

Article

Development of Bio-Based Thermosetting Resins from Maltodextrin–Itaconate Systems Toward Styrene-Free Unsaturated Polyesters

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Abstract

The transition to sustainable thermosetting resins is frequently hindered by the trade-off between high bio-based content and processability. This study reports a novel strategy in developing a highly bio-based, styrene-free unsaturated polyester resin (UPR) by leveraging maltodextrin-derived mixed esters dissolved in dimethyl itaconate (DMI). Unlike conventional polysaccharide-based systems that suffer from extreme viscosity, our functionalized prepolymer–DMI system achieves a low-viscosity curing solution without requiring petroleum-derived diluents such as styrene. Fourier-transform infrared spectroscopy confirmed the formation of a robust crosslinked network via the complete consumption of C=C bonds. Consequently, the cured resin exhibits exceptional thermal and mechanical performance, outperforming many existing bio-based analogs: a glass transition temperature (T_g) reaching 141 °C, a decomposition onset near 250 °C, and superior dimensional stability with a linear thermal expansion coefficient as low as 77 ppm/°C. Demonstrating a fully renewable, easy-to-process formulation with a flexural strength of 44 MPa, this work provides a design template for the next generation of high-performance, eco-friendly industrial thermosets.

Keywords: high bio-based unsaturated polyester resin; maltodextrin-derived prepolymer; styrene-free radical crosslinking



Academic Editors: Concepción Valencia-Barragán, Esperanza Cortés Triviño, Adrián Tenorio-Alfonso and Clara Delgado-Sánchez

Received: 3 February 2026

Revised: 27 February 2026

Accepted: 2 March 2026

Published: 6 March 2026

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1. Introduction

The global push toward a decarbonized and circular economy requires the polymer industry to develop materials with lower environmental impact across their entire life cycle. This has led to a strong demand for bio-based thermosetting resins with high biomass content, particularly in applications such as coatings, adhesives, and composites, which are currently heavily reliant on petrochemicals. Although conventional thermosets offer superior mechanical strength, heat resistance, and durability upon curing, their inherently crosslinked nature severely hinders their recyclability and biodegradability. Indeed, the chemically crosslinked nature of unsaturated polyester resins (UPRs) restricts their recovery for feedstock recycling. However, for applications such as coatings, where environmental discharge is a concern, potential biodegradability is a highly desirable attribute. High-biomass UPRs are therefore anticipated to be a significant solution to address both of these aspects [1]. Moreover, replacing fossil fuel-based thermosets with renewable analogs

remains a central challenge in sustainable polymer chemistry [2,3]. For example, UPRs rely on fossil fuel feedstocks and volatile styrene as reactive diluents, rendering them environmentally undesirable. Life-cycle analyses have shown that the carbon footprints of UPRs can be reduced by up to 57% by switching to fully renewable alternatives [4]. This potential has driven active research into the development of fully bio-based UPRs wherein both the polyacid and polyol components originate from sustainable sources [5,6].

Among the renewable monomers investigated to date, itaconic acid (IA) is a promising building block obtained via the fermentation of sugars by *Aspergillus terreus*, offering a nontoxic and structurally versatile platform for polyester synthesis [7]. Notably, the α,β -unsaturated dicarboxylic structure of IA imparts it with dual functionality, serving both as an ester-forming component and as a site for radical polymerization [8–10], thereby rendering it a renewable analog for maleic acid derivatives. Although IA possesses a dicarboxylic structure similar to that of maleic acid, its lack of geometrical isomerization and the higher reactivity of its exo-methylene double bond reduce the structural heterogeneity often observed in maleate-based UPR systems. This versatility has been exploited in the design of bio-based UPRs with properties comparable to those of their petrochemical counterparts. Furthermore, dimethyl itaconate (DMI) can be employed as a low-viscosity liquid derivative of IA [11], acting as both a monomer and a reactive diluent, and producing styrene-free formulations with improved safety and odor characteristics [12,13]. However, the resulting viscosity tends to be higher than those of styrene-based systems [14]; therefore, DMI is often used in combination with other reactive diluents, such as methacrylate derivatives.

Chemically crosslinked materials, including thermosetting resins, frequently incorporate polysaccharides as functional structural units to increase the biomass content, enhance biodegradability, improve mechanical performance, and enhance thermal resistance. In epoxy resin systems, the inherent chemical reactivity of the polysaccharide hydroxyl groups can be directly exploited in curing reactions, and such approaches have been extensively investigated for decades. For instance, in cellulose-based systems, chemical modifications such as acetylation [15] and/or hydroxyethylation [16] significantly improve compatibility with epoxy resin matrices, resulting in enhanced impact strength through improved interfacial adhesion and energy dissipation mechanisms.

In the case of UPRs, which are predominantly crosslinked via radical polymerization, the functionalization of resin systems has been explored using polysaccharides as particulate or nanoscale additives to enhance mechanical and thermal performance [17–19]. While these filler-based approaches can improve strength at low loading levels, they often face challenges related to dispersion and interfacial adhesion. In contrast to the particulate- and filler-based approaches described above, no studies have investigated the use of polysaccharides as molecularly dissolved prepolymer components in UPR curing solutions. One key advantage of polysaccharides is their high chemical tunability, which allows precise control of their compatibility with reactive monomers and the design of polysaccharide-based prepolymers optimized for UPR formulations. However, the dissolution of high-molecular-weight polymers in UPR curing solutions generally results in a dramatic increase in viscosity. This results in severe processability issues, making such systems impractical for conventional resin-processing techniques. This fundamental limitation hinders the direct use of polysaccharides as reactive prepolymer components in UPR systems.

To overcome this limitation, the use of low-molecular-weight oligosaccharides, such as maltodextrin (MD), represents a viable strategy. Indeed, chemically crosslinked networks incorporating maltodextrin as a structural component have been previously reported [20,21], particularly in hydrogel systems. However, to the best of our knowledge,

there have been no reports describing the use of maltodextrin-derived prepolymers in UPR systems. The introduction of unsaturated double bonds into the prepolymer system could therefore enable radical cross-linking of UPRs, potentially combining the biodegradability of carbohydrates with the mechanical durability of polyesters. Moreover, employing DMI as a curing medium is an attractive strategy to mitigate the typical miscibility and viscosity issues encountered with polar polysaccharide-based resins.

From both environmental and industrial perspectives, the development of styrene-free thermosetting resins is of critical importance because styrene, although widely used, is classified as a volatile hazardous air pollutant. Although various unsaturated fatty acid- and terpene-based monomers have been investigated for this purpose [22], these systems often contain abundant α,β -disubstituted double bonds. Their intrinsic low radical polymerization reactivity requires additional chemical modification such as methacrylation to achieve sufficient reactivity. In contrast, certain terpene-derived monomers, such as limonene, and bio-based monomers, such as IA, possess α,α -disubstituted double bonds, which confer relatively higher radical polymerization reactivity. Consequently, these compounds have strong potential for direct use as reactive diluents without the requirement for further functionalization.

Building on these insights, the present study aims to develop a novel UPR system derived from a maltodextrin derivative and DMI. This strategy involves the introduction of unsaturated ester groups into maltodextrin via controlled acylation, yielding a prepolymer with pendant double bonds. The obtained prepolymer is dissolved in DMI and subjected to thermal curing without external crosslinkers or styrene to form a rigid thermoset. This approach is expected to yield a styrene-free, carbohydrate-rich UPR with high biomass content. The maltodextrin derivatization, curing behavior, thermal stability, and mechanical performance of the resin are evaluated, and the effects of the prepolymer structure on both crosslinking and the glass transition temperature (T_g) are examined to guide the design of next-generation renewable UPRs.

2. Materials and Methods

2.1. General

Maltodextrin with different dextrose equivalent (DE) values (T100: DE = 8.0–9.9, T180: DE = 14.0–19.9, and T200: DE = 20.0–25.9) was purchased from Sansho Co., Ltd. (Osaka, Japan). Based on these DE values, the average degrees of polymerization were estimated to be ~4.5, 6.0, and 11 glucose units, denoted as MD_{4.5}, MD₆, and MD₁₁, respectively. Dimethylacetamide (DMAc; anhydrous, 99.8%) and cobalt(II) acetylacetonate (97.0%) were obtained from Sigma-Aldrich Co. (St. Louis, MO, USA), while methacryloyl chloride (>97.0%) was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Acetyl chloride (>98.0%), DMI (>98.0%, containing 100 ppm hydroquinone as a stabilizer), and methyl ethyl ketone peroxide (MEKPO, ~50% in dimethyl phthalate) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Methanol (>99.8%) and acetone (>99.5%) were obtained from Kanto Chemical Co. (Tokyo, Japan). All reagents were used as received without further purification.

Proton nuclear magnetic resonance (^1H NMR) spectra were measured using an ECS-600 spectrometer (JEOL, Tokyo, Japan). The viscosities of the curing solutions were measured using a rotational viscometer (TV-25; Toki Sangyo Co., Ltd., Tokyo, Japan). Fourier-transform infrared (FT-IR) spectroscopy was performed using a Nicolet iS10 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Dynamic mechanical analysis (DMA) was performed using a DMS6100 instrument (Seiko Instruments Inc., Chiba, Japan). Thermogravimetric analysis (TGA) was performed using a DTG-60AH analyzer (Shimadzu Co., Kyoto, Japan), while thermomechanical analysis (TMA) was performed

using an EXATAR SS7100C instrument (Seiko Instruments Inc., Chiba, Japan). The flexural properties of the cured resins were evaluated using a universal testing machine (AG-5kN Xplus; Shimadzu Co., Kyoto, Japan). Distilled water was prepared using the WG203 Auto Still system (Yamato Scientific Co., Ltd., Tokyo, Japan).

2.2. Chemical Synthesis of the Prepolymers—Maltodextrin Acetate Methacrylate

Maltodextrin was vacuum-dried at 70 °C for 24 h, and the dried sample (100 g) was placed in a two-necked flask. The flask was purged with argon gas, DMAc (1.8 L) was added, and the mixture was stirred at 70 °C for 2 h to dissolve the maltodextrin. Methacryloyl chloride (1.3–2.0 equiv. per anhydroglucose unit (AGU)) was dissolved in DMAc (100 mL) and placed in a dropping funnel. This solution was added dropwise to the maltodextrin solution over 10 min, followed by stirring at 70 °C for 3 h to complete the methacryloylation reaction. After cooling the reaction mixture in a water bath to 25 °C, a solution of acetyl chloride (2.5 equiv. per AGU) in DMAc (100 mL) was added dropwise at 25 °C. The mixture was then stirred at 40 °C for 21 h to complete the acetylation reaction. Then, methanol (200 mL) was added to quench the residual acylating reagents, and the reaction mixture was concentrated at 80 °C using a rotary evaporator. The resulting solid was washed repeatedly with distilled water until the filtrate reached a neutral pH. The product was dissolved in acetone, and the insoluble components were removed by centrifugation and subsequent vacuum filtration. The acetone was then removed under reduced pressure to obtain the final product. The dry weight of the product was measured, and the recovered mass of the maltodextrin backbone was calculated based on the degree of substitution (DS), as described below. The yield was defined as the ratio of the recovered maltodextrin mass to the initial maltodextrin mass.

The DS of the acyl groups was determined by quantitative ^1H NMR (qNMR) spectroscopy. To avoid peak overlap caused by the residual hydroxyl protons in maltodextrin and water, trifluoroacetic acid was added to the sample solution immediately before measurement. The DS of the methacryloyl groups was calculated from the ratios of the integrated intensities of the vinyl protons ($=\text{CH}_2$, 5.55–6.40 ppm) to those of the glucose-unit protons (AGU, 3.00–5.55 ppm). As the methyl protons of the acetyl group ($-\text{C}(\text{O})\text{CH}_3$) and the methacryloyl group ($=\text{C}(\text{CH}_3)-$) both appear in the 1.70–2.40 ppm region, their peaks overlapped and could not be separated. Therefore, the DS of the acetyl groups was calculated by subtracting the estimated intensity of the methacryloyl methyl signal (calculated as 1.5 times the $=\text{CH}_2$ integral) from the total integrated intensity in this region. Moreover, as the terminal hydroxyl groups significantly affect the DS estimation for lower molecular weight samples, the average numbers of hydroxyl groups and AGU hydrogen atoms per molecule were calculated based on the average degree of polymerization. Consequently, the 4.5-mer, 6-mer, and 11-mer maltodextrins were estimated to contain 15.5, 20, and 35 hydroxyl groups and 31.5, 42, and 77 AGU hydrogen atoms, respectively. The DS values were expressed as molar percentages calculated from these hydrogen ratios.

2.3. Viscosity Measurement of the Curing Solutions Before Crosslinking

The viscosities of the curing solutions were measured at 40 °C, which is above the melting point of DMI (i.e., 37 °C). Specifically, for each sample, DMI was melted at 40 °C and a predetermined amount of maltodextrin derivative was added and dissolved completely under stirring. The resulting solution was transferred to a small sample adapter, and the rotor was set in place. After the temperature stabilized at 40 °C, the viscosity was recorded at discrete shear rates only after a steady-state value was reached to avoid transient pre-shear effects, rather than using a continuous ramp mode.

2.4. Thermal Curing Procedure and Characterization of the Cured Materials

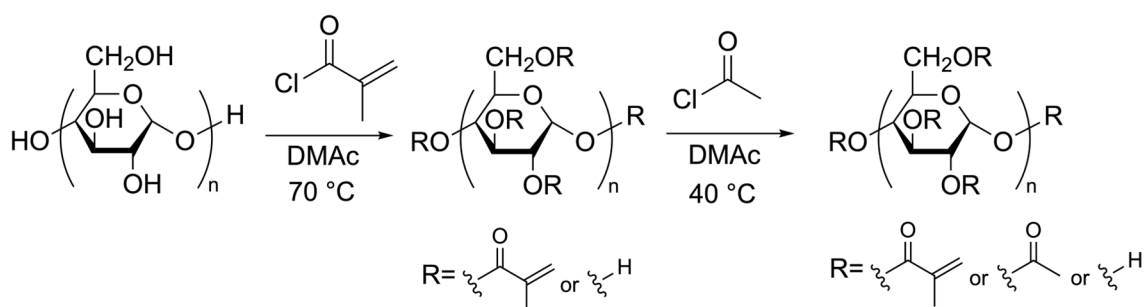
Cobalt(II) acetylacetonate (0.6 wt% of the total curing solution) was added to DMI and stirred at 40 °C to achieve uniform dispersion. A predetermined amount of maltodextrin derivative was then added and completely dissolved at 40 °C, followed by which the solution was degassed under reduced pressure (40 °C, 10 kPa) for 20 min. Subsequently, a MEKPO solution (6 wt% of the total curing solution) was added as an initiator, and the mixture was stirred for 5 min prior to degassing in an ultrasonic bath at 40 °C for 20 min. The prepared curing solution was poured into molds coated with a release agent (KS-707, Shin-Etsu Chemical Co., Ltd., Japan), pre-cured at 60 °C for 24 h, and then post-cured at 120 °C for 3 h. The consumption of unsaturated C=C bonds during curing was monitored by FT-IR spectroscopy (KBr method).

The thermal decomposition temperatures of the cured resins were evaluated by TGA under a flow of nitrogen gas (50 mL/min). Specimens for the physical property measurements were prepared using different molds depending on the test requirements. For flexural testing, a mold with dimensions of 60 mm × 15 mm × 2 mm was used to prepare the cured samples according to the procedure described above. Flexural tests were conducted according to the JIS K7017 method [23], and the results were analyzed using a two-tailed *t*-test with five replicates (*n* = 5) for each condition. Statistical significance was defined as *p* < 0.05. For the DMA measurements, samples were prepared using molds with dimensions of 50 mm × 10 mm × 2 mm, and three-point flexural tests were performed at a frequency of 1 Hz. For TMA, the test pieces molded for flexural testing were cut into 5 mm × 5 mm × 2 mm specimens, and measurements were performed under a flow of nitrogen gas (50 mL/min) between 0 and 180 °C.

3. Results and Discussion

3.1. Synthesis of the Prepolymers—Maltodextrin Acetate Methacrylate

Using three types of maltodextrin with average degrees of polymerization of 4.5, 6, and 11, respectively, as raw materials, mixed esters were synthesized by stepwise esterification of the maltodextrin hydroxyl groups with an appropriate amount of methacryloyl chloride, followed by acetyl chloride (Scheme 1). The total DS of the hydroxyl groups in the maltodextrin molecules was maintained constant between 81 and 83%, and several mixed esters with varying methacryloyl/acetyl ratios were synthesized (Table 1). These mixed esters (prepolymers) were denoted by MD_{XX}(DS_{acetyl}/DS_{methacryloyl}), where the subscript “XX” denotes the average degree of polymerization of maltodextrin, while DS_{acetyl} and DS_{methacryloyl} are the substitution degrees (mol%) of the acetyl and methacryloyl groups, respectively. The corresponding prepolymers were obtained in good yields of 86–95%.



Scheme 1. Synthesis of maltodextrin acetate methacrylate.

Table 1. Compositional details for the synthesized maltodextrin acetate methacrylates.

Entry	Abbreviation	DS _{acetyl} (%)	DS _{methacryloyl} (%)	DS _{total} (%)	Yield (%)
1	MD ₁₁ (53/28)	53	28	81	94
2	MD ₆ (51/31)	51	31	81	86
3	MD ₆ (55/28)	55	28	83	87
4	MD ₆ (60/21)	60	21	81	88
5	MD _{4.5} (57/26)	57	26	83	95

DS_{acetyl}, DS_{methacryloyl}, and DS_{total} represent the degree of acetylation, methacryloylation, and sum of them, respectively.

The chemical structures of the synthesized prepolymers were determined using FT-IR and NMR spectroscopy, as demonstrated in Figure 1 for MD_{4.5}(57/26). From the FT-IR spectrum, it can be seen that the peak derived from the stretching vibration of the sugar hydroxyl groups ($\sim 3300\text{ cm}^{-1}$) was significantly attenuated after the reaction. Additionally, peaks originating from the methacryloyl C=O and C=C groups appeared at 1720 and 1637 cm^{-1} , respectively, while the peak derived from the acetyl C=O group appeared at 1743 cm^{-1} . These assignments were confirmed by comparison with standard IR spectra of methyl methacrylate and methyl acetate obtained from the Spectral Database for Organic Compounds (SDBS) [24,25]. These results confirm successful esterification of the hydroxyl groups with methacryloyl and acetyl moieties.

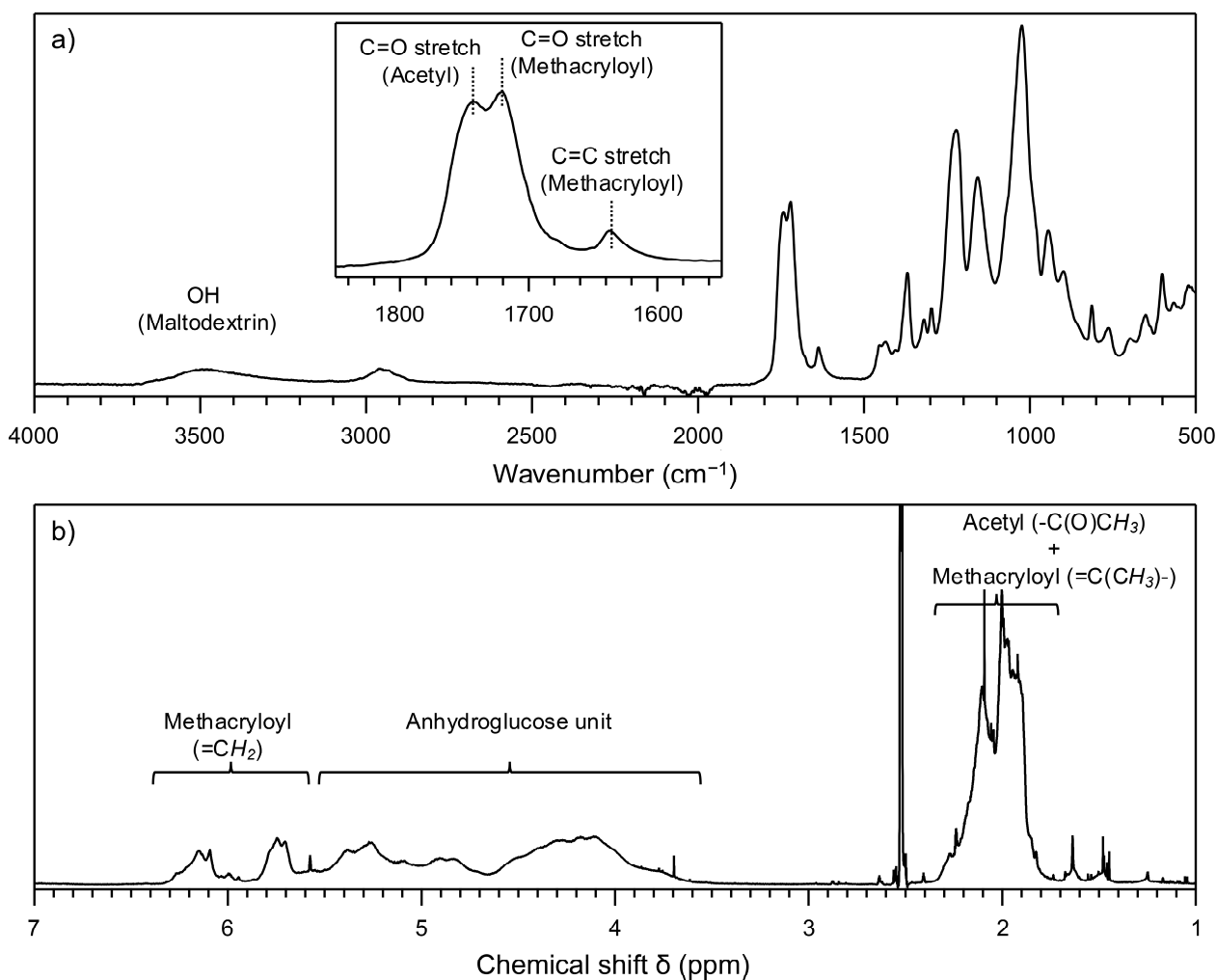


Figure 1. (a) FT-IR (ATR) and (b) ^1H NMR spectra of MD_{4.5}(57/26). The NMR spectrum was recorded in DMSO- d_6 .

In the ^1H NMR spectrum, peaks corresponding to the hydrogen atoms in the glucose ring were observed at 3.5–5.5 ppm, while those of the methacryloyl and acetyl groups were observed at 5.6–6.4 and 1.7–2.3 ppm, respectively. The methacryloyl DS was calculated from integration of the peak areas corresponding to the glucose ring protons and the vinyl ($=\text{CH}_2$) protons of the methacryloyl moiety. The acetyl DS was determined by initially calculating the sum of the acetyl and methacryloyl DS values and then subtracting the methacryloyl DS, as described in the experimental section. When calculating the DS, if the double bonds in the methacryloyl groups are consumed by any unexpected side reactions, the $\text{DS}_{\text{acetyl}}$ may be overestimated compared to the actual value. However, any extra peaks in the NMR spectrum were negligible, suggesting that unexpected side reactions had no significant impact on the calculated DS. The FT-IR and NMR spectra of other prepolymers possessing different average degrees of polymerization and substitution are shown in Figures S1 and S2, respectively. All samples exhibited comparable spectra, differing only in their peak intensities, thereby confirming the successful synthesis of all target prepolymers.

3.2. Evaluation of the Physical Properties of the Curing Solutions

Initially, the dissolution capacities of the different prepolymers were evaluated in DMI at 40 °C (Table S1). Regardless of the molecular weight, MD derivatives containing ≤ 28 mol% $\text{DS}_{\text{methacryloyl}}$ completely dissolved in DMI, even at a concentration of 50 wt%. However, when the $\text{DS}_{\text{methacryloyl}}$ content reached 31 mol% ($\text{MD}_6(51/31)$), some undissolved residues were observed. Based on these results, subsequent prepolymer evaluations were performed using ≤ 28 mol% $\text{DS}_{\text{methacryloyl}}$.

The synthesized prepolymers were dissolved in DMI at concentrations ranging from 30 to 50 wt%. Using a rotational viscometer, the viscosities of the resulting curing solutions were measured at 40 °C. The viscosity of a commercially available UPR curing solution was also measured to determine the target viscosity range (Figure S3a), affording a value of ~ 1200 mPa·s at low shear rates and a reduced viscosity of < 200 mPa·s at higher shear rates. The target viscosity range was therefore set at 200–1200 mPa·s. For the $\text{MD}_6(55/28)$ prepolymer, it was observed that the viscosity of the curing solution was also dependent on the shear rate, with higher shear rates resulting in lower viscosities. Additionally, upon plotting the viscosity at 50 s^{-1} shear rate against the prepolymer concentration, a concentration of ≤ 40 wt% was sufficient to provide a viscosity within the target range (Figure 2a). However, at a higher prepolymer concentration of 50 wt%, the viscosity increased sharply and exceeded the target value. Curing solutions containing prepolymers derived from MD_6 and MD_{11} exhibited higher viscosities than commercial products, suggesting that their use in spray-up or hand lay-up processes (commonly employed for manufacturing fiber-reinforced plastics for boats, large tanks, bathtubs, etc.) may be challenging. However, for the prepolymer derived from $\text{MD}_{4.5}$, the viscosity remained below 1000 mPa·s even at a prepolymer concentration of 50 wt%, reflecting the comparatively low viscosity of the curing solution. Furthermore, as shown in Figure 2b, the curing solution derived from $\text{MD}_{4.5}(57/26)$ exhibited non-Newtonian behavior and shear-rate-dependent viscosity reduction at all prepolymer concentrations between 30 and 50 wt%. Upon plotting the log of the shear stress versus the log of the shear rate, the viscosity change closely resembled the behavior of a Bingham fluid, similar to that of the commercial prepolymer solution (Figure S3b). According to this model, the fluid exhibits a yield stress, beyond which it behaves as a Newtonian fluid.

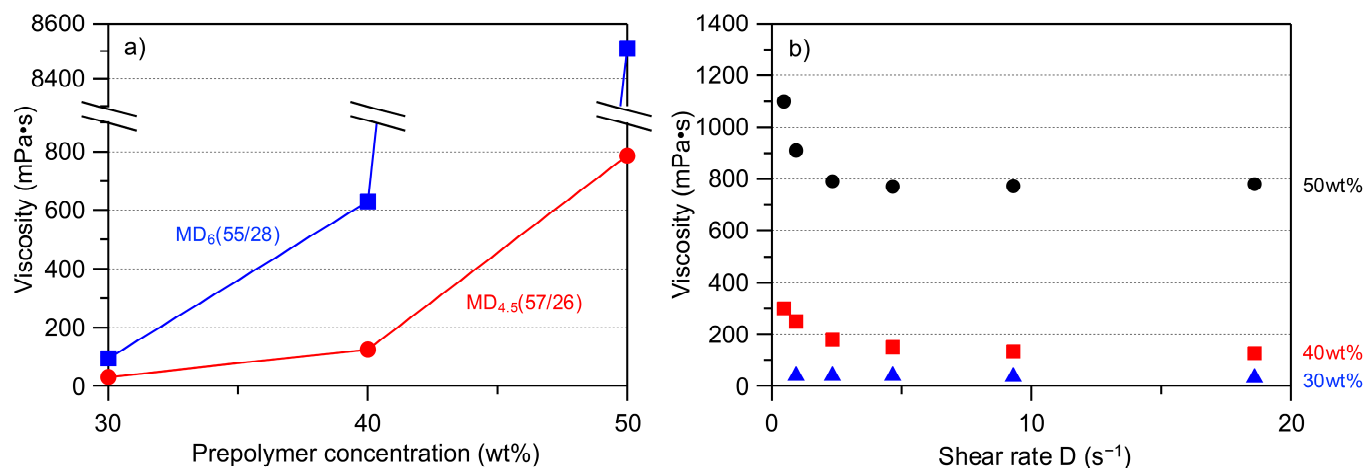


Figure 2. (a) Viscosities of the curing solutions composed of DMI and MD_{4.5}(57/26) (red line) or MD₆(55/28) (blue line) at prepolymer loadings of 30–50 wt%. The viscosity was measured at 40 °C using a shear rate of 50 s⁻¹. (b) Dependence of the curing solution viscosity on the shear rate. The curing solutions were composed of DMI and MD_{4.5}(57/26) at prepolymer loadings of 30 wt% (blue triangles), 40 wt% (red squares), and 50 wt% (black circles).

3.3. Thermal Treatment of the Curing Solutions

Subsequently, the thermal curing behavior of the curing solution was employed using MD_{4.5}(57/26) as the prepolymer. After thermal curing, the FT-IR spectrum was recorded in the attenuated total reflectance (ATR) mode and compared with that of the original curing solution (Figure 3). The peaks derived from the methacryloyl C=O and C=C groups (i.e., at 1720 and 1637 cm⁻¹, respectively) completely disappeared after curing, confirming completion of the radical polymerization reaction.

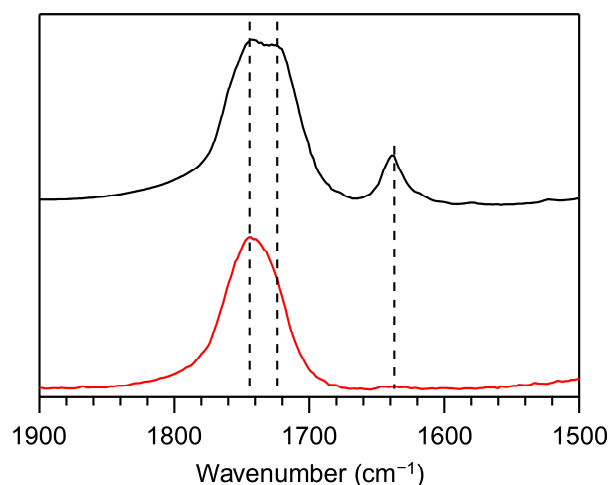


Figure 3. FT-IR spectra (KBr method) recorded for the resin composed of MD_{4.5}(57/26) and DMI (50 wt%) before (black line) and after (red line) curing. The vertical dashed lines are provided as visual guides to facilitate an easier comparison of peak positions and intensity changes during the reaction.

3.4. Mechanical Properties of the Thermally Cured Resins

Thermal curing of the MD_{4.5}(57/26) solution was performed in a strip mold for flexural testing, and the resulting sample pieces were tested at ambient conditions. The resulting stress–strain curves are shown in Figure 4a, and the corresponding flexural strengths, moduli, and breaking strains of the specimens are given in Figure 4b and Table 2. At a prepolymer concentration of 30 wt%, the breaking stress was 35.8 ± 3.9 MPa,

while a prepolymer concentration of 40 wt% afforded a higher breaking stress of 44.0 ± 3.4 MPa ($p = 0.015$ vs. 30 wt%). However, upon increasing the concentration to 50 wt%, the breaking stress decreased to 28.0 ± 6.6 MPa ($p = 0.010$ vs. 40 wt%). In contrast, the prepolymer concentration had no significant effect on the flexural moduli of the cured resins. Consequently, the increased breaking strength observed at higher prepolymer concentrations was attributed to the increased crosslink densities. However, as the distance between crosslink points became shorter at higher prepolymer concentrations, the sample became brittle and the breaking strength decreased. Although an increase in crosslink density typically enhances the modulus of elasticity, the flexural moduli remained relatively constant even at 50 wt% prepolymer concentration. This behavior can be attributed to the sharp increase in the initial viscosity of the 50 wt% curing solution (Figure 2a), which likely creates diffusion limitations for the reactive species during the crosslinking process. Such high viscosity may lead to a less homogeneous network and the formation of microvoids or internal defects within the matrix, thereby counteracting the expected increase in modulus and causing the observed reduction in breaking strength. The optimal prepolymer concentration was therefore determined to be 40 wt%. For comparison, thermally cured resins were prepared using 30 and 40 wt% MD₆(55/28), and their flexural strengths were evaluated, affording values of 19.7 ± 6.7 and 35.2 ± 5.4 MPa, respectively. In both cases, the flexural strength was lower than those of the corresponding MD_{4.5}(57/26) resins (Figure S4). This may be because of the longer prepolymer chain length of MD₆(55/28), allowing the material to be more flexible.

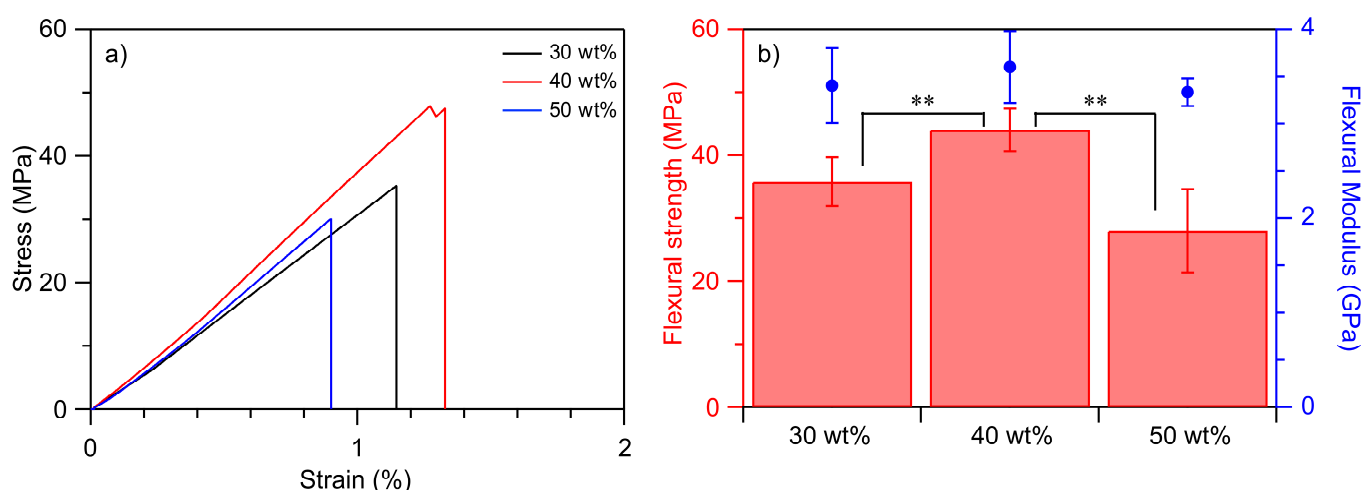


Figure 4. Flexural tests performed for the cured resins composed of MD_{4.5}(57/26) and DMI with prepolymer concentrations of 30, 40, and 50 wt%. (a) Stress–strain curves and (b) flexural strengths and Young’s moduli. Results are presented as the mean $\pm$ SD. Statistical significance is reflected by ** $p < 0.05$.

Table 2. Bending performance of the cured resins.

Entry	Prepolymer Concentration (wt%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Breaking Strain (%)
1	30	35.8 ± 3.9	3.4 ± 0.40	1.1 ± 0.4
2	40	44.0 ± 3.4	3.4 ± 0.38	1.2 ± 0.4
3	50	28.0 ± 6.6	3.3 ± 0.15	1.2 ± 0.2

3.5. Dynamic Viscoelastic Behavior of the Thermally Cured Resin

The dynamic viscoelasticity of the thermally cured resin composed of MD_{4.5}(57/26) was evaluated at different temperatures (Figure 5). In the cured material containing 30 wt% prepolymer, the storage modulus remained almost unchanged up to ~ 80 °C, whereas the

loss modulus increased with increasing temperature. In other words, the cured material was in a glassy state below 80 °C. Thereafter, both the storage and loss moduli decreased with increasing temperature and, beyond ~160 °C, the storage modulus reached a plateau, indicating transition to the rubbery state (Figure 5a). Additionally, the $\tan \delta$ value (i.e., the ratio of the loss modulus to the storage modulus) reached its maximum at 125 °C, reflecting the T_g of the polymer chain. Upon increasing the prepolymer content to 40 and 50 wt%, the temperature at which the maximum $\tan \delta$ value was obtained rose slightly to 132 and 141 °C, respectively (Figure 5b,c). As the FT-IR results indicated almost complete reaction of the double bonds at these concentrations, the obtained results suggested that increasing the prepolymer concentration increased the crosslinking density. This shortened the distance between crosslink points, thereby increasing T_g . Moreover, the cured resin became harder at higher prepolymer concentrations, consistent with the reduced $\tan \delta$ peak intensities under these conditions. Furthermore, a slight broadening of the peak width at half-height was observed with increasing prepolymer content. This change suggests increased polydispersity and a wider distribution of relaxation times within the crosslinked network as the structure becomes more densely packed. This reflects the complex homogeneity of the carbohydrate-rich matrix. For the cured resin based on the MD₆(55/28) prepolymer, the T_g was determined to be 118 and 125 °C at 30 and 40 wt% of the prepolymer, respectively, representing slightly lower values than those of the MD_{4.5}(57/26)-based resin (Figure S5).

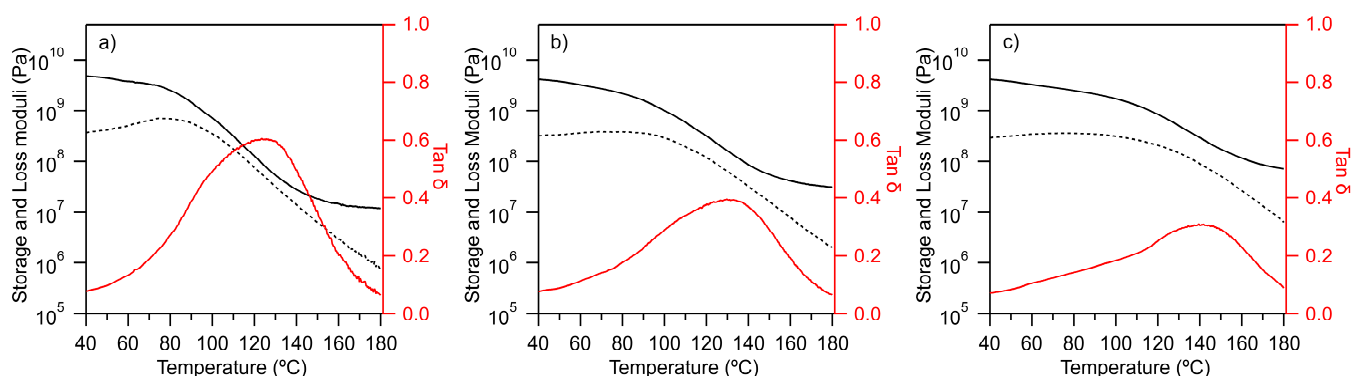


Figure 5. DMA profiles of the DMI resins incorporating (a) 30 wt%, (b) 40 wt%, and (c) 50 wt% MD_{4.5}(57/26) as the prepolymer. The storage (solid black line) and loss (dashed black line) moduli and $\tan \delta$ values (red line) are plotted against the temperature.

3.6. Thermal Stability of the Cured Resin

TGA measurements were performed to evaluate the thermal decomposition temperature of the thermally cured resin incorporating the MD_{4.5}(57/26) prepolymer (Figure 6a–c). Upon increasing the prepolymer concentration from 30 wt% to 40 and 50 wt%, the 5%-weight-loss temperature (T_{d5}) decreased slightly from 260 °C to 259 and 251 °C, respectively. Notably, the thermal stability of all the UPRs was sufficiently high for common use. The derivative thermogravimetry (DTG) curves clearly resolve two distinct decomposition stages. The first stage, centered at ~340 °C, corresponds to the decomposition of the DMI-derived crosslinked segments [26], whereas the second stage at ~370 °C is attributed to the thermal degradation of the carbohydrate-derived maltodextrin backbone (Figure S6). Notably, the intensity of the first peak gradually diminishes as the prepolymer concentration increases from 30 to 50 wt%. This trend is consistent with the decreasing mass fraction of DMI in the final cured resin as it is replaced by a higher proportion of the maltodextrin derivative. This two-stage thermal decomposition was also observed for the MD₆(55/28) resin system (Figure S7).

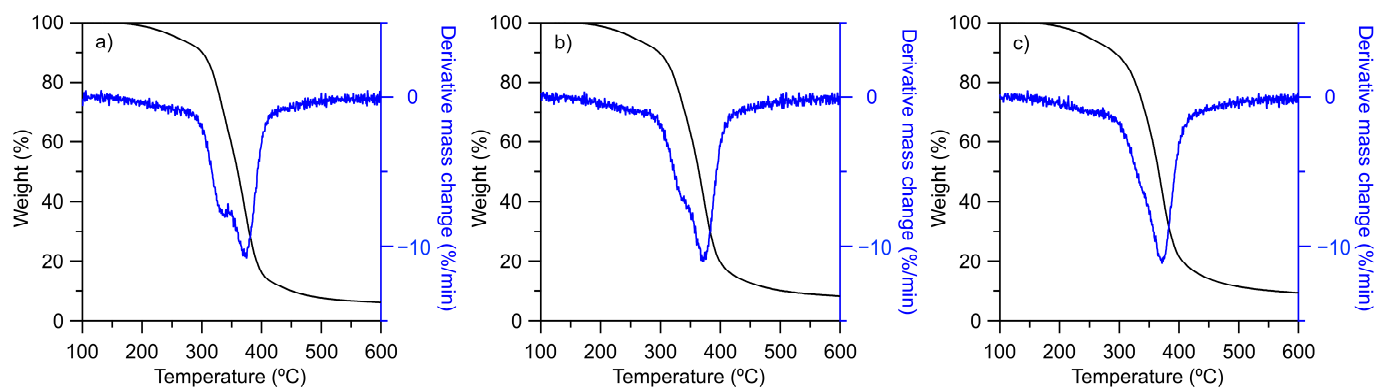


Figure 6. TGA profiles recorded for the cured DMI resins incorporating (a) 30 wt%, (b) 40 wt%, and (c) 50 wt% MD_{4.5}(57/26) prepolymer. The blue lines represent the first derivative of mass change (DTG).

3.7. Dimensional Stability of the Cured Resin

The thermal expansion behavior of the thermally cured resin incorporating the MD_{4.5}(57/26) prepolymer was subsequently analyzed using TMA, wherein the percentage of sample expansion and its first derivative (dL/dT) were plotted as a function of temperature (Figure 7). The derivative curves, representing the instantaneous coefficient of thermal expansion, more clearly highlight the transition to the rubbery state at T_g , which is otherwise subtle in the raw expansion plots. The average linear thermal expansion coefficient in the range of 0–50 °C (i.e., below the T_g) was found to be 77–89 ppm °C^{−1}, indicating a slight dependence on the prepolymer concentration. These values are at the lower end of the typical range reported for UPRs (i.e., 55–120 ppm °C^{−1}) [27]; in other words, the UPRs developed in this study possess better dimensional stability than do typical UPRs. At a prepolymer concentration of 30 wt%, the linear expansion coefficient was significantly reduced upon increasing the temperature from ~80 and 120 °C. According to the DMA results (Figure 5a), the loss modulus reached its maximum at ~80 °C, indicating that the β -relaxation process of the polymer side chains had essentially reached completion at this temperature. Meanwhile, the α -relaxation associated with cooperative main-chain motion occurred at T_g (i.e., ~125 °C). Therefore, in the temperature region between the completion of β -relaxation and the onset of α -relaxation, the contribution of local molecular motions to macroscopic thermal expansion became weak. Simultaneously, slight densification owing to molecular packing and structural relaxation may have occurred, leading to the release of residual internal stress. Consequently, the thermal expansion behavior was suppressed in this temperature range. Similar behavior was observed for the thermally cured resin incorporating the MD₆(55/28) prepolymer at a concentration of 30 wt% (Figure S8).

Notably, the properties of the present prepolymers and thermally cured resins are comparable to those reported for itaconate-based UPRs, as summarized in Table S2. For example, Spasojevic et al. [9] reported bio-based unsaturated polyesters with moderate-to-high T_g values (65–153 °C) and tensile strengths of 20–55 MPa, which were prepared using an itaconate-based prepolymer and diluents. While a direct numerical comparison is somewhat limited because many existing systems are evaluated based on tensile strength rather than the flexural strength reported here, the T_g (125–141 °C) and mechanical integrity (flexural strength of 44 MPa) of the present system demonstrate its high-performance potential, suggesting that the incorporation of a carbohydrate backbone does not compromise mechanical or thermal performance. However, despite similar prepolymer weights, the viscosity of the curing solution was ~25% lower for the maltodextrin-based system than for the itaconate ester-based system. This is advantageous from the viewpoint of the UPR curing process. For instance, during resin transfer molding, a lower viscosity facilitates resin

injection, prevents air entrapment (void formation), and allows for increased production speed. Furthermore, during the spray-up and filament winding processes, a lower viscosity allows the resin to impregnate the filaments more rapidly and uniformly, preventing spray nozzle clogging and enabling stable atomization.

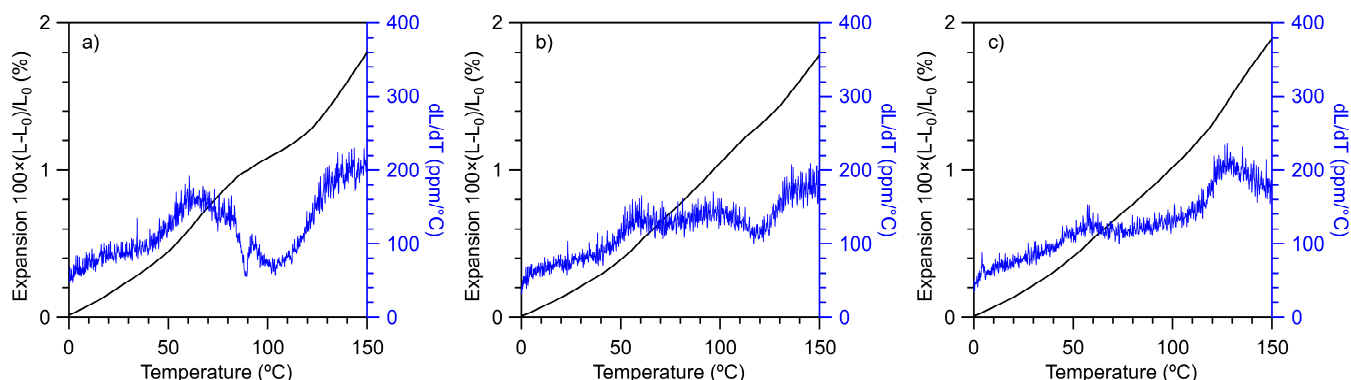


Figure 7. TMA profiles recorded for the cured DMI resins incorporating (a) 30 wt%, (b) 40 wt%, and (c) 50 wt% of the MD_{4.5}(57/26) prepolymer. The blue lines represent the first derivative of the thermal expansion curves (dL/dT).

In another study, Hofmann et al. [28] synthesized polyesters using furan dicarboxylic acid and fumaric acid as dicarboxylic acids, along with 1,3-propanediol and isosorbide as diols. They developed a UPR in which 2-hydroxyethyl methacrylate was blended with styrene at a 1:1 weight ratio for use as the reactive diluent. Even at a high prepolymer concentration of 60 wt%, they successfully maintained a low viscosity (<1300 mPa·s), and the tensile strength reached a sufficiently high value of 57 MPa. However, this formulation requires a 20 wt% loading of styrene, thereby not achieving a completely styrene-free system. Although the present IA–maltodextrin system exhibits a slightly lower strength than that reported by Hofmann et al., the incorporation of 20 wt% styrene increased the flexural strength to a comparable value of 54.2 ± 3.2 MPa. Consequently, when considering a styrene-free system, the present prepolymer, composed mainly of maltodextrin and DMI-derived carbon, achieved comparable or even higher biomass ratios.

Overall, these comparisons suggest that the prepolymer system developed herein possesses thermal and mechanical properties comparable to those of previously reported bio-based unsaturated polyesters, while also featuring a novel carbohydrate-based backbone architecture that may afford benefits such as improved curing solution processability and the potential for future biodegradation studies. In the near future, the UPRs are expected to be further functionalized by optimizing the combination of bio-derived reactive monomers and diluents with a suitably modified maltodextrin derivative.

4. Conclusions

This study demonstrated that maltodextrin can be successfully functionalized with unsaturated ester groups and combined with dimethyl itaconate (DMI) to produce a highly bio-based, styrene-free, carbohydrate-rich unsaturated polyester-type thermoset. Owing to its low molecular weight and tunable degree of substituents, the maltodextrin-mixed ester was highly miscible with DMI, thereby avoiding the severe viscosity and processability challenges typically associated with polysaccharide-based resins. The resulting cured materials exhibited well-defined crosslink formation, thermal stability, and mechanical rigidity, indicating that carbohydrate-derived prepolymers can serve as viable structural components in renewable unsaturated polyester resin systems. Furthermore, these results

provide design guidelines for next-generation bio-based thermosetting resins with low environmental impact.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050645/s1>, Figure S1: FT-IR(ATR) spectra of maltodextrin acetate methacrylate with different substitution ratios. (a) MD₁₁(53/28), (b) MD₆(51/31), (c) MD₆(55/28), and (d) MD₆(60/21); Figure S2: ¹H NMR spectra of maltodextrin acetate methacrylate with different substitution ratios. (a) MD₁₁(53/28) measured in CDCl₃, (b) MD₆(51/31), (c) MD₆(55/28), and (d) MD₆(60/21) measured in DMSO-*d*₆; Figure S3: (a) Change in viscosity of a commercial unsaturated polymer resin (Rigolac) with shear rate. (b) Relationship between the logarithms of shear stress (S) and shear rate (D) for the curing solutions: commercial unsaturated polymer resin (Rigolac) and the mixtures prepared using 30–50 wt% MD_{4.5}(57/26) and DMI; Figure S4: Flexural tests performed for the cured resins comprising MD₆(55/28) and DMI at different prepolymer weight ratios (30 and 40 wt%). (a) Stress–strain curves and (b) flexural strengths and Young’s moduli, presented as the mean ± SD; Figure S5: DMA profile of the cured DMI resins containing (a) 30 wt% and (b) 40 wt% MD₆(55/28) prepolymer. The storage (solid black line) and loss (dashed black line) moduli and Tan δ values (red line) are plotted against temperature; Figure S6: TGA profile of the MD_{4.5}(57/26) prepolymer; Figure S7: TGA profiles of the cured DMI resins incorporating (a) 30 wt% and (b) 40 wt% of the MD₆(55/28) prepolymer; Figure S8: TMA profiles of the cured DMI resins incorporating (a) 30 wt% and (b) 40 wt% of the MD₆(55/28) prepolymer; Table S1: Solubility of the maltodextrin derivatives in DMI; Table S2: Performance metrics of the present maltodextrin-based thermosets in comparison with previously reported highly bio-based UPRs.

Author Contributions: Conceptualization, N.W. and K.T.; Methodology, R.S., N.W. and K.T.; Validation, R.S., N.W. and K.T.; Formal Analysis, N.W.; Investigation, R.S., N.W. and K.T.; Data Curation, R.S. and N.W.; Writing—Original Draft Preparation, R.S. and N.W.; Writing—Review and Editing, R.S., N.W. and K.T.; Visualization, R.S. and N.W.; Supervision, N.W. and K.T.; Project Administration, K.T.; Funding Acquisition, N.W. and K.T. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Japan Science and Technology Agency (JST) COI-NEXT Program (grant number: JPMJPF2102 for K.T.) and the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant numbers: 18H02253 for K.T., and 21K05704 for N.W.).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding authors.

Acknowledgments: This research was supported by the Yamaha Corporation. NMR measurements were performed at the Research Institute for Instrumental Analysis of Kanazawa University, and DMA and TMA measurements were conducted at the Industrial Research Institute of Ishikawa. During the preparation of this manuscript, the authors used ChatGPT-5.1 for the purpose of refining English expression. The authors have reviewed, revised, and approved the final content and take full responsibility for the content of this publication.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AGU	anhydroglucose unit
DS	degree of substitution
DE	dextrose equivalent
DMAc	dimethylacetamide
DMI	dimethyl itaconate
DMA	dynamic mechanical analysis

FT-IR	Fourier-transform infrared
¹ H NMR	Proton nuclear magnetic resonance
IA	itaconic acid
MD	maltodextrin
MEKPO	methyl ethyl ketone peroxide
qNMR	quantitative ¹ H NMR
T _g	glass transition temperature
TGA	thermogravimetric analysis
TMA	thermomechanical analysis
UPR	unsaturated polyester resin

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