.
- [14] M. Li, C. Zhu, T. Fu, et al. (2022), "Effect of water on amine-based deep eutectic solvents (choline chloride + monoethanolamine): Structure and physicochemical properties", *Journal of Environmental Chemical Engineering*, **10**(1), DOI: 10.1016/j.jece.2021.106952.
- [15] A. Faraone, D.V. Wagle, G.A. Baker, et al. (2018), "Glycerol hydrogen-bonding network dominates structure and collective dynamics in a deep eutectic solvent", *The Journal of Physical Chemistry B*, **122**(3), pp.1261-1267, DOI: 10.1021/acs.jpcc.7b11224.
- [16] M. Zdanowicz, K. Sałasińska (2023), "Characterization of thermoplastic starch plasticized with ternary urea-polyols deep eutectic solvent with two selected fillers: Microcrystalline cellulose and montmorillonite", *Polymers*, **15**(4), DOI: 10.3390/polym15040972.
- [17] R. Banerjee, S.S. Ray (2023), "Role of rheology in morphology development and advanced processing of thermoplastic polymer materials: A review", *ACS Omega*, **8**(31), pp.27969-28001, DOI: 10.1021/acsomega.3c03310.
- [18] R.A. Gómez-López, C.E. Montilla-Buitrago, H.S. Villada-Castillo, et al. (2023), "Co-plasticization of starch with glycerol and isosorbide: Effect on retrogradation in thermo-plastic cassava starch films", *Polymers*, **15**(9), DOI: 10.3390/polym15092104.
- [19] L.E. McWilliams, N.A. Valley, S.N. Wren, et al. (2015), "A means to an interface: Investigating monoethanolamine behavior at an aqueous surface", *Physical Chemistry Chemical Physics*, **17**(33), pp.21458-21469, DOI: 10.1039/C5CP02931G.
- [20] A.F. Chamorro, M. Palencia, T.A. Lerma (2025), "Physicochemical characterization and properties of cassava starch: A review", *Polymers*, **17**(12), DOI: 10.3390/polym17121663.
- [21] M. Zdanowicz (2021), "Deep eutectic solvents based on urea, polyols and sugars for starch treatment", *International Journal of Biological Macromolecules*, **176**, pp.387-393, DOI: 10.1016/j.ijbiomac.2021.02.039.
- [22] M. Zdanowicz (2020), "Starch treatment with deep eutectic solvents, ionic liquids and glycerol: A comparative study", *Carbohydrate Polymers*, **229**, DOI: 10.1016/j.carbpol.2019.115574.
- [23] J.P. Florez, M. Fazeli, R.A. Simão (2019), "Preparation and characterisation of thermoplastic starch composite reinforced by plasma-treated poly(hydroxybutyrate) PHB", *International Journal of Biological Macromolecules*, **123**, pp.609-621, DOI: 10.1016/j.ijbiomac.2018.11.070.
- [24] J. Staker, S. Schott, R. Singh, et al. (2024), "Influence of choline chloride/urea and glycerol plasticizers on the mechanical properties of thermoplastic starch plastics", *Polymers*, **16**(6), DOI: 10.3390/polym16060751.
- [25] U.A. Weerasinghe, T. Wu, P.L. Chee, et al. (2024), "Deep eutectic solvents towards green polymeric materials", *Green Chemistry*, **26**(15), pp.8497-8527, DOI: 10.1039/D4GC00532E.
- [26] D.K. Owens, R.C. Wendt (1969), "Estimation of the surface free energy of polymers", *Journal of Applied Polymer Science*, **13**(8), pp.1741-1747, DOI: 10.1002/app.1969.070130815.
- [27] D.H. Kaelble (1970), "Dispersion-polar surface tension properties of organic solids", *The Journal of Adhesion*, **2**(2), pp.66-81, DOI: 10.1080/0021846708544582.
- [28] M. Zdanowicz (2023), "Influence of urea content in deep eutectic solvents on thermoplastic starch films' properties", *Applied Sciences*, **13**(3), DOI: 10.3390/app13031383.
- [29] A. Surendren, A.K. Mohanty, Q. Liu, et al. (2022), "A review of biodegradable thermoplastic starches, their blends and composites: Recent developments and opportunities for single-use plastic packaging alternatives", *Green Chemistry*, **24**(22), pp.8606-8636, DOI: 10.1039/D2GC02169B.
- [30] M. Huang, J. Yu, X.F. Ma (2005), "Ethanolamine as a novel plasticiser for thermoplastic starch", *Polymer Degradation and Stability*, **90**(3), pp.501-507, DOI: 10.1016/j.polymdegradstab.2005.04.005.
- [31] M. Esmaeili, G. Pircheraghi, R. Bagheri, et al. (2019), "Poly(lactic acid)/coplasticized thermoplastic starch blend: Effect of plasticizer migration on rheological and mechanical properties", *Polymers for Advanced Technologies*, **30**(4), pp.839-851, DOI: 10.1002/pat.4517.