

Supplementary Materials

Biodegradable Polymeric Foams Based on Modified Castor Oil, Styrene, and Isobornyl Methacrylate

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Methods

Synthesis of castor oil glycerides

60.0 g of castor oil and 13.1 g of glycerol (1:2.2 mole ratio) were charged in a three necked 500 ml round bottom flask equipped with inert gas inlet (Ar), thermometer, Liebig condenser and mechanical stirrer. The mixture was heated to 180 °C. 0.5 phr Ca(OH)₂ was added to the mixture. The mixture was heated to 200 °C for 1.5h. After 1.5h the reaction vessel was plunged into salted ice water to rapidly cool to 15 °C whilst stirring rapidly. Any excess glycerol remained in the mixture and no further purification was performed. The product was a golden-brown liquid at room temperature.

Synthesis of maleated castor oil glycerides

To the castor oil glycerides (COG) previously prepared, 59.0 g of MA was added in the reaction vessel. Hydroquinone (0.10 phr) and N,N-DMBA (0.15 phr) were added as free radical inhibitor and accelerant, respectively. The mixture was heated in an oil bath to 100 °C with continuous stirring under inert atmosphere (Ar) for 3.5 h. MA that sublimed on the reaction vessel walls was regularly melted back into the reaction mixture by pouring hot silane oil over the outside of the vessel. At the end of the reaction, any excess MA remained in the mixture, and the product was used for polymerization without any further purification. The product was a yellow/brown highly viscous liquid at room temperature.

Results and Discussion

Synthesis of maleated castor oil glycerides

The synthesis of MACOG was performed by a two-step “one-pot” procedure. Firstly, COG was produced via a base catalyzed glycerolysis with castor oil and glycerol, using Ca(OH)₂ as catalyst. The COG product had an acid value (AV) of 8.54 ± 0.0048 mg KOH/g, and a saponification value (SV) of 143.27 ± 0.82 mg KOH/g, resulting in $0.0025 \pm 1.46 \times 10^{-5}$ moles of ester groups per gram of COG. The maleation reaction was performed for 3.5 h, at which point the product had an AV of 258.16 ± 0.74 mg KOH/g, and SV of 552.66 ± 2.66 mg KOH/g, resulting in $0.0053 \pm 4.74 \times 10^{-5}$ moles of ester bonds per gram of MACOG.

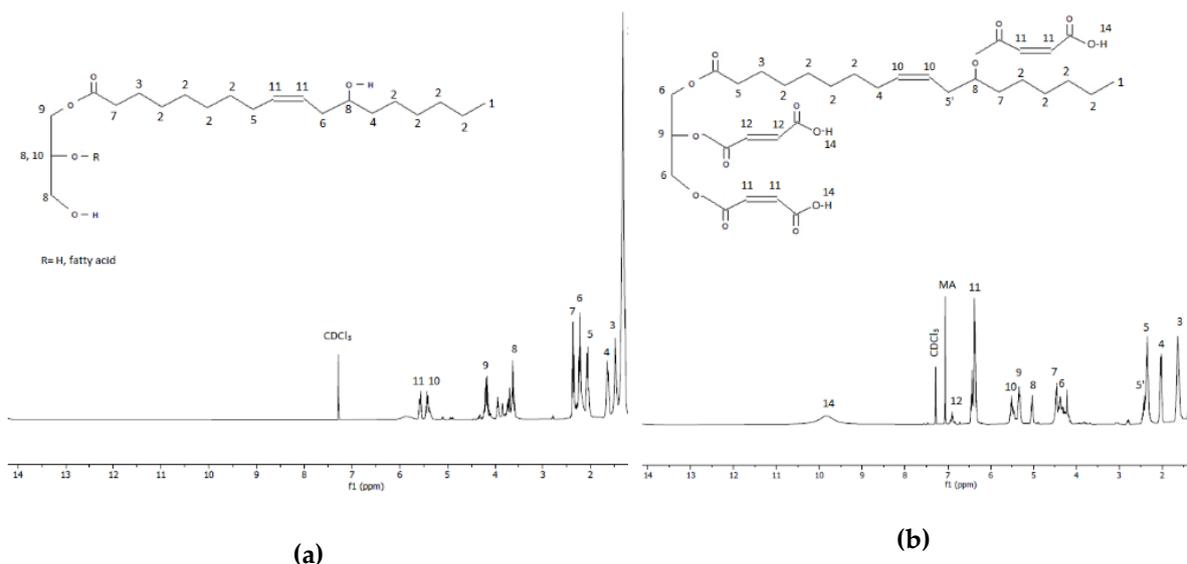


Figure S1: ^1H NMR spectra of a) COG and b) MACOG.

For COG, ^1H NMR was performed using CDCl_3 solvent at a frequency of 400.22 MHz at 293.4K over 8 scans, presented in Figure S1a. A triplet at 0.89 ppm related to terminal $-\text{CH}_3$, a multiplet in the range of 1.25-1.40 ppm related to $-\text{CH}_2-$ on the fatty acid, a quartet at 1.47 ppm related to $-\text{CH}_2-\text{CH}(\text{OH})-$, a triplet at 1.65 ppm related to $\beta-\text{CH}_2-\text{CH}_2-(\text{CO})\text{O}-$, a quartet at 2.07 ppm and a triplet at 2.23 ppm related to $\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$ and $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-$, respectively, and a multiplet in the range of 2.26-2.41 related to $\alpha-\text{CH}_2(\text{CO})\text{O}-$. Due to COG being a mixture of predominantly monoglyceride and diglyceride with a minor fraction of triglyceride and glycerol, there were various hydroxyl groups and esters present on the glycerol centre. A multiplet in the range of 3.54-3.76 ppm related to $\text{CH}-\text{OH}$ and CH_2-OH on the glycerol centre and $\text{CH}(\text{OH})$ on the fatty acid.[1] A quartet of triplets at 4.18 ppm related to $\text{CH}_2-\text{O}(\text{CO})-$ methylene on the glycerol centre, a multiplet at 5.34-5.47 ppm related to $-\text{CH}-\text{O}(\text{CO})-$ methine attached to the glycerol centre and a multiplet in the range of 5.52-5.63 ppm related to $-\text{CH}=\text{CH}-$ unsaturation on the fatty acid.[2-5]

For MACOG, ^1H NMR was performed using CDCl_3 solvent at a frequency of 400.22 MHz at 293.3 K over 8 scans, presented in Figure S1b. A triplet at 0.85-0.93 ppm related to terminal $-\text{CH}_3$, a quintet at 1.30 ppm related to $-\text{CH}_2-$ on the fatty acid, a triplet at 1.63 ppm related to $\beta-\text{CH}_2-\text{CH}_2(\text{CO})\text{O}-$, a quartet at 2.02 ppm related to $\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$. A multiplet in the range of 2.36-2.49 ppm related to $\alpha-\text{CH}_2(\text{CO})\text{O}-$ and $-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}(\text{CO})-$, a multiplet in the range of 4.24-4.42 ppm related to $\text{CH}_2-\text{O}(\text{CO})-$ methylene on the glycerol centre, a quartet at 4.46 ppm related to $\text{CH}_2-\text{CH}_2-\text{CH}-\text{O}(\text{CO})$ on the fatty acid, a quartet at 5.03 ppm related to $\text{CH}-\text{O}(\text{CO})-$ maleate on the fatty acid, a quartet at 5.32 ppm related to $-\text{CH}=\text{CH}-$ unsaturation on the fatty acid, and a triplet of doublets at 5.5 ppm related to $-\text{CH}-\text{O}(\text{CO})-$ methine attached to the glycerol centre. A multiplet in the range of 6.30-6.49 ppm related to $-\text{CH}=\text{CH}-$ of the maleate group and a multiplet in the range of 6.83-6.96 ppm related to $-\text{CH}=\text{CH}-$ of the fumarate group. The singlet at 7.06 ppm related to unreacted MA. The broad singlet at 9.83 ppm related to the $-\text{COOH}-$ on the maleate/fumarate groups.[3, 6] Comparative to COG, the peaks related to $\text{CH}(\text{OH})$, $\text{CH}-\text{OH}$ and CH_2-OH diminished for MACOG, which suggested that the majority of the hydroxyl groups present on COG were consumed during the maleation reaction. Furthermore, new peaks appeared for MACOG related to $\text{CH}-\text{O}(\text{CO})-$ and $\text{CH}_2-\text{O}(\text{CO})-$ of maleates/fumarates appear, suggesting that the esterification reaction was successful.[4, 7, 8]

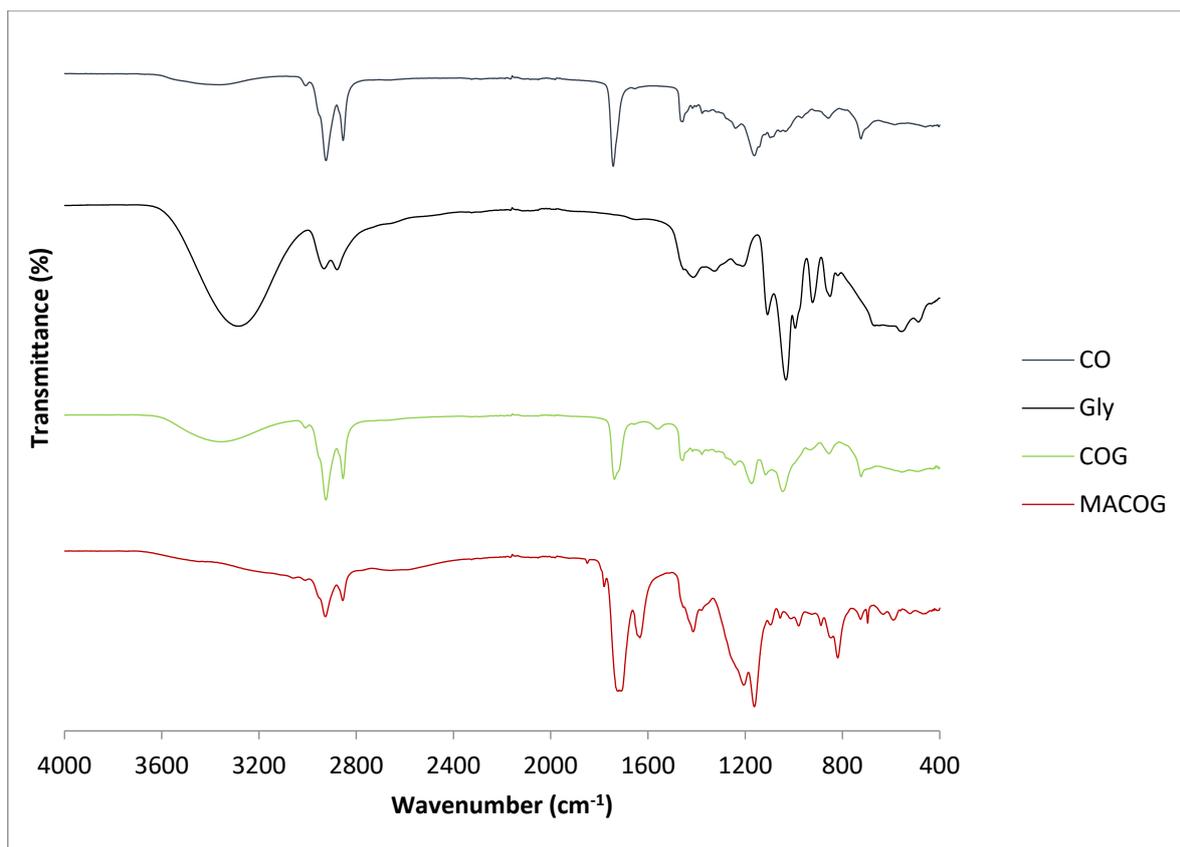


Figure S2: ATR-FTIR spectra of castor oil (CO), glycerol (gly), COG, and MACOG.

Table S1. ATR-FTIR peak assignments for castor oil (CO), glycerol, COG, and MACOG.

	CO	Glycerol	COG	MACOG	Ref.
$\nu(\text{O-H})$	3364	3283	3362	-	[9-11]
$\nu_{\text{as}}(\text{C-H}_2)$	2924	2932	2924	2926	[11-13]
$\nu_{\text{s}}(\text{C-H}_2)$	2853	2878	2854	2856	[11-13]
$\nu(\text{C=O})$	1742	-	1737	1723	[10, 14, 15]
$\nu(-\text{C}=\text{C}-)$	1633	-	1633	1633	[16]
$\nu(\text{C-O-H})$	1240	1226	-	-	[2, 14, 15, 17]
$\nu(\text{C-O})$ and $\delta(\text{C-H})$	1162	-	1165	1159	[2, 14, 15]
$\nu(\text{C-O-H})$ secondary	1095	1108	1115	-	[18, 19]
$\nu(\text{C-O-H})$ primary	-	1032	1045	-	[18, 19]
$\gamma(\text{O-H})$	858	851 + 650-600	855 + 650-600	-	[17, 20]
$\rho(\text{C-H}_2)$	723	-	723	725	[15]

The ATR-FTIR spectra of castor oil (CO), glycerol, COG, and MACOG are presented in Figure S2, with some of the common absorption peak assignments summarized in Table S1. Additional absorption peaks were also present for the aforementioned compounds. For glycerol, the peak at 1326 cm^{-1} was assigned to the $\delta(\text{C-H})$ of the methine [20]. For COG, the intensity of the hydroxyl $\nu(\text{O-H})$ at 3362 cm^{-1} increased compared to castor oil, due to the relative increase in hydroxyl group functionality on the product. The peak at 1563 cm^{-1} was assigned to the $\nu(\text{COO}^-)$ of the carboxylate salt, which was a soap product formed during the glycerolysis reaction with $\text{Ca}(\text{OH})_2$ and free fatty acids [9, 21-24]. An additional peak related to $\nu(\text{C-O})$ of primary hydroxyl groups was observed at 1045 cm^{-1} , which was not present on the castor oil triglyceride spectrum.

For MACOG, the peak due to $\nu(\text{O-H})$ in the 3500 cm^{-1} region present on COG diminished, and was replaced by $\nu(\text{O-H})$ for maleate acid groups with a broad peak between $3400\text{-}2500\text{ cm}^{-1}$ [25]. This was indicative that the majority of hydroxyl groups were consumed during the anhydride esterification

reaction and the formation of maleate half esters occurred [6]. Weak peaks at 1853 cm^{-1} and 1783 cm^{-1} were indicative that there was a cyclic anhydride present, although the weak absorption intensity suggested that the majority of MA was successfully consumed [8, 26, 27]. The peak at 1723 cm^{-1} was assigned to the carbonyl valence bond $\nu(\text{C}=\text{O})$, which was more intense than that of castor oil and COG and indicated more ester groups were present due to the formation of maleate half-esters. Moreover, it shifted down from 1742 cm^{-1} for castor oil due to the influence of the carbonyl contribution of the carboxylic acid groups on the maleate half esters. Relative to castor oil and COG, an increase in intensity of the peak at 1633 cm^{-1} assigned to the $\nu(\text{C}=\text{C})$ indicated the presence of double bonds from the maleate groups on the product [27]. The peak at 1414 cm^{-1} was assigned to the carboxyl $\nu(\text{C}-\text{O}-\text{H})$ [28]. The peak at 1052 cm^{-1} was assigned to the O-C-C ester group vibration [18]. This peak could also be due to the CO-O-CO vibration of the residual anhydride, although these are typically seen as broad peaks [29]. It has previously been suggested that the C=C-H out of plane bending vibration for the *trans* alkene fumarate group has a peak around 980 cm^{-1} [18, 30]. The presence of a peak in this area further implied that maleate groups may have isomerized to fumarates. The peak at 890 cm^{-1} was assigned to $\omega(\text{C}-\text{H}_2)$. The peak at 819 cm^{-1} was attributed to the $\gamma(\text{C}=\text{C}-\text{H})$ of the maleate group [5, 6]. The weak peak at 696 cm^{-1} was assigned to $\gamma(\text{C}=\text{C}-\text{H})$ in the *cis* conformation related to unsaturation on the fatty acid moieties [29].

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