

Harnessing terpenes for thermosetting polymers development: synthesis and characterization of myrcene- modified unsaturated polyester

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Abstract: This study explores the use of a myrcene-based monomer for synthesizing unsaturated polyesters, aiming to fully understand its impact on the polymerization process, curing, and the ultimate properties of the resulting materials. The polymerization involving different amounts of myrcene-based monomer (6, 12 and 24 wt%) with phthalic anhydride, maleic anhydride, propylene glycol, ethylene glycol, and diethylene glycol demonstrated similar trends in conversion (0.92-0.93), molar masses ($1400-1700 \text{ g}\cdot\text{mol}^{-1}$), and molar masses distributions (2-2.3) of the produced unsaturated polyesters. Moreover, detailed analysis using ^1H NMR spectroscopy revealed short chains formation in the myrcene-modified unsaturated polyesters via Ordelt reaction. Additional investigations such as dynamic and isothermal differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetric analysis, provided deeper insights into the relationship between the developed macromolecular structures and their final performance. These analyses examined the curing behavior, thermomechanical properties, and thermal stability of myrcene-modified unsaturated polyesters, both as solutions in styrene and as highly cured materials.

Introduction

In recent years, the search for sustainable materials has led researchers to explore bio-based monomers to create polymers that reduce reliance on fossil fuels and minimize carbon footprints. Among these, terpenes—especially β -myrcene—have gained attention due to their renewability¹. Found abundantly in plant sources, β -myrcene offers potential in polymer production, producing polymers with properties comparable to fossil-based alternatives and exhibiting good compatibility with carbon allotropes in composites. However, β -myrcene's application has been mainly limited to chain-growth polymerizations, with little research on its use in step-growth polymerizations^{2,3}.

Unsaturated polyester resins (UPRs) are important step-growth polymers widely used in industries such as automotive, construction, and medical devices due to their mechanical strength, processability, and cost-effectiveness. UPRs are versatile, allowing for backbone modification through various diols,

diacids, or anhydrides, and their radical copolymerization enables tailoring to specific application needs. Renewable monomers have recently been integrated into UPRs, demonstrating promising curing and mechanical properties⁴. Yet, myrcene's inclusion in UPRs remains underexplored.

This study investigates the synthesis, characterization, and performance of UPRs containing myrcene within the polymer backbone. It focuses on how myrcene influences polymerization and curing behavior, with additional evaluations including dynamic-mechanical analysis and thermal stability testing of the resulting thermosetting materials.

Experimental

Materials: Maleic anhydride (MAN), β -myrcene (My), ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), phthalic anhydride (PA) were purchased from Aldrich and used as received for synthesizing the unsaturated polyester resins. Styrene,

acetone, hexane, tetrahydrofuran (THF), and deuterated chloroform (CDCl₃) were used for dissolution and analysis.

Synthesis: A myrcene-maleic anhydride adduct (ManMy) was prepared as reported in literature⁵. On the other hand, unsaturated polyesters were synthesized by reacting ManMy, MAN, PA, EG, PG, and DEG at 180°C. The acid value (AV) was monitored to track reaction progress, and conversion was calculated. Purified polyesters were characterized by ¹H NMR and SEC. The obtained polyesters were dissolved in styrene at 70 wt.% (containing 100 ppm of hydroquinone).

For unsaturated polyester curing, 0.2 wt.% cobalt (II) 2-ethylhexanoate was dissolved in the unsaturated polyester/styrene solutions at room temperature, then cooled to 0°C. Methyl ethyl ketone peroxide (MEKP, 1.25 wt.%) was added, mixed for 30 seconds, and an aliquot (25-30 mg) was analyzed via DSC at 25°C. The remaining sample was cured at 25°C for 12 h, followed by post-curing at 100°C for 5 h. Cured materials underwent DMA from 0 to 180°C and TGA from 25 to 700°C under nitrogen.

Results and discussion

Synthesis of unsaturated polyesters containing the myrcene-based monomer

A series of experiments was conducted for investigating the impact of myrcene-based monomer content on polymerization behavior and its subsequent effect on physicochemical properties. The codes and proportions of the raw materials used are detailed in Table 1.

Table 1. Proportions of raw material used for the synthesis of unsaturated polyesters

Experiment	Molar percentage (mol%)					
	EG	PG	DEG	MAN	PA	ManMy
UP1	17.2	17.2	17.2	24	24.4	0
UP1-25My	17.2	17.2	17.2	18	24.4	6
UP1-50My	17.2	17.2	17.2	12	24.4	12
UP1-100My	17.2	17.2	17.2	0	24.4	24

Conversion as a function of reaction time was monitored, and results are shown in Figure 1. Initially, all reactions exhibited a rapid conversion increase within the first 400

minutes ($p = 0.75-0.77$), followed by a gradual rise, eventually becoming constant at conversion = 0.92-0.93. This behavior aligns with polycondensation process, where early-stage conversion is driven by abundant reactive sites (hydroxyl and carbonyl groups), while later stages slow due to factors like byproduct formation, reduced reactive sites, and diffusion limitations. The presence of myrcene-based monomer (6, 12, and 24 mol%) did not hinder the polymerization, thus achieving high conversions (0.92-0.93) and M_n values ranging from 1400 to 1700 g·mol⁻¹ ($\bar{D} = 2.01-2.37$).

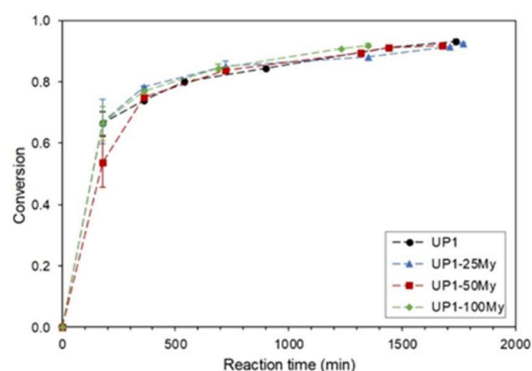


Figure 1. Conversion as a function of time for polymerizations with different content of ManMy

Structural analysis of the obtained unsaturated polyesters

¹H NMR spectroscopy was conducted to elucidate the macromolecular structure of the synthesized unsaturated polyesters, whose spectra are disclosed in Figure 2.

The UP1 spectrum (Figure 2a) is discussed first as a reference. Signals *a* and *b* are assigned to phthalate protons, while *c* and *c'* correspond to fumarate and maleate protons, respectively. Signal *d* indicates the methine proton in the 1,2-propyleneoxy unit, and signals *e* and *f* represent methylene groups from various glycol-derived units. Signal *g* corresponds to methyl protons in the 1,2-propyleneoxy unit. These results match prior literature⁶.

In myrcene-modified unsaturated polyesters (Figures 2b–d), signals *a* to *g* were observed as in UP1. However, in UP1-100My, maleate and fumarate protons (*c* and *c'*) disappeared,

as expected. New signals at 5.04 and 5.35 ppm correspond to the unsaturation proton in the cyclic (*i*) and vinylidene terminal group (*j*) of the ManMy unit. A group of signals between 1.73 and 2.58 ppm (*k*) is attributed to methine and methylene protons in the ManMy unit, while signal *l* corresponds to terminal methyl groups in ManMy. These signals intensified as ManMy content increased from 6 to 24 mol%.

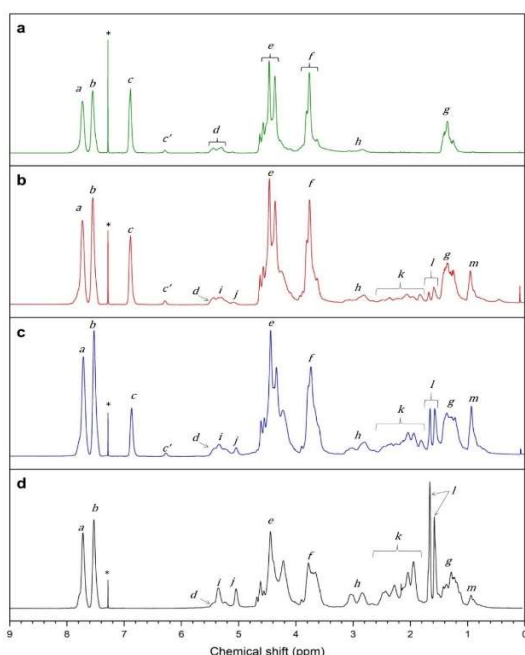


Figure 2. ^1H spectra of unsaturated polyester containing (a) 0, (b) 6, (c) 12 and (d) 24 mol% of ManMy

A key aspect in the synthesis of unsaturated polyesters involves both the isomerization of maleate to fumarate units and the formation of saturated structures via etherification between maleate/fumarate units and glycols (Ordelt reaction). These reactions significantly affect the thermal and mechanical properties of the cured resins.

A detailed analysis of the ^1H NMR spectra allowed the estimation of isomerization percentage using Equation 1, where I_c and $I_{c'}$ represent the integral values of signals *c* and c' , respectively. The isomerization percentages were 95.7% for UP1, 94.03% for UP1-25My, and 92.66% for UP1-50My. These values are similar to those of propylene glycol-based polyesters, known for high reactivity with styrene.

$$\text{Eq. 1 } \%isomerization = \frac{I_c}{I_c + I_{c'}} * 100$$

For the Ordelt reaction, signals between 2.7 and 3.2 ppm (*h*) indicate saturation. The saturation extent (SE) was calculated using Equation 2 where I_x represents the integral value of the signal indicated in the subplot, and results showed SE values of 0.204 for UP1, 0.313 for UP1-25My, 0.528 for UP1-50My, and 0.633 for UP1-100My. These results suggest that myrcene's carbon-carbon bonds show a high propensity for forming short branches through the Ordelt reaction, reducing the available reactive sites compared to theoretical values, similar to polyesters derived from itaconic acid^{7,8}. These structural features may influence the performance of the corresponding unsaturated polyester/styrene systems, which will be discussed in subsequent sections.

$$\text{Eq. 2 } SE = \frac{I_h}{I_h + I_c + I_{c'} + I_i + I_j}$$

The relationship between chemical structure and curing behavior of unsaturated polyesters is crucial for developing new resins. In this study, the unsaturated polyesters were cured using a MEKP/cobalt(II) 2-ethylhexanoate system (1.2 wt.% and 0.2 wt.%, respectively) and analyzed via dynamic DSC. Notably, UP1-100My exhibited no exothermic transition, while UP1, UP1-25My, and UP1-50My displayed broad exothermic transitions with enthalpy (ΔH) values of 678, 106, and 79 $\text{J} \cdot \text{g}^{-1}$, respectively. These transitions began at 45–50°C, with peaks at approximately 68°C, 112°C, and 158°C in all three samples.

The absence of an exothermic transition in UP1-100My suggests that the remaining carbon-carbon double bonds in the myrcene moiety were unable to cure under these conditions. This was confirmed by casting in an aluminum mold, where UP1-100My remained in liquid form. In contrast, the other polyesters exhibited ΔH values inversely proportional to their myrcene content. Their curing likely occurred through copolymerization of styrene with the residual fumarate/maleate units, resulting in lower ΔH values.

On an industrial scale, unsaturated polyester-based composites are typically processed at low temperatures, between 20 and 40°C. Understanding the curing behavior in this temperature range is essential for assessing their applicability. To explore this, isothermal DSC assays were conducted. The resulting thermograms, shown in Figure 3, reveal that the exotherms began at nearly the same time (ca. 4 min) for all samples, indicating similar initiation regardless of the ManMy content. However, the reference polyester exhibited a higher exothermic value ($\Delta H = 96 \text{ J}\cdot\text{g}^{-1}$) compared to the myrcene-modified resins, which ranged between 50 and 52 $\text{J}\cdot\text{g}^{-1}$.

The overall conversion during curing was estimated using Equation 3, where ΔH_R is the enthalpy from dynamic DSC and ΔH_t is the heat released at time t . Figure 3b shows the conversion trends for the reference and myrcene-modified polyesters. The conversion increased over time, correlating with the ManMy content, and plateaued at 14.2%, 47.1%, and 64.8% for UP1, UP1-25My, and UP1-50My, respectively. This behavior can be explained by the availability of carbon-carbon double bonds. With fewer active sites and a constant amount of initiator, more double bonds are converted to single bonds, but with less heat release.

$$\text{Eq. 3 } \% \text{ conversion} = \frac{\Delta H_t}{\Delta H_R} * 100$$

Since achieving highly cured unsaturated polyester resins with high conversion at 25°C was not possible, the samples underwent post-curing at 100°C for 5 h. This process resulted in conversion rates of 87.9%, 92.8%, and 89.7% for UP1, UP1-25My, and UP1-50My, respectively, as calculated using Equation 4. The post-curing enthalpy values ($\Delta H_{R, \text{post-curing}}$) were 82.93, 7.68, and 8.14 $\text{J}\cdot\text{g}^{-1}$. These conversion rates are high, aligning with the maximum range (90-95%) reported for unsaturated polyesters.

$$\text{Eq. 4 } \% \text{ conversion} = 1 - \frac{\Delta H_{R, \text{post-curing}}}{\Delta H_R} * 100$$

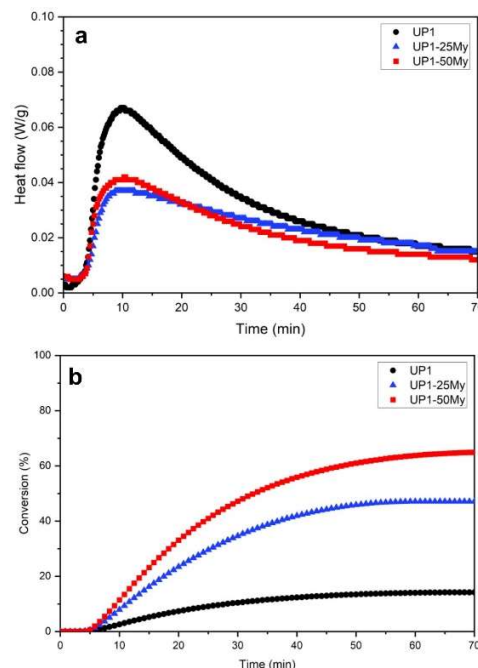


Figure 3. (a) Isothermal DSC and (b) global conversion of carbon-carbon double bonds to carbon-carbon single bonds for the obtained unsaturated polyesters/styrene initiated by MEKP/cobalt (II) 2-ethylhexanoate system.

Thermo-mechanical performance of cured myrcene-modified unsaturated polyesters

Dynamic mechanical analysis (DMA) was used to evaluate the thermo-mechanical properties of the highly cured unsaturated polyesters. The results, shown in Figure 4, reveal that the storage modulus decreased with increasing ManMy content. At 25°C, the storage modulus values were 2941 MPa for UP1, 2115 MPa for UP1-25My, and 1013 MPa for UP1-50My.

In terms of tan delta, UP1 showed a broad peak beginning at 35°C and ending at 165°C, with a maximum at 107°C and a noticeable shoulder between 50-60°C. The tan delta curves for UP1-25My and UP1-50My started at similar temperatures to UP1 (30-35°C) but ended at lower temperatures (140-145°C), with peaks at 83°C and 70°C, respectively. The shoulder seen in UP1 was nearly absent in the myrcene-modified polyesters, likely due to peak overlap. The temperature corresponding to the maximum tan delta is considered the glass transition temperature (T_g), and the T_g decreased as ManMy content increased.

The lower T_g values in the myrcene-modified polyesters compared to the reference can be attributed to reduced crosslinking density in the polymer network. The myrcene-derived segments in UP1-25My and UP1-50My likely do not participate in crosslink formation, limiting crosslinking to the remaining fumarate units. This reduced crosslinking density lowers both T_g and the storage modulus. Additionally, the presence of 6% and 12% myrcene-derived segments increases the polymer network's mobility, further lowering T_g and storage modulus while broadening and increasing the tan delta curve⁹. The low-temperature shoulder (50-60°C) is likely due to free or grafted polystyrene formed from residual styrene, as the overall conversion for the cured materials ranged between 87.9% and 92.8%.

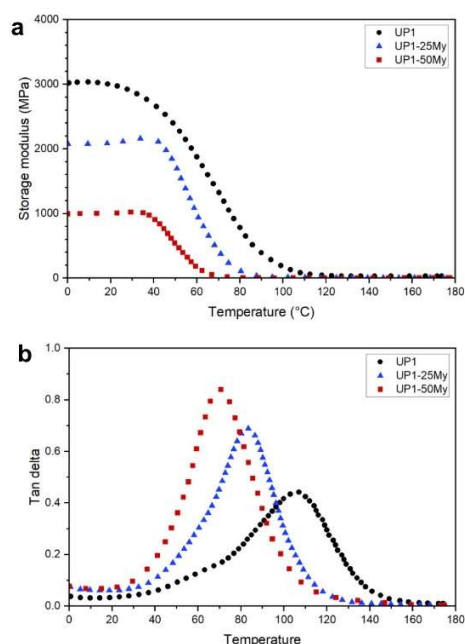


Figure 4. (a) Storage modulus and (b) Tan delta as a function of temperature derived from DMA of the obtained unsaturated polyesters

Figure 5 displays the thermogravimetric analysis (TGA) traces for the cured materials, revealing consistent degradation patterns across all samples, regardless of composition and network structure. These patterns unfolded in two distinct stages: the first one, beginning at 150°C and ending at 290°C, this stage showed a 10% weight loss, attributed to the degradation of both free and grafted polystyrene, which has lower thermal stability than cross-linked polystyrene. The second

stage, starting immediately at 291°C and continuing until 450°C, this stage accounted for the most significant weight loss (~86%), primarily affecting the polyester-polystyrene network. The degradation stage occurring at 600°C involved the oxidation of residual carbonaceous materials by changing the atmosphere from N_2 to O_2 .

The results indicate that incorporating myrcene-based monomers into the synthesized unsaturated polyesters does not significantly impact the thermal stability of the cured materials compared to the reference polyester.

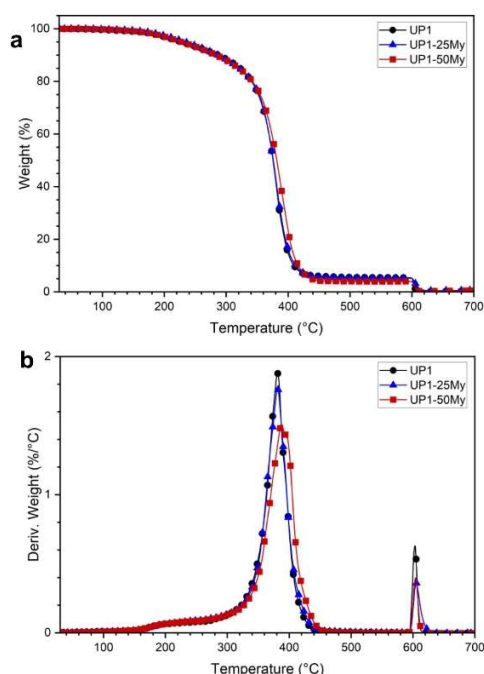


Figure 5. (a) Weight percentage and (b) derivative weight as a function of temperature derived from TGA of the obtained unsaturated polyesters

Conclusions

The synthesis of myrcene-modified unsaturated polyesters was investigated to understand their polymerization behavior and physicochemical properties. Polymerization followed typical polycondensation patterns, with consistent molar mass and dispersity across different myrcene contents (ManMy). 1H NMR revealed key structural features, including saturated structures in the ManMy moiety as a result of Ordeli reaction, and high maleate-to-fumarate isomerization.

Regarding the curing behavior, DSC analyses showed the myrcene moiety's carbon-carbon double bonds did not react with styrene, suggesting crosslinking primarily occurred through styrene and fumarate polymerization.

Concerning the thermo-mechanical properties of fully cured polyesters, DMA highlighted reduced crosslinking density and glass transition temperature (T_g) in myrcene-modified polyesters, linked to increased polymer network mobility. TGA showed consistent thermal stability across all ManMy compositions.

Overall, incorporating myrcene introduces non-polar groups into unsaturated polyester chains without disrupting polymerization, yielding thermally stable materials with high potential for composites with non-polar reinforcements like graphene.

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